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Experimental study of the interaction of vacancy defects with Y, O and Ti solutes to better understand their roles in the nanoparticles formation in ODS steels

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General introduction

Nuclear energy is an attractive source to meet the global growth of energy demands. Starting from the first small nuclear reactors made in the 1950s, nuclear power grows greatly till nowadays. The 437 reactors currently in operation produce 369 GW (e); most of them (83%) are in OECD countries where the power generated with nuclear fuel -350 plants- represents 25% of the total energy produced, compared to 16% worldwide. In the European Union this fraction reaches an average of 34%, while in France it is 73.3% till 2013, the highest percentage in the world.

As a result of the great potential of nuclear energy, the future nuclear reactor, Generation-IV, is in development. Compared to the currently operating systems (Gen II), Generation-IV designs will use fuel more efficiently, reduce waste production, be economically competitive, and meet stringent standards of safety and proliferation resistance. It is important to notice that the service conditions of these Gen-IV systems will be drastically different. The operating temperature of currently operating reactors (Gen II) does not exceed 400°C, whereas for Gen IV it is much higher. In addition, higher irradiation damage than in Gen II, are expected for Gen IV. These service conditions would affect the microstructural stability and mechanical properties of structural materials. Thus, the adapted materials development would be a key factor for Gen IV to succeed.

Several candidate materials have been suggested for structural applications in Gen- IV reactors: F-M steel, Austenitic stainless steels, Oxide-dispersion strengthened (ODS) alloys, Ni-base alloys, Graphite, Refractory alloys and Ceramics. Among these, ODS materials afford many benefits. They show not only negligible swelling under irradiation, owing to their ferritic bcc structure but equally outstanding creep properties, owing to the nano-reinforcements present in the matrix. This material is expected to be used for claddings, targets and some other core and fuel structures in Gen- IV reactors.

In this context, a French research program CPR ODISSEE (funded by AREVA, CEA, CNRS, EDF, Mécachrome- contract n°070551) has been launched since 2011. This program focus on the scientific problems about the fabrication, microstructure, physical and mechanical properties of ODS under conditions similar to Gen IV fission and fusion reactors. Both experimental and modeling works are involved in this program. Multi- scale characterizations are preformed: APT (Atomic Probe Tomography), TEM (Transmission Electronic Microscopy), SANS (Small-Angle Neutrons Scattering), XRD (X-Rays Diffraction), XPS (X-ray Photoelectron Spectrometry), and EXAFS (Extended X-Ray Absorption Fine Structure). The ab initio, clusters dynamic etc. modelings are also realized.

It is known that the excellent properties of ODS steels are induced by the fine dispersion of nanoparticles. But the atomic scale clustering mechanism of these nanoparticles is not yet cleared. Although there are some simulation works which try to shed light on the nucleation route, the lack of experimental data for fundamental properties of nanoparticle constitutions (vacancy, Y, Ti, O) makes these works difficult to be validated. In this context, the present thesis using positron annihilation spectroscopy (PAS) and secondary ion mass spectrometry (SIMS) has the objectives of answering to the following questions:

- How the solutes (Y, Ti, O, Cr) interact with vacancies in bcc Fe matrix.
- How vacancies evolve with the annealing temperatures.

- How the solutes (Y, Ti, O, Cr) diffuse in the matrix.
- What is the earliest stage of solute clustering.

The results obtained would help to better understand how the oxide nanoclusters nucleate and what is their kinetic precipitation path and to explain the structure of nanoclusters observed in previous studies.

This thesis is composed of four chapters.

The chapter I presents the scientific context and summarizes the previous studies related to the present one. The future nuclear power plants, especially the nuclear fission GEN IV, are firstly introduced. The development of ODS alloys is briefly explained: their elaboration process, their chemical composition and their mechanical properties. The microstructure evolution at high temperature and under irradiation is also discussed. Then, the characterization of oxide nanoparticles and their clustering mechanism at different scales (macroscopic and atomic scale) are described. Finally, the properties of point defects in bcc Fe and bcc FeCr matrixes have been presented.

The chapter II describes the materials and experimental techniques used in this thesis. The preparation methods of the Fe and FeCr virgin materials are firstly explained. The irradiation/implantation conditions are then reported and the defects and solutes depth profiles as calculated by SRIM are shown. Finally, the principle of the positron annihilation spectroscopy (PAS) and secondary ion mass spectrometry (SIMS) techniques are explained and the experimental conditions are detailed.

The chapter III is focused on the study of the properties of vacancy defects induced in bcc Fe and FeCr matrixes. The Fe and FeCr virgin samples qualities after preparations are firstly checked by positron annihilation spectroscopy. Then, the vacancy defects formation in Fe and FeCr matrix induced by He irradiation is studied. Finally, the evolution of vacancy defects as a function of temperature is revealed.

In the chapter IV the interaction between vacancy and yttrium, titanium and oxygen atoms are studied in bcc Fe. The introduction of vacancy defects and Y, Ti, O atoms by implantations is firstly presented. Then, the nature and depth distribution of the implanted elements (Y, O) and of the detected defects are reported. Then from the evolution of O and Y depth profiles and of the defects distributions, the Y, and O effect on annealing behavior of vacancy defects is studied. With these results, the Y, Ti, O-vacancy interactions are revealed. Finally, a mechanism, at atomic scale, of ODS nanoparticles formation is proposed.

At the end of this manuscript, the general conclusion is drawn and some perspectives are proposed.

Chapter I.

Bibliography

I. Bibliography

This chapter presents the scientific context and summarizes the previous studies related to the present thesis. The future nuclear power plants, especially the nuclear fission GEN IV, are firstly introduced in section I.1. Their severe service conditions, high temperature and great irradiation damage, require the development of new structural materials. Oxide Dispersion Strengthened (ODS) alloys are among the most prospective candidates because of their excellent properties.

In section I.2, the development of ODS alloys is briefly introduced. Their elaboration process and the strategy of the chemical composition choice are explained. Then, their mechanical properties and the microstructure evolution at high temperature and under irradiation are presented.

As explained in the previous section, the nanoclusters in ODS steels are believed critical to the high temperature strength and potential radiation resistance. Thus, in section I.3, the existing works about the characterization of nanoparticles (chemical composition, distribution, number density, size and structure) and their clustering mechanism at different scales (macroscopic and atomic scale) are described. Then, the role of vacancy defects is discussed.

In section I.4, the properties of point defects in bcc Fe and bcc FeCr matrixes have been firstly presented. They are the basis to understand the interaction between vacancy defects and the elements (Y, Ti, O) which constitute the oxide nanoclusters in bcc iron which is presented in the following.

Finally, the conclusions have been drawn in section I.5 and the objectives of the present thesis are explained in section I.6.

I.1. Future Nuclear power plants

In this section, the different generations of nuclear reactors are introduced, especially the GEN IV nuclear fission reactors. Their severe service conditions, high temperature and great irradiation damage, require the development of new structural materials. Oxide Dispersion Strengthened (ODS) alloys are among the most prospective candidates because of their excellent properties.

I.1.1. Brief history of nuclear energy reactors

Nuclear energy is an attractive source to meet the global growth of energy demands. Starting from the first small nuclear reactors made in the 1950s, nuclear power grows greatly till nowadays. The 437 reactors currently in operation produce 369 GW (e); most of them (83%) are in OECD countries where the power generated with nuclear fuel- 350 plants- represents 25% of the total energy produced, compared to 16% worldwide ^[1]. In the European Union this figure reaches an average of 34%, while in France it is 73.3% till 2013, the highest percentage in the world ^[2].

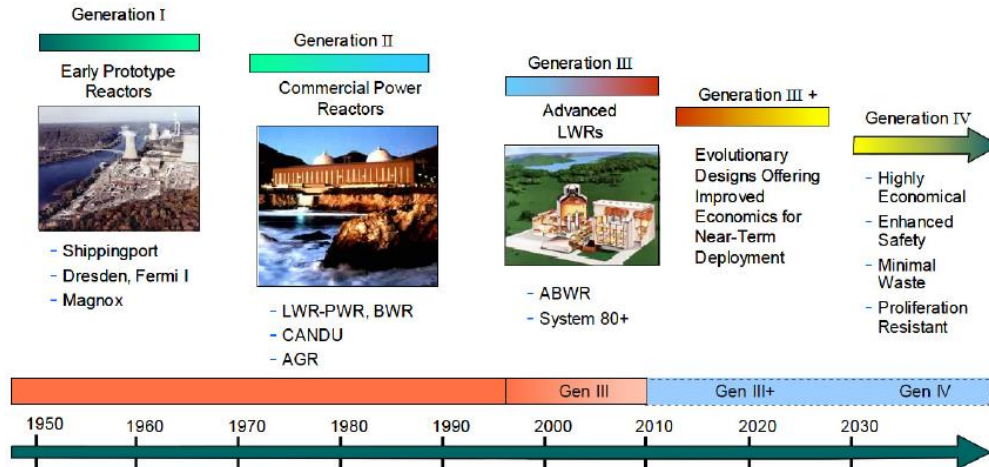


Figure I-1: Overview of the generations of nuclear power systems ^[3].

The progress of nuclear power systems is expressed in terms of generations, as shown in Figure I-1. All these systems are based on nuclear fission reaction: uranium nucleus bombarded with neutrons split into few isotopes of lighter elements with release of energy and emission of neutrons. The first nuclear fusion experimental reactor ITER, based on the fusion reaction, is also in construction adjacent to the Cadarache facility in the south of France. But the commercialization of fusion nuclear reactor is in the far future.

Gen I consists of early prototype reactors from the 1950 and 1960s, such as Shippingport (1957–1982) in Pennsylvania, Dresden-1 (1960–1978) in Illinois, Calder Hall-1 (1956–2003) in the United Kingdom ^[4] and G1 (1955- 1968) in Marcoule, France. This kind of reactor typically ran at power levels that were ‘proof-of-concept’. They mostly used natural uranium fuel, used graphite or heavy water as moderator and CO₂ as a coolant. All of them are now stopped. Gen II refers to a class of commercial reactors designed to be economical and reliable. Designed for a typical operational lifetime of 40 years, prototypical Gen II reactors include pressurized water reactors (PWR), CANada Deuterium Uranium reactors (CANDU), boiling water reactors (BWR), advanced gas-cooled reactors (AGR), and Vodo-Vodyanoi Energetichesky Reactors (VVER). Gen II systems began operation in the late 1960s and most of them still in operation in the West were manufactured by one of three companies: Westinghouse, AREVA, and General Electric (GE). The economics of existing Gen II plants and of those under construction or in the planning stage are generally favorable, particularly in Asia. For example, China’s existing and planned civilian power fleet is based on the PWR. Two important designs used in China are the improved Chinese PWR 100 (the CPR- 1000) and the standard PWR 600 MW and 1000 MW designs (the CNP series). Gen III nuclear reactors are essentially Gen II reactors with evolutionary, state-of-the-art design improvements. These improvements are in the areas of fuel technology, thermal efficiency, modularized construction, safety systems (especially the use of passive rather than active systems), and standardized design. Improvements in Gen III reactor technology have aimed at a longer operational life, typically 60 years of operation, potentially to greatly exceed 60 years, prior to complete overhaul and reactor pressure vessel replacement. In this condition, several European projects like PERFORM 60 have been launched to predict the effects of radiation for reactor materials using 60 years foreseen plant life

time. Advanced Generation III (so-called Generation III+) which is an evolutionary development of Gen III is under construction in several countries, for example the 'European Pressurized Reactor' (EPR). This reactor designed by Areva is now under construction in Finland, France and China.

Gen IV reactors have been developed to help meet the world's future energy needs. This results in the formation of the Generation- IV International Forum (GIF). The nine founding members are those that signed the GIF Charter in July 2001: Argentina, Brazil, Canada, France, Japan, the Republic of Korea, the Republic of South Africa, the United Kingdom and the United States. Subsequently, the GIF Charter was signed by Switzerland in 2002, Euratom in 2003, and the People's Republic of China and the Russian Federation in 2006 ^[5]. Generation-IV designs will use fuel more efficiently, reduce waste production, be economically competitive, and meet stringent standards of safety and proliferation resistance.

1.1.2. GEN IV nuclear fission reactor

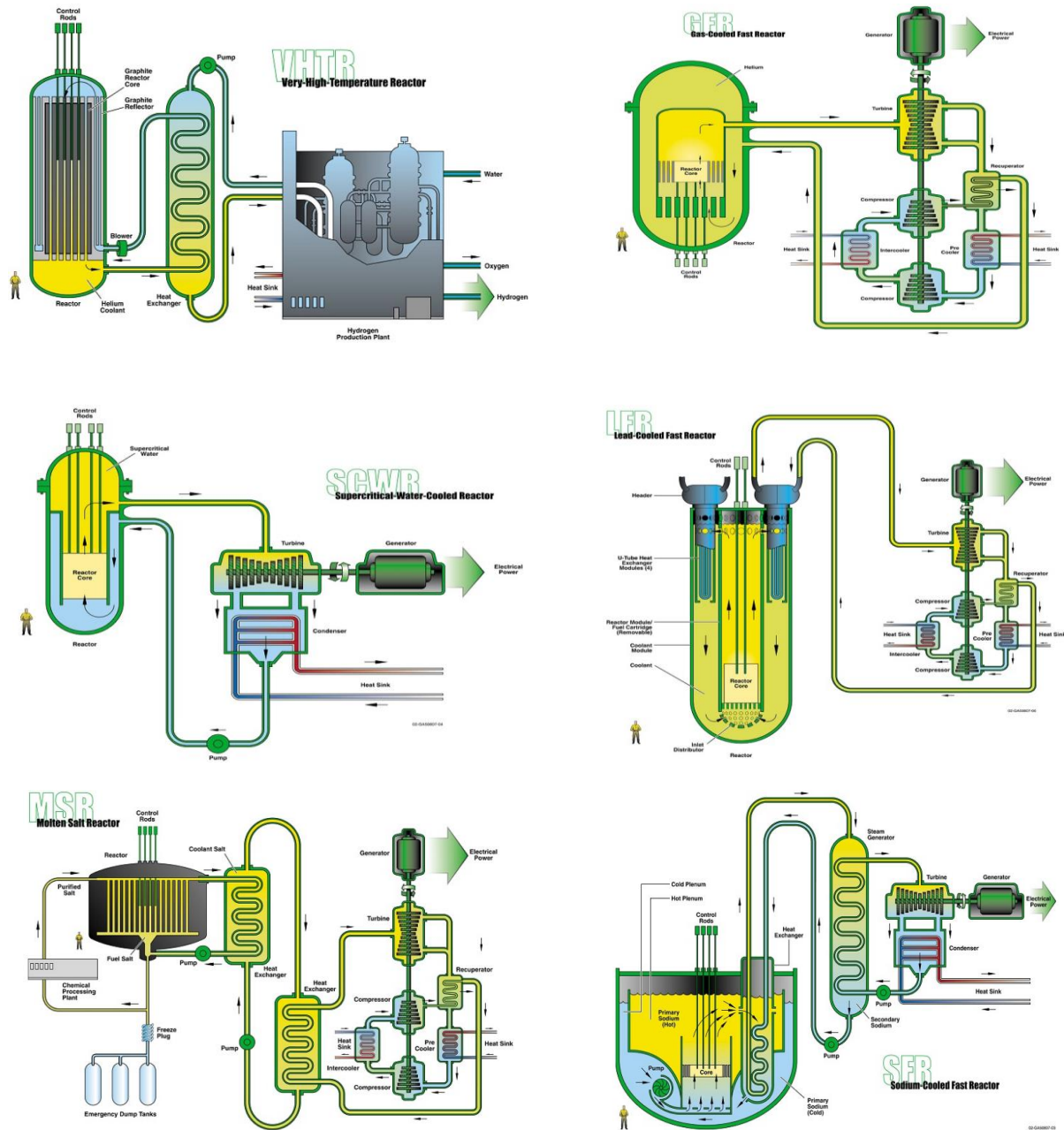
Eight technology goals have been defined for Generation IV systems in four broad areas as shown in Table I-1: sustainability, economics, safety and reliability, and proliferation resistance and physical protection.

Goals for Generation IV Nuclear Energy Systems	
Sustainability-1	Providing sustainable energy generation that meets clean air objectives and provides long-term availability of systems and effective fuel utilization for worldwide energy production.
Sustainability-2	Minimizing and managing their nuclear waste and notably reduce the long-term stewardship burden, thereby improving protection for the public health and the environment.
Economics-1	Having a clear life-cycle cost advantage over other energy sources.
Economics-2	Having a level of financial risk comparable to other energy projects.
Safety and Reliability-1	Operations will excel in safety and reliability.
Safety and Reliability-2	Having a very low likelihood and degree of reactor core damage.
Safety and Reliability-3	Eliminating the need for offsite emergency response.
Proliferation Resistance and Physical Protection	Increasing the assurance that they are very unattractive and the least desirable route for diversion or theft of weapons-usable materials, and providing increased physical protection against acts of terrorism.

Table I-1: Goals for Generation IV nuclear energy systems ^[6].

With these goals in mind, some 100 experts evaluated 130 reactor concepts before GIF selected six reactor technologies for further research and development. These include: the Gas-cooled Fast Reactor (GFR), the Lead-cooled Fast Reactor (LFR), the Molten Salt Reactor (MSR), the Supercritical Water-cooled Reactor (SCWR), the Sodium-cooled Fast Reactor (SFR) and the Very High Temperature Reactor (VHTR). Three systems (GFR, LFR, and SFR) are named fast reactors and other three thermal reactors according to the energy of produced neutrons.

Fast Reactors have a unique capability as sustainable energy source; the closed fuel cycle allows significantly improving the usage of natural resources and the minimization of volume and heat load of high-level waste. Among the fast reactor systems, the sodium-cooled fast reactor (SFR) has the most comprehensive technological basis, thanks to the experience gained internationally from operating experimental, prototype and commercial size reactors ^[7]. In the past, SFR was selected in Europe with several achievements: Rapsodie, Phénix, PFR, KnKII, and Superphénix. Since the definitive shut down of Phenix in March 2010, no more plants are in operation in Europe. Elsewhere, the sodium technology has been selected by several countries, such as Japan (with Joyo and Monju and JSFR, Japan Sodium-cooled Fast Reactor), Russia (with the BN 600 in operation and the BN 800 reactor), India (with the FBTR and the PFBR prototype), China (with CEFR, China Experimental Fast Reactor) and the United States (with the advanced recycling reactor project). In 2006, following the President Chirac decision, France launched a project to build a sodium-cooled fast reactor (SFR) prototype by 2020, open to industrial and international partnerships. This could be considered as the first step towards a renewed European initiative.



	Neutron spectrum	Coolant	Temperature (°C)	Fuel	Fuel cycle	Size(s) (MWe)
Sodium-cooled fast reactors (SFR)	Fast	Sodium	550	U-238 and MOX	Closed	50, 1700
Very high temperature gas reactors (VHTR)	Thermal	Helium	1000	UO ₂ prism or pebbles	Open	275
Gas-cooled fast reactors (GFR)	Fast	Helium	850	U-238	Closed	300, 1500
Supercritical water-cooled reactors (SCWR)	Thermal or fast	Water	625	UO ₂ or MOX	Open (thermal) or closed (fast)	1700
Lead-cooled fast reactors (LFR)	Fast	Pb or Pb-Bi	480–800	U-238	Closed	10–100, 600
Molten salt reactors (MSR)	Epithermal	Fluoride salts	700–800	UF in salt	Closed	1000

Figure I-2: Schematic overview of the different Generation IV reactors ^[6]. Reference information is also presented ^[8].

I.1.3. Service conditions for structural materials in Gen IV reactor

Figure I-3 compares the proposed operating temperatures and displacement damage dpa (displacement per atom) levels for structural materials in the six Generation IV concepts and fusion energy systems with the existing knowledge base ^[9]. It is noted that the operating temperature of currently operating reactors (Gen II) does not exceed 400°C, whereas for Gen IV it is much higher. In addition, higher damage doses than in Gen II, are expected for some of these systems (for example, SFR). These service conditions will affect the microstructural stability and mechanical properties of structural materials. For example, in the case of the sodium- cooled fast reactor (SFR) concept, a closer- packed fuel- element bundle core is designed as shown in Figure I-4. It involves larger- diameter fuel pins, fitted with thinner spacer wires, inserted between the cladding tubes, than were used in the Phénix or Superphénix (SPX) fast reactors^[10]. To inhibit any excessive deformation of the fuel pins, it is essential that the cladding material exhibits little swelling under irradiation. At the same time, in order to achieve optimization in economic terms, the burnup values being considered will result in doses higher than those allowed for the cladding material used in Phénix, namely 15- 15 Ti austenitic steels. New alloys thus must be developed.

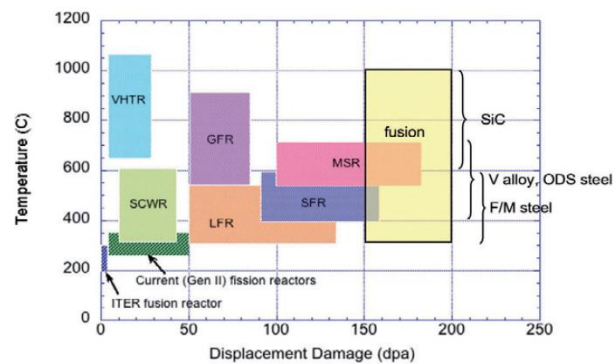


Figure I-3: Overview of operating temperatures and displacement damage dose regimes for structural materials in current (Generation II) and proposed future (Generation IV) fission and fusion energy systems ^[9].



Figure I-4: (a) Part of a PWR fuel assembly, comprising short fuel cladding segments fitted with endplugs, and part of one of the spacer grids. An actual fuel assembly may comprise as many as 17x 17 rods, each more than 4 m long. (b) Sectional view of the fuel and cladding used for the Phénix and Superphénix fast reactors, and for the future SFR. The fuel is shown in black, the metal cladding in gray, while the central cavity, holding no fuel, is shown in yellow ^[10].

I.1.4. Candidate structural materials

Several candidate materials have been suggested for structural applications in Gen- IV reactors: F-M steel, Austenitic stainless steels, Oxide-dispersion strengthened (ODS) alloys, Ni-base alloys, Graphite, Refractory alloys and Ceramics ^[11]. Among these materials, ODS materials afford many benefits. They afford not only negligible swelling under irradiation, owing to their ferritic bcc structure -by contrast to austenitic grades, which feature a fcc structure- but equally outstanding creep properties, owing to the nano-reinforcements present in the matrix. This material is expected to be used for claddings, targets and some other core and fuel structures of Gen- IV reactors. ODS EUROFER steel could also be used for structural applications in fusion power reactors up to about 650°C. The plate supporting the tungsten tiles in the European dual coolant lithium-lead (DCLL) breeding blanket concept and the cartridge within the finger-like parts of the European He-cooled divertor concept are presently foreseen to be made of ODS EUROFER ^[12]. The use of ODS Reduced- Activation Ferritic (RAF) steels with higher creep strength up to about 750°C and reasonable fracture toughness at ambient and intermediate temperatures will provide these components with additional integrity margin and lifetime ^[13].

In this context, a French research program CPR ODISSEE (funded by AREVA, CEA, CNRS, EDF, Mécachrome- contract n°070551) has been launched since 2011. This program focus on the scientific problems about the fabrication, microstructure, physical and mechanical properties of ODS under conditions similar to Gen IV fission and fusion reactors. Both experimental and modeling works are involved in this program. Multi- scale characterizations are preformed: APT, MET, DNPA, DRX, XPS, and EXAFS. The AB initio, clusters dynamic etc. modelings are also realized. The present thesis using positron annihilation spectroscopy (PAS) will be a complementary study of the point defects effect on ODS nanoparticles formation for ODISSEE program. In addition, another ongoing thesis realized by C.BAROUH in CEA- Saclay with Dr.Fu focus on the multi-scale simulation for the same science context which is based on the experimental results of this thesis.

I.1.5. Conclusions

In this section, the different generations of nuclear reactors have been introduced, especially the GEN IV nuclear fission reactors. The operating temperature of currently operating reactors (Gen II) does not exceed 400°C, whereas for Gen IV it is much higher. In addition, higher damage doses than in Gen II, are expected for some of these Gen IV systems (for example, SFR). These service conditions will affect the microstructural stability and mechanical properties of structural materials. New alloys thus must be developed. Several candidate materials have been suggested, ODS materials afford many benefits among them. They afford not only negligible swelling under irradiation, owing to their ferritic bcc structure- by contrast to austenitic grades, which feature a fcc structure- but equally outstanding creep properties, owing to the nano- reinforcements present in the matrix. This material is expected to be used for claddings, targets and some other core and fuel structures of Gen- IV reactors. ODS EUROFER steel could also be used for structural applications in fusion power reactors up to about 650°C.

I.2. Oxide dispersion strengthened (ODS) alloys

In this section, the development of ODS alloys is briefly introduced. Their elaboration process and the strategy of the chemical composition choice are explained. Then, their mechanical properties and the microstructure evolution at high temperature and under irradiation are presented.

I.2.1. Development of ODS alloys

a) History

Oxide Dispersion Strengthened (ODS) alloys typically consist of a high temperature metal matrix - such as iron aluminide, iron chromium, iron-chromium-aluminium, nickel chromium or nickel aluminide - with small oxide particles of alumina (Al_2O_3) or yttria (Y_2O_3) dispersed within it. The ODS alloys began to be formally developed since the birth of mechanical alloying developed by John Benjamin and his colleagues^[14] around 1966 as a method to produce ODS alloys on an industrial scale.

Since 1980s, the superior high temperature mechanical properties of ODS ferritic or martensitic steels have attracted attention for advanced nuclear power plants applications such as fast and fusion reactors^[15]. These materials are based on Fe-Cr matrix and reinforced by nanometer scale oxide (for example, $\text{Y}_2\text{Ti}_2\text{O}_7$) particles. ODS ferritic steels are being developed and investigated for nuclear fission and fusion applications in Japan^[16-18], Europe^[19, 20], and the United States^[21]. Various kinds of ODS ferritic or martensitic steels have been developed both in laboratory and industry, for example commercial ODS steel 'MA957' produced by INCO Alloys International in United States and experimental ODS steel '12YWT' elaborated by Kobe Steel Ltd in Japan. In France, CEA has developed the ODS materials since twenty years and the Fe-13/18CrWTi ferritic ODS alloys have been considered as reference materials for new ODS alloys development^[20].

b) Elaboration process

The manufacturing process of the ODS ferritic or martensitic cladding tubes is shown in Figure I-5. The pre-alloyed powders (Fe, Cr, W, Ti...) which are prepared by argon gas atomization have a size of micrometers. They are mechanically alloyed with yttrium oxide powders which have a size of nanometers under hydrogen or an inert atmosphere like argon^[22] in an attrition ball mill for about 48 hours. These mechanically alloyed powders are canned, degassed, sealed and consolidated by powder metallurgical processes, as Hot Extrusion (HE) or Hot Isostatic Pressing (HIP). Then cold or warm rolling and different recrystallization heat treatments are applied to produce final form of cladding tubes^[17].

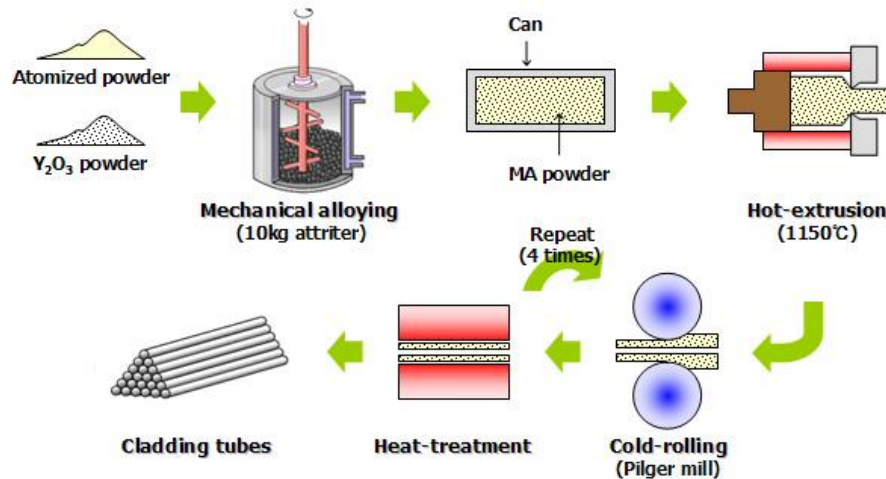


Figure I-5: Elaboration process of ODS cladding tubes ^[23].

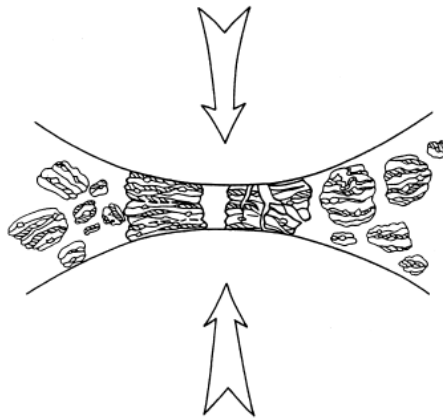


Figure I-6: Ball-powder-ball collision of power mixture during mechanical alloying ^[14].

Mechanical alloying is the critical process to alloy the starting constituents. During high-energy milling, the powder particles are repeatedly flattened, cold welded, fractured and rewelded. Some amount of powder is trapped between two steel balls during their each collision as shown in Figure I-6. This impact plastically deforms the powder particles resulting in work hardening and fracture. The new surfaces created enable the particles to weld together leading to an increase in particle size as indicated by points a, b in Figure I-7 which shows how powders evolve as a function of milling time ^[14]. At this early stage, a broad range of particle sizes develops and the particle composite have a characteristic layered structure consisting of various combinations of the starting constituents. With continued deformation, the particles get work hardened and fracture resulting in size reducing as shown by point c. At this stage, the tendency to fracture predominates over cold welding and the structure of the particles is steadily refined. After milling for a certain duration, steady-state equilibrium is reached when welding balances fracture. At this stage, the particle size distribution is narrow as indicated by point d because particles larger than average are reduced in size at the same rate that those smaller than average grow by agglomerating. Each particle contains all of the starting ingredients in the proportion they were mixed together.

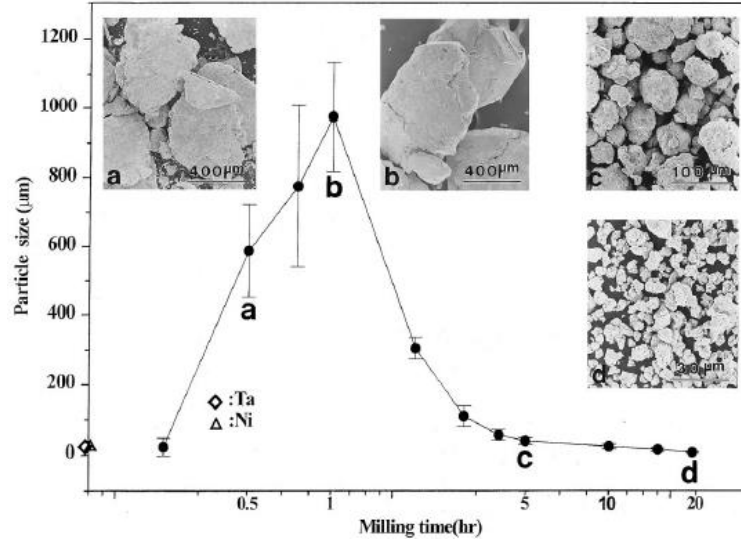


Figure I-7: Particle size distribution in function of milling time ^[14].

High energy ball milling results in the formation of crystal defects such as dislocations, vacancies, stacking faults, and increased number of grain boundaries in the grains. The presence of this defect structure enhances the diffusivity behavior of solute elements. The excess vacancies introduced are considered by some researchers having the critical role in nanoparticles formation and stabilization ^[24].

c) The choice of chemical composition

The ferritic or martensitic Fe-Cr matrix (bcc structure) is chosen for ODS steels to avoid the swelling under irradiation which represents a major inconvenience of austenitic steels. Martensitic structure is obtained after the quench from the austenitic region (γ) as shown in the binary Fe-Cr phase diagram presented in Figure I-8. The range of this austenitic region depends largely on others alloying elements, such as carbon and azote. As shown in Figure I-9 the range of γ region enlarges with the increase of C and N content. This is because some of the alloying elements (Mn, C, N, Ni...) are austenitic stabilizers and also others (Cr, W, Ti, Mo, V, Si, Al...) are ferritic stabilizers. The effectiveness of austenitic stabilizers could be evaluated by the equivalent content of Ni, while ferritic formers are evaluated by the equivalent content of Cr as calculated by equation 1 ^[25].

$$\text{Ni}_{\text{equivalent}} (\text{wt}\%) = (\% \text{Ni}) + (\% \text{Co}) + 0.5(\% \text{Mn}) + 0.3(\% \text{Cu}) + 30(\% \text{C}) + 25(\% \text{N})$$

$$\begin{aligned} \text{Cr}_{\text{equivalent}} (\text{wt}\%) = & (\% \text{Cr}) + 2(\% \text{Si}) + 1.5(\% \text{Mo}) + 5(\% \text{V}) + 1.75(\% \text{Nb}) + 0.75(\% \text{W}) \\ & + 1.5(\% \text{Ti}) + 5.5(\% \text{Al}) + 1.2(\% \text{Ta}) + 1.2(\% \text{Hf}) + 1.0(\% \text{Ce}) + 0.8(\% \text{Zr}) + 1.2(\% \text{Ge}) \end{aligned} \quad (1)$$

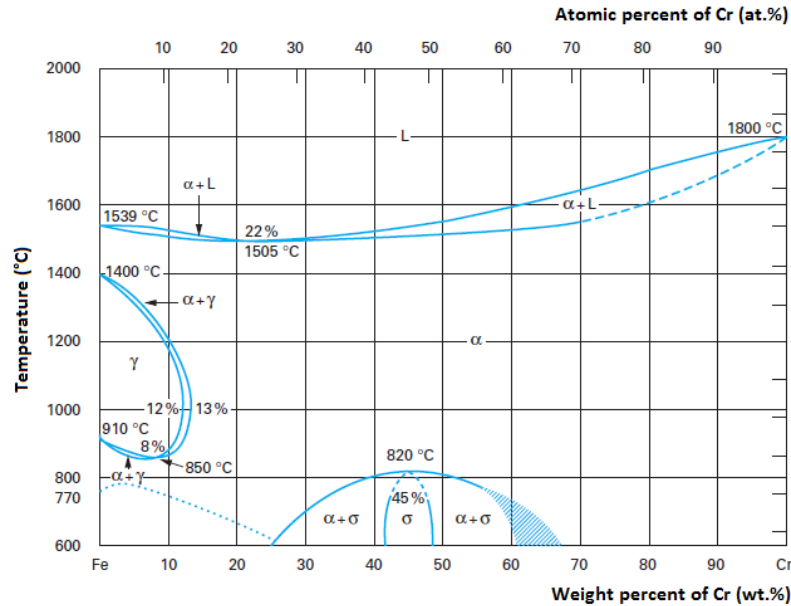


Figure I-8: Fe-Cr phase diagram ^[26].

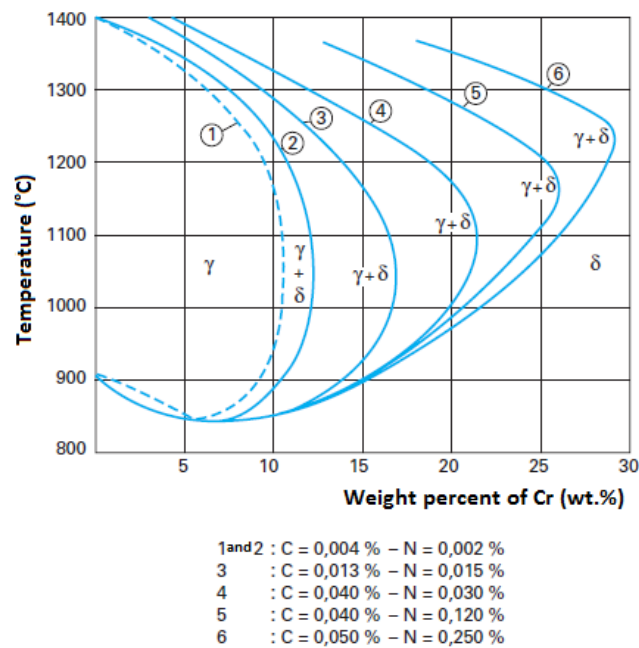


Figure I-9: Influences of carbon and azote on the range of austenitic region (γ) ^[26]

The structure of the steel could be estimated owing to the Schaeffler-Schneider diagram ^[27] using Ni and Cr equivalent as shown in Figure I-10. Martensitic or ferritic ODS steels both exhibit excellent creep properties and both types could be retained for the nuclear application. Martensitic ODS can only be used at temperatures below 800°C in order to avoid high temperature phase transformation into austenite ^[20]. In comparison to martensitic ODS, ferritic ODS is envisaged for application at temperatures in excess of 1100°C ^[20]. Bamboo-like grain structure observed after hot extrusion in ferritic ODS steels leads to the decrease of creep rupture strength in the bi-axial direction compared to the uni-axial

direction^[16]. Recrystallization process was demonstrated successfully to decrease the degree of anisotropy of ODS ferritic steels in the direction of extrusion^[28]. The microstructure of a martensitic ODS steel is usually isotropic by using martensitic transformation^[29]. Generally, ferritic steels exhibit higher DBTT compared to martensitic ones.

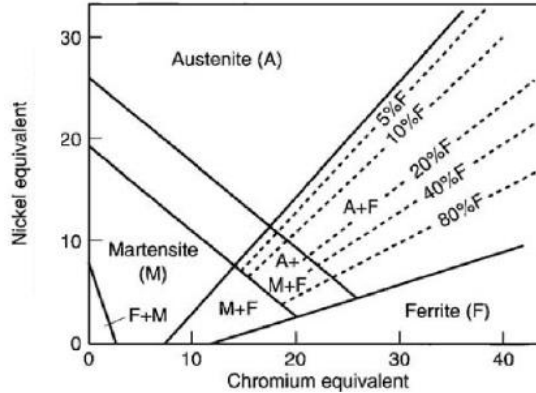
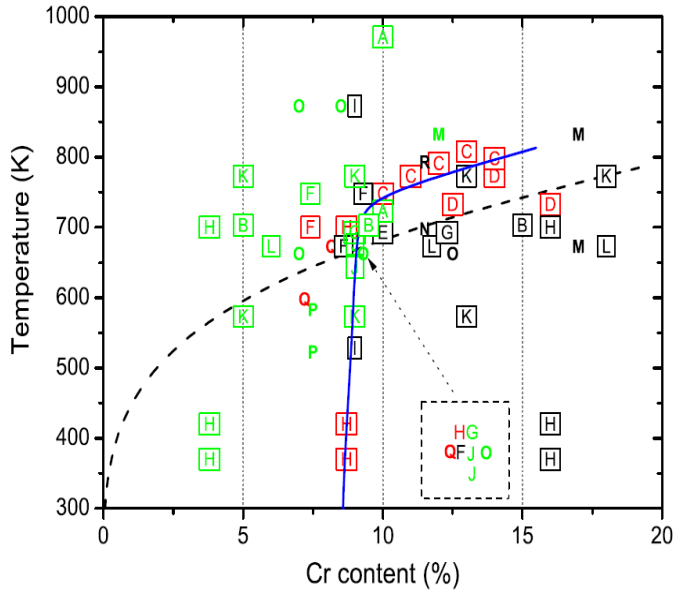


Figure I-10: Schaeffler-Schneider diagram^[27]

FeCr based steels with high Cr concentrations are known to undergo hardening and embrittlement after thermal ageing^[30] (named as '475°C embrittlement') due to α (rich in iron)- α' (rich in chromium) phases separation. However this separation could occur in temperature range of 400°C...550°C depending on the chemical composition of the steel and the irradiation conditions could also change this temperature range^[31]. The exact position of α - α' miscibility gap is still under debate. As shown in Figure I-11, Bonny et al.^[31] have proposed the position of α - α' phase boundary by summarizing the experimental data of literature regarding α' precipitation in FeCr binary alloys and FeCr based steels. In the figure, green coloured data stands for absence of α' precipitation in works; black for observed α' precipitation; red are α - α' phase boundary points suggested in corresponding works. Using these points the α - α' phase boundary line is drawn as shown in blue solid line: (i) a steep line connecting two points at ~8.5%Cr at 300K and ~10%Cr at 750K; (ii) from the latter point a line passing by point of 14%Cr at ~810K extending to higher Cr content points. It should be noted that these works were realized under thermal aging and irradiation exposure as shown in Figure I.11 (b) could induce or enhance Cr precipitation.



Symbol in Figure	Observation method	Treatment	Material
A	TEM	Triple beam (He, De, Fe), 4 MeV, 10 dpa	Binary Fe-Cr
B	DNS & RM	Heat treatment	Binary Fe-Cr
C	M-R	Heat treatment	Binary Fe-Cr
D	M-R	Heat treatment	Binary Fe-Cr
E	TEM	n-irr, 23-30 dpa	Binary Fe-Cr
F	M-R	p-irr, 16 MeV, 0.2-0.4 dpa	Binary Fe-Cr
G	TEM	n-irr, 140-200 dpa	Binary Fe-Cr
H	M-R	e-irr, 5.5 MeV, <10 dpa	Binary Fe-Cr
I	TEM	n-irr, 0.3 dpa	Binary Fe-Cr
J	TEM	n-irr, 10-40 dpa	Binary Fe-Cr
K	M-R & TEM	e-irr, 5.5 MeV, $2 \times 10^{18} \text{ e/m}^2$ for 10 h	Binary Fe-Cr
L	TEM	n-irr, 26 dpa	Binary Fe-Cr
M	TEM	Heat treatment & n-irr, 30-114 dpa	Steels: F17, EM12, HT9, EM10
N	TEM & EDS	n-irr, 36 dpa	Steel: JLF (Cr, W, V, Ta)
O	TEM	n-irr, 20-60 dpa	Steels (Fe-xCr-2W-0.2V, Ta)
P	TEM	p-irr, 490 MeV, 0.5-9.2 dpa	Steel: F81H
Q	SANS	Heat treatment & n-irr, 0.7-2.9 dpa	RA-steels: LA-type (W-Mn-V) Steels: HT9, T91, EM10, F82H
R	TEM	n-irr, 3-89 dpa	Steel: EP450

Figure I-11: (a) α - α' phase boundary shown in blue solid line (b) list of the experimental data indicated in the figure [31].

The corrosion resistance of ODS steels increases with chromium content and the minimum concentration of chromium necessary to obtain an effective passive layer of chromium oxide is about 10.5 to 11wt.% [32]. The spent nuclear fuel refining requires the dissolution of the uranium or the plutonium oxide in the nitric acid. It is important to maintain the integrity of the cladding as much as possible so high Cr content alloys are of interest to resist to the corrosion by nitric acid.

Hence, the Cr concentration is one of the key parameters to be optimized in order to guarantee the best corrosion resistance and also favourable mechanical properties. As shown in Table I-2, different ODS steels are being developed, for example Fe-18Cr-1W-0.3Ti by CEA France [20]. These ODS steels contain different amounts of Cr (9-18wt.%). Concerning other alloying elements, most of them are tungsten, titanium and yttria. Tungsten (W) is added to strengthen the material. Yttria (Y_2O_3) increases creep strength but decreases ductility of ODS steel by solid solution hardening [17]. Ti contributes to the formation of the Y-Ti-O oxide nanoparticles in finer size resulting in an increase of creep rupture strength [33-35]. The Ti effect is explained in the section I.3.1(a). Carbon (C) contamination could be introduced during fabrication of ODS steel [36]. Carbides, such as $\text{Cr}_{16}\text{Fe}_6\text{MoC}_6$, precipitate during the tempering process after quenching. They increase the material hardness and strength [37]. In addition, excess oxygen which is defined as the total content of oxygen in ODS steel minus the oxygen coming from Y_2O_3 is also an important parameter influencing mechanical properties of material. Ohtsuka et al. [38, 39] showed that when the atomic ratio between excess oxygen and titanium in the steel is close to 1, fine and dense distribution of oxide particles can be achieved resulting in higher temperature strength. But higher excess of oxygen (more than 0.1wt.%) may result in coarser nanoparticles and reduce mechanical properties. Excess oxygen content is introduced during the early stage of MA process and could be reduced by application of a high purity Ar (99.9999 wt.%) [39] atmosphere during MA.

Alloy	Composition (wt.%)										
	Fe	Cr	W	Ti	Mo	Mn	V	Ta	C	Y ₂ O ₃	Other
ODS Eurofer 97	bal.	9	1.1	-	-	0.4	0.2	0.12	0.11	0.3	0.03N
Mm13	bal.	8.9	2	0.21	-	-	-	-	0.13	0.36	0.01N; 0.05Si
12YWT	bal.	12	3	0.4	-	-	-	-	-	0.25	-
14YWT	bal.	14	3	0.4	-	-	-	-	-	0.3	-
MA957	bal.	14	-	0.9	0.3	-	-	-	0.01	0.25	-
MA ODS-H	bal.	15	2	-	-	-	-	-	0.03	0.35	4Al; 0.8Zr
Fe-18Cr1W ^[20]	bal.	18.1	0.95	0.26	-	0.31	-	-	0.03	0.56	Si 0.3; Ni 0.2

Table I-2: ODS Ferritic or martensitic alloy compositions for nuclear applications

I.2.2. Mechanical properties of ODS steel at high-temperature and under irradiation

Advanced nuclear power plants operate at high temperatures and under irradiation. Such exposures cause materials damage of components during service. In this part, the mechanical behavior of ODS steels such as stress rupture, creep, fatigue, swelling and etc. under these severe serving conditions will be discussed.

a) ODS steel mechanical properties at high temperature

As shown in [Figure I-12 \(a\)](#)^[40], ultimate tensile strength in function of temperature for Eurofer 97^[41] (Fe-9wt.%Cr ferritic/martensitic steel), ODS Eurofer^[41] (Fe-9wt.%Cr-0.3wt.%Y₂O₃ ferritic/martensitic steel), 14Cr ODS^[42] (Fe-14wt.%Cr-0.3wt.%Ti-0.3wt.%Y₂O₃ ferritic steel) and bimodal-grained ODS^[40] (Fe-14wt.%Cr-0.3wt.%Ti-0.3wt.%Y-0.1wt.%O ferritic steel) is compared. For all four steels, the tensile strength decreases with increasing temperature. It appears that all the three types of ODS steel have higher tensile strength than Eurofer steel in the temperature up to 875K. But compared to Eurofer 97 steel, 14 Cr ODS steel exhibit a low tensile ductility as shown in [Figure I-12 \(b\)](#). It is caused by the nano-crystalline structure of ODS steel which limits intragranular dislocation activity. D. Zhao et al.^[40] fabricate an ODS ferritic steel with bimodal grain size distribution by mixing micron-sized grains (5-10 μm) into the matrix (100-300 nm). Compared with 14Cr ODS ferritic steel, its elongation increases by 60-180% over the whole temperature range and ultimate strength is not severely weakened. The ductility is achieved in the bimodal samples through plastic deformation of the coarse grains^[43].

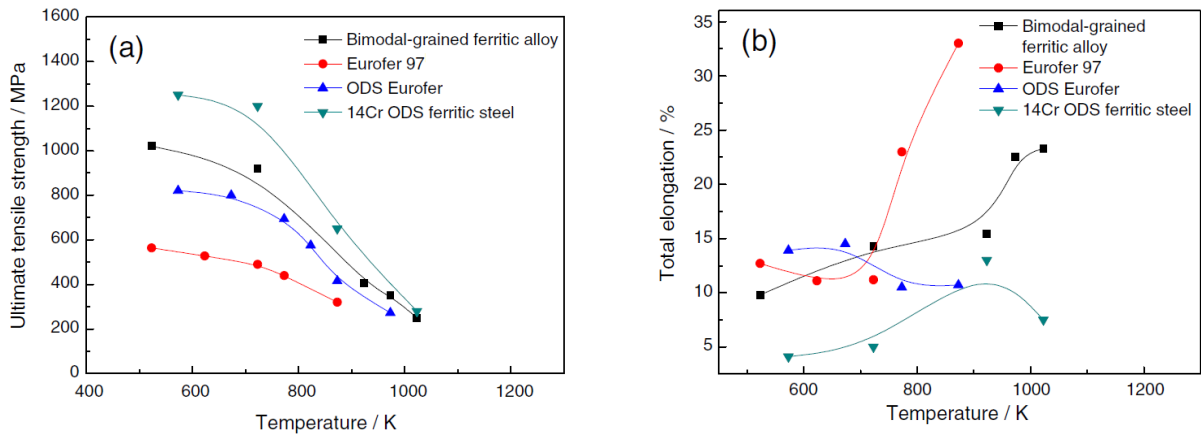


Figure I-12: Comparison of ultimate tensile strength (a) and total elongation (b) in function of temperatures for Eurofer 97^[41], ODS Eurofer^[41], 14Cr ODS ferritic steel^[42] and Bimodal-grained ODS ferritic alloy^[40].

The ODS steel has good thermal creep resistance at high operating temperatures ($T > 550^{\circ}\text{C}$). G. Yu et al.^[44] perform thermal creep experiments at various temperatures ranging between 450°C and 750°C on the EUROFER 97 ferritic/martensitic steel and two European ODS steels (EUROFER 97 steel as matrix reinforced by 0.3wt.% Y_2O_3). The Larson-Miller parameter, P , versus applied stress was determined for these alloys as shown in Figure I-13. T_k is the test temperature (in Kelvin) and t_m is the creep life (in hours). It is remarked that the creep strength of both ODS steels is much higher than that of the EUROFER 97 alloy. For a given applied stress value, the Larson-Miller parameter is larger, about 1.5 for both ODS steels with respect to the EUROFER 97 alloy, which corresponds to a temperature increase of about 65°C for a given rupture time and indicates that both ODS steels could be used up to a maximum temperature that is about 65°C higher.

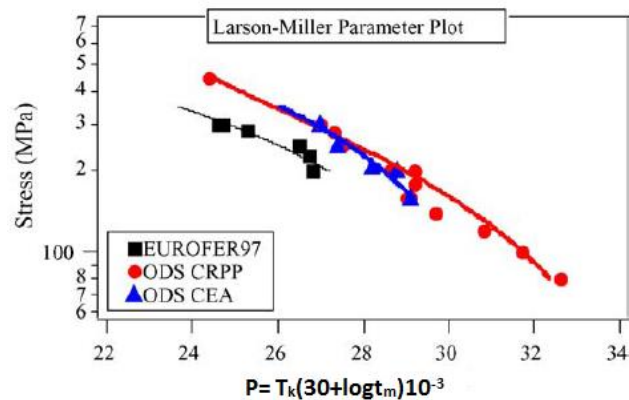


Figure I-13: Larson-Miller parameter P versus applied stress for the EUROFER 97 alloy and two ODS steels^[44].

b) ODS steel mechanical properties in irradiation exposure

Swelling occurs as a result of irradiation introduced point-defect agglomerations or voids which increase the volume. As shown in Figure I-14, ferritic-martensitic ODS steels show a much better swelling behavior than austenitic steels because of their bcc structure.

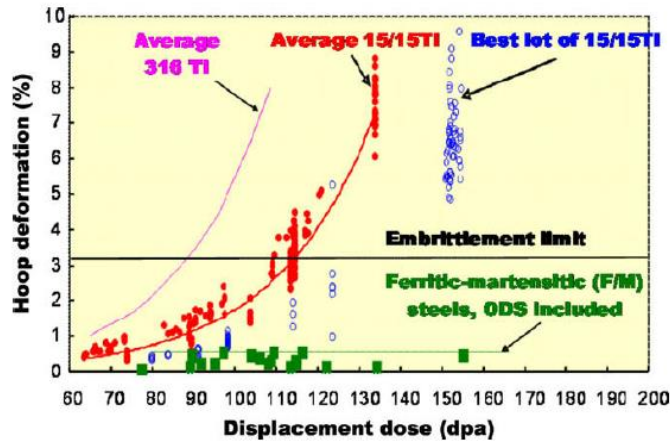


Figure I-14: Hoop deformation of different grades of austenitic Phénix claddings and ferritic/martensitic (F/M) materials versus dose at temperatures between 675 and 825 K ^[45].

Helium is introduced as a result of transmutation reactions in nuclear plants. It diffuses to all kinds of sinks: point defects, dislocations and grain boundaries. It could form intragranular as well as intergranular clusters and bubbles. Helium bubbles at the grain boundaries considerably reduce toughness of a material ^[46]. J. Chen et al. ^[47] study the ODS ferritic steel, PM2000, implanted with α -particles under stress at different irradiation temperatures. The trapping of helium at the surfaces of Y_2O_3 particles at 773 K is observed as shown in Figure I-15. When bubbles grow on the Y_2O_3 /matrix interface, larger particles became truncated, indicating a strong binding between particles and bubbles. Very fine homogeneously distributed particles can act as sinks for helium preventing it from the formation of detrimental voids along the grain boundaries and thus reduce high-temperature helium embrittlement.

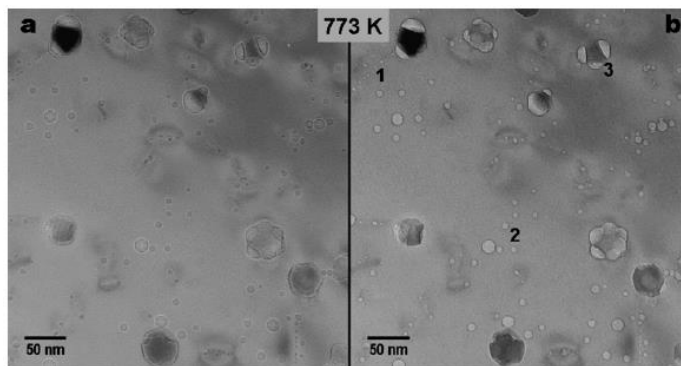


Figure I-15: Migration of helium to oxide dispersoids in the ferritic ODS alloy PM2000. a) over- focus b) under- focus ^[47]

1.2.3. Microstructure evolution of ODS alloy under irradiation

The changes of mechanical properties of materials during irradiation arise from their microstructural changes caused by physical effects of radiation damage. For example, radiation-induced defect clusters serving as strong obstacles to dislocation motion can cause radiation hardening; radiation-induced segregation and precipitation can lead to localized corrosion or grain boundary embrittlement; vacancy accumulation can cause void swelling creating unacceptable volumetric expansion; helium produced by nuclear reaction precipitating into bubbles on grain boundaries can cause intergranular fracture etc ^[9]. The nanoclusters in ODS steels play a major role in the high temperature strength and potential radiation resistance. Thus, in the current section, the studies about stability of these nanoclusters under irradiation are briefly described.

There is no common conclusion regarding the stability of oxide particles under irradiation. Some studies show that nanoclusters are stable under low damage dose (0.7, 1, 5, 10 dpa) at 300°C ^[48] and 500°C ^[49]. No modification of size, shape or chemical composition was detected at 20 dpa at 200°C, 500°C, 700°C ^[50], 60 dpa, 650°C ^[51] or 150 dpa, 670°C ^[52]. Other studies show a decrease of the average size of nanoclusters after ion irradiation for doses 1 dpa, 525°C ^[53] and 1.4 dpa, 443°C ^[54]. Oxide particles were found to dissolve slightly at 20 dpa, 380°C ^[55] and to be amorphous with modified shapes at 33 dpa, 400°C ^[56]. According to M-L. Lescoat et al. ^[57], the direct comparison of average mean sizes or number densities before and after irradiation in these investigations could possibly raise questionable conclusions, since the nanoclusters distribution varies from areas to areas in such materials. Thus, M-L. Lescoat et al. ^[57] study the stability of the Y-Ti-O nanoclusters of a Fe18Cr1W0.3Ti + 0.6Y₂O₃ ODS steel under ion irradiation up to 45 dpa at 500°C by using in situ Transmission Electron Microscopy (TEM) technique. The processed images of the micrographs obtained before irradiation and at 23 dpa are shown in Figure I-16. The 1-4 numbered large oxides prove that the same region is followed under irradiation. The image at 23 dpa shows nanoclusters which coincide with 5-6 nm Y-Ti-O circled before irradiation, thus indicating that Y-Ti-O nanoclusters are apparently stable up to 23 dpa at 500°C. The determination of size evolution is not relevant here because the images to be compared before and after irradiation are either Bright Field or Dark Field micrographs.

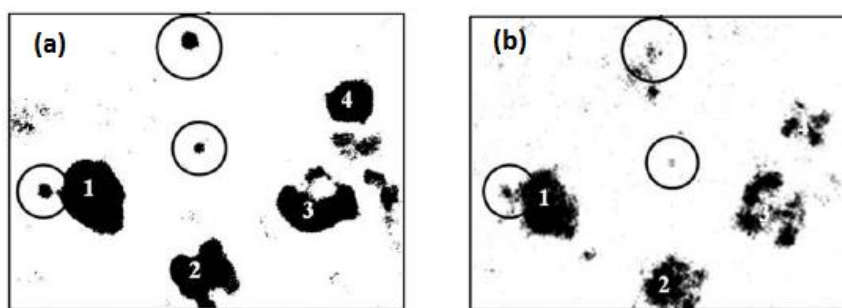


Figure I-16: In situ stability of typical nano-precipitates in Fe18Cr-Y₂O₃ under irradiation up to 23 dpa. Processed images a) BF TEM before irradiation b) DF TEM at 23 dpa ^[57].

1.2.4. Conclusions

ODS ferritic or martensitic steels are based on Fe-Cr matrix and reinforced by nanometer scale oxide (for example, Y₂Ti₂O₇) particles. They are being developed and investigated for nuclear fission and fusion

applications in Japan ^[16-18], Europe ^[19, 20], and the United States ^[21]. To fabricate the ODS alloys, several procedures are performed. Mechanical alloying is considered as the critical step. It results in the formation of crystal defects such as dislocations, vacancies, stacking faults, and increased number of grain boundaries in the grains. The presence of this defect structure enhances the diffusivity behavior of solute elements. The excess vacancies introduced are considered by some researchers having the critical role in nanoparticles formation and stabilization ^[24].

The ferritic or martensitic Fe-Cr matrix (bcc structure) is chosen for ODS steels to avoid the swelling under irradiation. ODS steels contain different amounts of Cr (9-18wt.%) which guarantee the good corrosion resistance and also favourable mechanical properties. The addition of Yttria (Y_2O_3) particules increases creep strength of ODS steel by solid solution hardening ^[17]. Ti contributes to forming the Y-Ti-O nanoparticles in finer size resulting in an increase of creep rupture strength ^[33-35].

The ODS steel has good thermal creep resistance at high operating temperatures ($T > 550^\circ C$). It also shows a much better swelling behavior than austenitic steels because of their bcc structure. In addition, very fine homogeneously distributed particles can act as sinks for helium preventing it from the formation of detrimental voids along the grain boundaries and thus reduce high-temperature helium embrittlement. The nanoclusters in ODS steels are considered as stable under irradiation.

1.3. Formation mechanism of oxides nanoparticles in ODS alloy

As explained above, the nanoclusters in ODS steels are believed critical to the high temperature strength and potential radiation resistance. Thus, in this section, the existing works about the characterization of nanoparticles (chemical composition, distribution, number density, size and structure) and their clustering mechanism at different scales (macroscopic and atomic scale) are described. Then, the role of vacancy defects is discussed.

1.3.1. Characterization of nanoparticles

a) Chemical composition, distribution, number density and size

H.Sakasegawa et al. ^[58, 59] have studied the commercial ODS ferritic alloy MA957, with nominal compositions of Fe-14Cr-0.3Mo-1.0Ti-0.25 Y_2O_3 in wt%, by using the Field Emission Gun- Transmission Electron Microscope (FE- TEM: JEOLJEM-2010F, Spot size: less than 2 nm) with an Energy Dispersive X-ray Spectrometry system (EDS: Oxford Link-ISIS). As shown in Figure I-17 (a), TEM image of sample shows that there exist both very small particles less than about 5 nm in size and coarse aggregated particles about 200 nm in size. The nature of these different types of oxides depends on their size as shown in Figure I-17 (b):

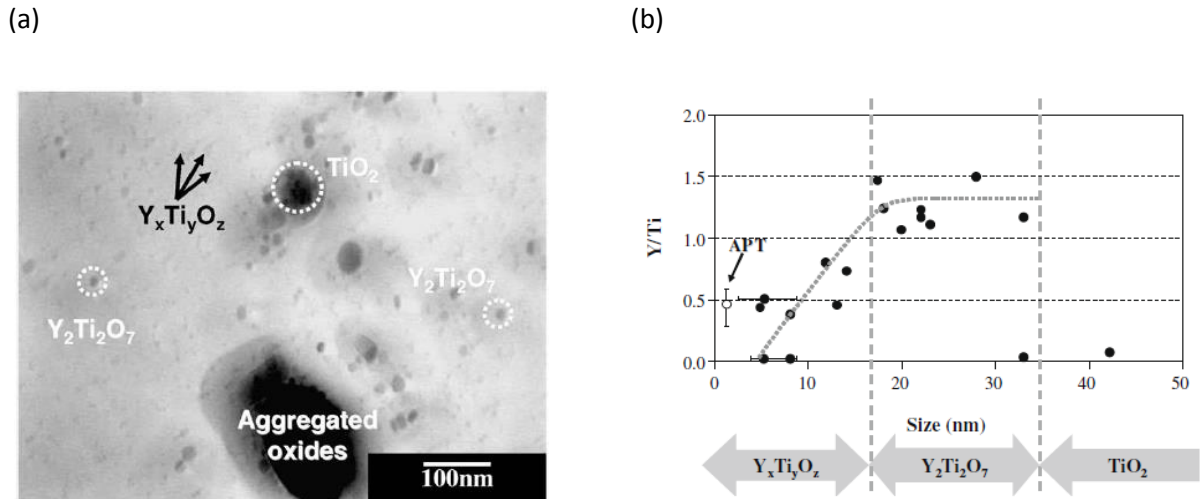


Figure I-17: (a) TEM image of extraction replica of MA957 showing different types of precipitates. (b) Correlation between chemical composition and size of oxide particles ^[58].

- 1) Non- stoichiometric very small Y-, Ti-, O- enriched clusters from ~2 to ~15 nm ($Y/Ti < 1$);
- 2) Stoichiometric $Y_2Ti_2O_7$ particles from ~15 nm to ~35nm (Y/Ti constant at ~1.4);
- 3) TiO_2 particles larger than ~35 nm with low yttrium content.

The ratio of yttrium content divided by the titanium one increases with increasing particle size up to 15 nm and then saturates in the range up to 35 nm. The non-stoichiometric very small Y-, Ti-, O- enriched clusters have been experimentally confirmed as playing a major role in strengthening of the steel ^[60]. The Y/Ti ratio of most very small particles is less than about 0.5 and thus it is suggested that the appropriate increase of the titanium content compared to the yttrium one could be an effective way to increase the number of very small oxide particles by modifying the chemical composition of the bulk. However, the added titanium could also contribute to the formation of TiO_2 particles with larger sizes which degrade the creep property of ODS alloys ^[61].

The stability and evolution mechanism of non-stoichiometric nanoclusters ($Y_xTi_yO_z$) of MA957 ODS alloy during annealing at 1473 K for one hour are also studied by H.Sakasagawa et al. ^[59]. As shown in Figure I-18(a), the correlation between Y/Ti and size for $Y_xTi_yO_z$ particles did not change. Some $Y_xTi_yO_z$ particles with higher original yttrium content could become $Y_2Ti_2O_7$ particles. As for $Y_2Ti_2O_7$, the maximum size increased from about 30 nm to about 45 nm. The evolution of oxide particles could be explained by yttrium diffusion during annealing as illustrated in Figure I-18(b).

It is also noted that large titanium oxides existing in material have a Y-enriched shell as shown in Figure I-20. The difference of the Y/Ti ratio between the centre and the edge of a particle is observed. The result obtained by Yamashita et al. ^[62] support this structure. These titanium oxide particles with the Y-enriched shell grow during annealing at 1473 K as shown in Figure I-19. It is noted that the doubled value of the shell thickness increase is equal to the value of the increase in diameter of particle. Thus, the growth of such large titanium oxide particles can be interpreted by the growth of thickness of the Y-

enriched shell. Yttrium diffusion probably controlled the evolution mechanism for the large titanium oxide particle as illustrated in Figure I-20.

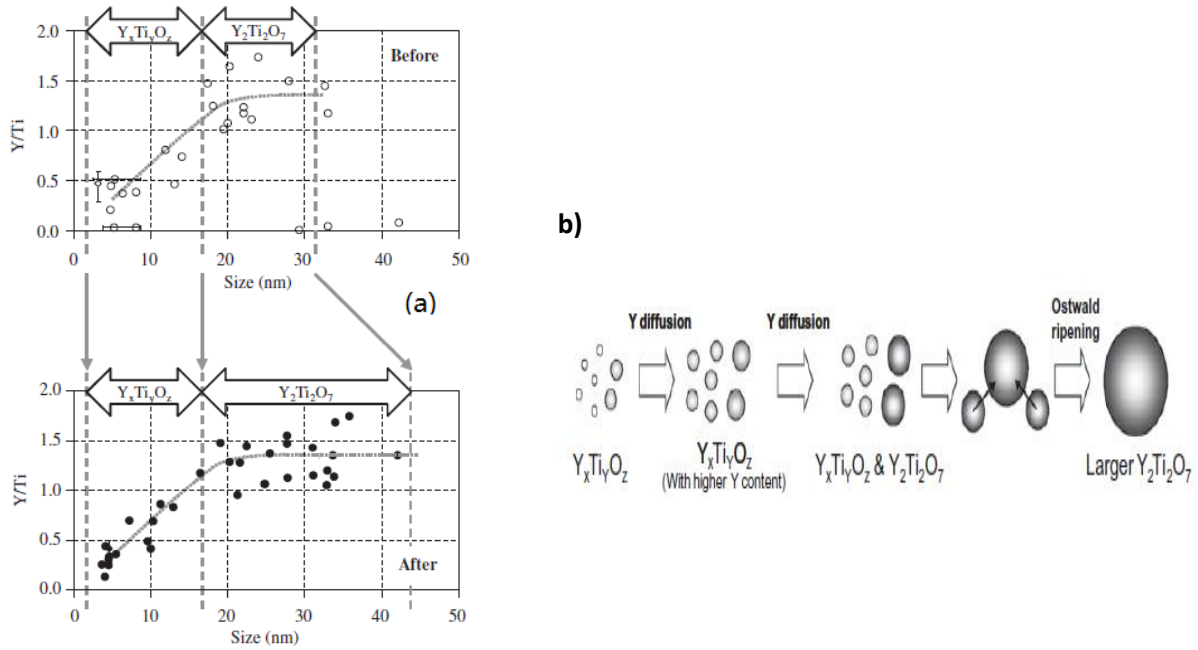


Figure I-18: (a) Correlation between Y/Ti ratio and size of the nanoparticles before and after annealing. (b) Schematic illustration for evolution mechanism of $Y_xTi_yO_z$ and $Y_2Ti_2O_7$ oxides [59].

These results suppose that yttrium diffusion has an important role in the evolution of the oxides. M. Allinger determined the yttrium diffusion coefficient in iron by fitting a classical nucleation-growth-coarsening model to small-angle neutron scattering data [63, 64]. The experimental values are calculated by equation 2. With these values, the Y diffusivity is approximately 400 times less than Fe at 1125 K. The Y diffusion coefficient in bcc Fe is also calculated using Le Claire's nine frequency model by D. Murali et al. [65]. It is noted that the diffusion coefficient of Y calculated by them is three orders of magnitude higher than the value obtained by experiment [63, 64]. But the calculated diffusion coefficient of host Fe is one order of magnitude lower than the experimental value. Thus in this calculation, the Y diffusivity is higher than that of Fe. The contradiction between experiment and calculation shows more direct experimentation of diffusion of Y in pure bcc Fe is necessary.

$$D_{Fe}^{Fe} = 6 \times 10^{-4} \exp\left(-\frac{2.91 \text{ (eV)}}{k_B T}\right) (\text{m}^2 \text{ s}^{-1})$$

$$D_Y^{Fe} = 1 \times 10^{-5} \exp\left(-\frac{3.10 \text{ (eV)}}{k_B T}\right) (\text{m}^2 \text{ s}^{-1})$$

$$D_O^{Fe} = 4 \times 10^{-5} \exp\left(-\frac{1.67 \text{ (eV)}}{k_B T}\right) (\text{m}^2 \text{ s}^{-1}). \quad (2) [63]$$

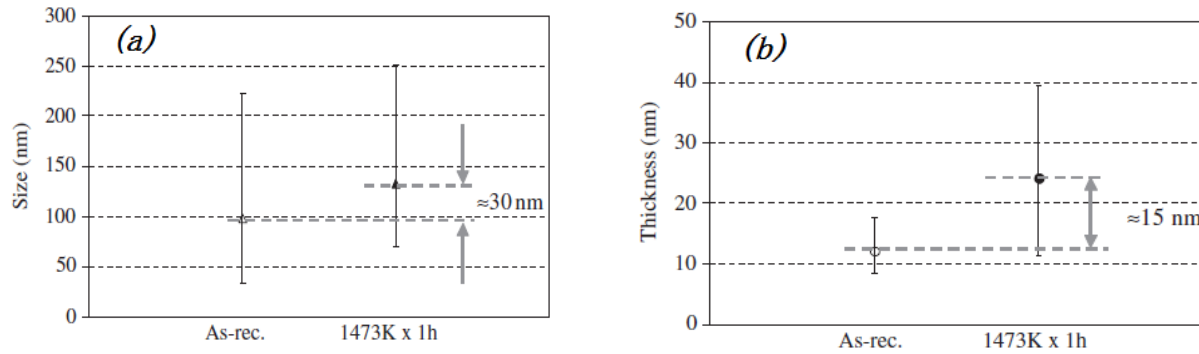


Figure I-19: (a) change of diameter and (b) of shell thickness of titanium oxide nanoparticles after annealing at 1473 K during 1 hour ^[59].

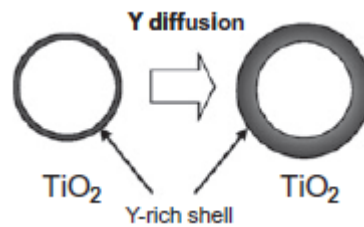


Figure I-20: Schematic illustration of the evolution mechanism of large titanium oxide nanoparticles ^[59].

In addition, many works have been realized to characterize microstructure of ODS steel by different techniques mainly by Transmission Electron Microscopy (TEM) and Atom Probe Tomography (APT). It should be noted that the size of the analysed particles is different between TEM and APT. APT observes very small oxides particles less than few nanometres in diameter, whereas TEM mainly analyses larger oxide particles with about several tens of nanometers in diameter. Thus, it is found that the nature of dispersed oxide particles varies in a wide range among different techniques. Summary of observed oxides in different ODS steels are shown in [Table I-3](#). It has to be noted that stoichiometric particles, like $\text{Y}_2\text{Ti}_2\text{O}_7$, TiO_2 , Y_2TiO_5 and YTiO_3 , are detected by TEM because of their relatively large size. On the contrary, non-stoichiometric very small Y-, Ti-, O- enriched clusters are detected by APT. It has also been noted that the Y/Ti ratio of these very small non- stoichiometric Y-, Ti-, O- enriched clusters is less than 1 and that the O concentration is high.

ODS alloy	Fabrication route	Characterization method	Oxides informations
Fe-12Cr-3W-0.4Ti+0.25Y ₂ O ₃ (Wt%) ^[60]	MA+HE at 1175°C	TEM; APT	TEM: Y ₂ Ti ₂ O ₇ , 19.8±7.6 nm; TEM: TiO ₂ : 50- 200 nm;
Fe-12Cr-3W-0.4Ti+0.3Y ₂ O ₃ (Wt%) ^[60]	MA+HE at 850°C	TEM; APT	TEM: TiO ₂ : >10 nm; APT: Fe-43.9±6.7%Ti-6.9±5.8%Y-44.7±4.0%O-1.1±1.1%Cr, 0.9±0.2nm, 1x10 ²³ m ⁻³
Fe-12Cr-2.5W-0.4Ti+0.25Y ₂ O ₃ (Wt%) ^[66]	MA+HE at 1150°C	APT	APT: Y-Ti-O rich nanoclusters, 1-5 nm, 1.1x10 ²⁴ m ⁻³
Fe-9Cr-0.5Ti+0.5Y ₂ O ₃ (Wt%) ^[67]	MA+HIP at 1050°C	TEM(EELS)	TEM: Y ₂ Ti ₂ O ₇ , ~10 nm;
Fe-19Cr-0.3W-0.3Ti+0.3Y ₂ O ₃ (Wt%) ^[68]	MA+HE	TEM(EDS), XRD	TEM: Y ₂ Ti ₂ O ₇ , ~3.7 nm;
Fe-16Cr-0.1Ti+0.35Y ₂ O ₃ (Wt%) ^[51]	MA+HE at 1150°C	TEM(EDX)	HRTEM: Y ₂ Ti ₂ O ₇ or Y ₂ TiO ₅ , ~11 nm;
Fe-14Cr-2W-0.3Ti+0.3Y ₂ O ₃ (at%) ^[69]	MA+HIP at 1150°C	APT, HRTEM	APT: Y:Ti _{1.75} :O _{3.5} , 2.5±0.1nm, 4±0.5x10 ²³ m ⁻³ ; HRTEM: YTiO ₃ , ~10 nm
Fe-14Cr-0.3Mo-0.9Ti+0.25Y ₂ O ₃ (Wt%) ^[70]	Commercial alloy as-received	APT	APT: Fe-32.9±5.3at%Ti-15.4±7.3%Y-39.9±6.9%O-1.7±1.7%Cr, 0.02±0.2%Mo, 1.2±0.4nm, 2x10 ²⁴ m ⁻³
Fe-14Cr-0.3Mo-0.9Ti+0.25Y ₂ O ₃ (Wt%) ^[70]	Commercial alloy annealed for 1h at 1300°C	APT	APT: Fe-21.3±7.9at%Ti-8.9±5.8%Y-47.8±23.3%O-4.2±4.2%Cr, 0.03±0.1%Mo, 1.7±0.4nm, 2x10 ²³ m ⁻³
Fe-12Cr-3W-0.4Ti+0.25Y ₂ O ₃ (Wt%) ^[71]	MA+HE at 1150°C	APT	APT: 21.6at.%Ti-17.2%Y-19.3%O-1.11%Cr-0.83%W, 3-5 nm

Table I-3: Summary of the nature, size and density of observed oxides in different ODS alloys. MA represents mechanical alloying; HE represents hot extrusion; HIP represents hot isostatic pressing.

b) Structure of nanoparticles

Marquis^[72] has studied the small nanoparticles of MA957 ODS alloy (nominal composition: 14Cr, 0.9Ti, 0.3Mo and 0.25Y₂O₃; hot extruded at ~1150°C) by APT. A core/shell structure is found for these nanoparticles. As shown in Figure I-21(a), the particles in MA957 with size ~4 nm consist of a Y, Ti, O rich core and a Cr rich shell. The core compositions are 42.8±3.6%O, 37.9±3.0%Ti, 14.6±1.2%Y, 4.6±1.0%Cr. As the size increases, the distinction between core and shell becomes clearer as illustrated in Figure I-21(b) for larger particles with size ~8 nm. Marquis suggested that this structure may be governed by the interfacial energy between the oxide phases and the surrounding matrix. The oxide particles may have a high nucleation barrier and the presence of a shell would decrease the interfacial energy, favouring the

nucleation of the oxide particles. This core/shell structure is also observed in other studies of ODS alloys [73-75]

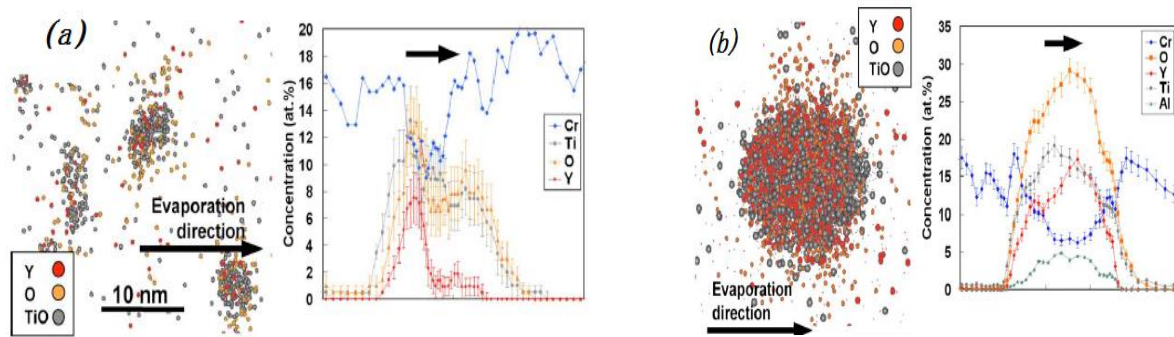


Figure I-21: 3D reconstructions of structures of particles (a) with size ~4 nm (b) with size ~8 nm in MA 957 [72].

Hsiung et al. [76-78] studied crystal and interfacial structures of oxide nanoparticles in 16Cr-4.5Al-0.3Ti-2W-0.37Y₂O₃ ODS ferritic steel by using high-resolution transmission electron microscopy (HRTEM) techniques. A structure with an Y₄Al₂O₉ core associated with a shell is observed in both large (>20 nm) and small nanoparticles (<10 nm). And it is noted that the shell is amorphous as shown in **Figure I-22**. The author suggests that amorphous shell results in a partial crystallization during consolidation of amorphous nanoparticles introduced by MA process. The solute-enriched shell forms when the solute depletion rate -due to the core building- is greater than the solute diffusion rate from the oxide/matrix interface during the crystallization stage. It is also remarked that the core/shell structure disappears after prolonged annealing treatment (900°C/168 h) for particle with diameter larger than 20 nm, indicating that these core/shell structures are far from chemical equilibrium.

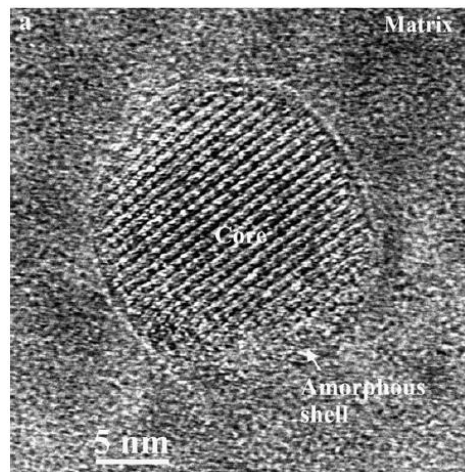


Figure I-22: HRTEM image of a large nanoparticle (>20 nm) in 16Cr-4.5Al-0.3Ti-2W-0.37Y₂O₃ ODS ferritic steel: incoherent interface associated with a core/shell structure [76].

I.3.2. Nanoparticles clustering mechanism

a) Macroscopic scale formation mechanism

Based on the observation of core/amorphous shell structure for oxide nanoparticles in 16Cr-4.5Al-0.3Ti-2W-0.37Y₂O₃ ODS ferritic steel, Hsiung et al. [76-78] have proposed a formation mechanism of nanoparticles including three stages as shown in Figure I-23(a):

- (1) Fragmentation of starting Y₂O₃ particles during early stages of MA;
- (2) Agglomeration and solid-state amorphization of Y₂O₃ fragments mixing with matrix constituents during later stages of MA. This initiates the formation of some clusters and agglomerates (designated as [MYO], M: alloying elements) in the Fe-Cr matrix;
- (3) Crystallization of the amorphous agglomerates larger than ~ 2nm to form oxide nanoparticles with a core/shell structure during the consolidation at 1150°C. Agglomerates or clusters smaller than ~ 2 nm remain amorphous as illustrated in Figure I-23(b).

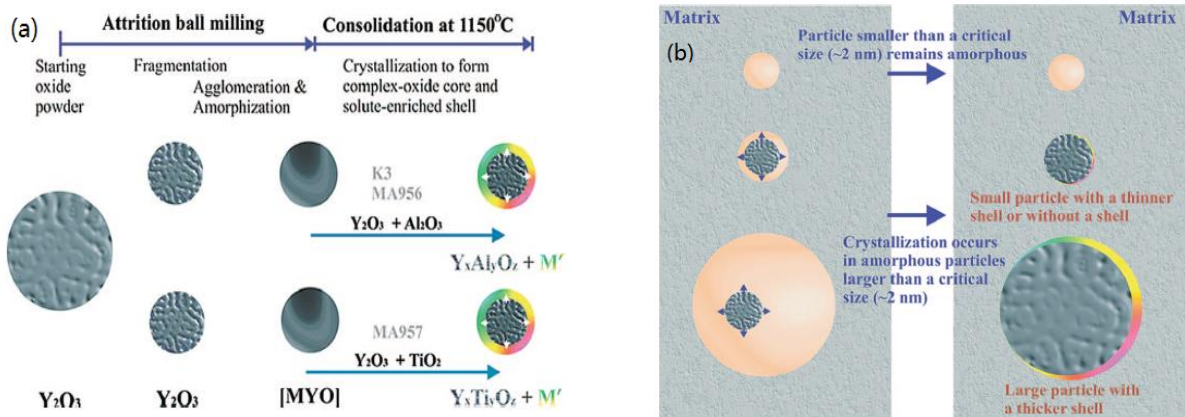


Figure I-23: (a) a three-stage mechanism for the formation of oxide nanoparticles containing a core/shell structure during MA and consolidation for Al as well as for Ti-containing ODS steel. (b) Size effect on the formation of core/shell structures in oxide nanoparticles. A solute-enriched shell can form in particles larger than 2 nm when solute depletion rate from the core is greater than solute diffusion rate from the oxide/matrix interface during the crystallization stage; a particle smaller than 2 nm remains amorphous [77].

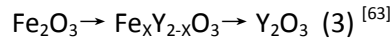
b) Atomic scale formation mechanism

The atomic-scale formation mechanism of these Y- Ti- O nanoparticles that affects the optimal processing method and their performance in extreme environments has not been clarified. Thus, it is necessary to understand their kinetic pathway of precipitation during MA and heat treatments.

C. Hin et al. [63, 79, 80] studied the homogeneous precipitation in Fe- Y- O and Fe- Ti- O ternary alloys during heat treatments by using Kinetic Monte Carlo simulations, shedding light on the complex kinetic

pathway to precipitation in Fe- Y- Ti- O quaternary alloys. The KMC simulations are performed on a rigid bcc lattice, with oxygen atoms placed on the octahedral sites and Fe, Ti or Y atoms placed on substitutional sites. Thus, the diffusion of Fe, Ti, Y and O atoms occurs by a realistic mechanism, which involves a vacancy or interstitial jump. The diffusion coefficients of Fe, Y, O ^[63] and Ti ^[79] in bcc iron are included as the kinetic parameters in the simulations. But it should be noted that these diffusion coefficients are not obtained by direct experimentation in pure bcc Fe, thus they could be discussed. The solubility limits and pair interaction energies (between entities: Fe, Y, Ti, O, vacancy) are included as the thermodynamic parameters.

For Fe- Y- O ternary alloys ^[63], three types of KMC simulations have been realized: 1) an iron solid solution with 0.12 at.% of Y and 0.18 at.% of O during isothermal heat treatment at 1125K; 2) an iron solid solution with 0.12 at.% of Y and 0.18 at.% of O during an anisothermal heat treatment, with a temperature heating rate of 20 K/min, up to 1125K; 3) an iron solid solution with 0.25 at.% of Y and 0.37 at.% of O during an anisothermal heat treatment. The similar kinetic precipitation path is observed for three conditions as explained by equation 3. There is an initial formation of a transient, metastable iron oxide phase Fe₂O₃, which forms due to the rapid diffusion of O relative to Y, and due to the existence of a driving force for iron oxides precipitation. After, it is followed by the nucleation of Y₂O₃ precipitates, which occurs within the Fe₂O₃. The phase, called Fe_xY_{2-x}O₃, grows with a decrease in Fe content and an increase in Y content. Finally, these precipitates are ultimately approaching the stoichiometric composition of Y₂O₃. An effect of the heat treatment can be observed looking at the size and number density of the precipitates. A higher density of smaller precipitates appears during the anisothermal heat treatment. The higher Y, O concentrations do also favor a higher density of smaller precipitates. The authors believe that the low Y diffusion coefficient accelerates the nucleation and early growth stages, but slows down the subsequent coarsening of the precipitate distribution. Again, the more direct experimentation of diffusion of Y in pure bcc Fe is necessary to validate this hypothesis.



For Fe- Ti- O ^[79] ternary alloys, KMC simulation has been realized for an iron solid solution with 0.25 at.% of Ti and 0.37 at.% of O during an anisothermal heat treatment, with a temperature heating rate of 20 K/min, up to 1125K. Compared to the third simulation for Fe- Y- O ternary alloys that has the same condition, the path of Fe- Ti- O precipitation is practically the same: formation of a Fe₂O₃ metastable phase followed by Fe_xTi_{2-x}O₃ precipitates approaching the stable Y₂O₃ phase. But their kinetics are not the same. At the end of the anisothermal heat treatment at 1125 K, the system remains with $4.2 \times 10^{24} \text{ m}^{-3}$ Fe_xY_{2-x}O₃ (with X ~ 0.5) precipitates containing 15 atoms per precipitate (~ 0.5 nm) for the Fe- Y- O alloy, while it remains a density of $5.2 \times 10^{23} \text{ m}^{-3}$ of Fe_xTi_{2-x}O₃ (with X ~ 1.2) precipitates containing 100 atoms per precipitate (~ 1.2 nm) for the Fe- Ti- O alloy. The system has just reached the coarsening type reaction of the Fe_xY_{2-x}O₃ precipitates, while it is almost the end of the coarsening type reaction of the Fe_xTi_{2-x}O₃ precipitates. Hence, 200 precipitates remain in the simulation box for the Fe- Y- O ternary alloy, while only 7 precipitates remain for the Fe- Ti- O system. The authors ascribe this difference to the diffusion coefficients difference between Y and Ti atoms. The authors consider that the Ti diffusion

coefficient is about 10^5 times faster than the Y diffusion coefficient, whatever the temperature during the anisothermal heat treatment.

First-principles studies realized by C.L. Fu et al. ^[81] identify a vacancy mechanism for nucleation of stable O-enriched nanoclusters in defect- containing Fe. Oxygen has high formation energy in the Fe lattice, indicating little solubility. But the authors found that the high affinity of O for vacancies reduces the O- vacancy pair formation energy essentially. Thus, they propose that the O- vacancy mechanism enables the nucleation of O- enriched nanoclusters, which attract solutes with high O affinities (Ti and Y).

But Jiang et al. ^[82] consider nanoparticles formation could take place without the presence of vacancies. Because these researchers think excess vacancies are not a persistent thermodynamic-energetic constituent of the Fe- Y- Ti- O system and will quickly annihilate at dislocations during high temperature powder consolidation. Their density functional theory (DFT) calculations show that $O_{int}+O_{sub}$ is the most stable pair followed by O-Y and O-Ti which could act as the basic building blocks for the initial formation of NCs (nanoclusters).

The ab initio calculations realized by A. Claisse and P. Olsson ^[83] show that a vacancy can increase considerably the binding energy for (Y, Ti, O) clusters. It is of prime importance when it comes to explaining the slow diffusion of an Y atom. The authors also find that the most stable cluster nuclei should form as planar structures of O and Y in the same fashion with Ti decorating the edge as shown in Figure I-24. The planar form of these clusters can be explained by the asymmetric O- O interaction. The ab initio study by L. Barnard et al. ^[84] discovered that nanoclusters that are structurally similar to bulk Ti and Y oxides are significantly more stable than nanoclusters that are restricted to the Fe lattice. But the work of A. Claisse and P. Olsson ^[83] shows that coherent planar structures are much more stable than the incoherent ones used in the work of L. Barnard et al. ^[84].

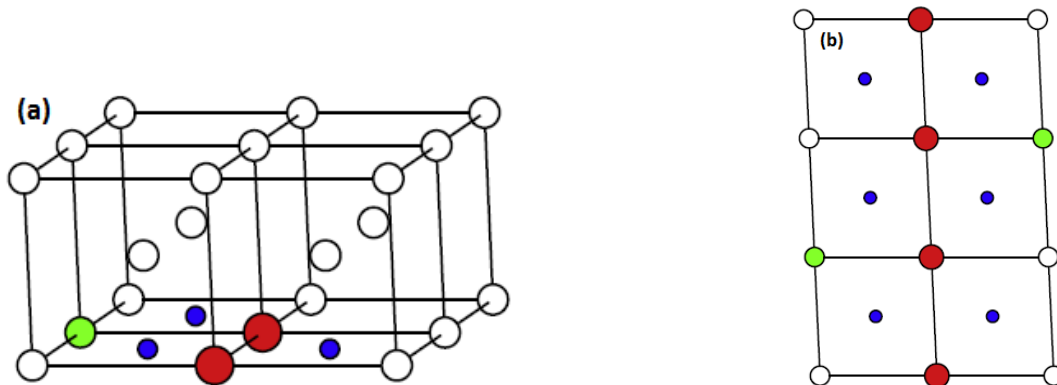


Figure I-24: Most stable configurations for (a) Y_2TiO_3 and (b) $(Y_2TiO_3)_2$. The blue atoms are oxygens, the red ones yttriums and the green ones titanium ^[83].

c) Role of vacancy in clustering

Jun Xu et al. ^[85] studied nanocluster associated vacancies in ODS ferritic steel by positron lifetime spectroscopy. Two types of materials have been compared. One is a MA ferritic steel containing Y, Ti, O nanoclusters (2- 4 nm in diameter) observed by atom probe tomography. The other is a similar MA steel

which does not contain nanoclusters and is called no- MA. By positron lifetime study, they indicate that vacancy clusters containing four to six vacancies have been found in the MA steel but not in the no- MA steel. Thus, they conclude that vacancies are a vital component of the nanoclusters in MA ODS steel. But it should be noted that the authors have not mentioned that positrons could be also trapped by Y, Ti, O nanoclusters without vacancies which could give a positron signal approaching the one given by vacancy clusters. In fact, positrons can be trapped in clusters of elements that have a higher positron affinity than that of the matrix. The positron affinities for elements in ODS steel are: Fe= -3.84 eV, Cr= -2.62 eV, Y= -5.31 eV, Ti= -4.06 eV^[86]. The affinity differences essentially represent the trapping energy for a positron. For example, a positron would be trapped in a pure Y phase in an iron matrix with a binding energy of about 1.5 eV^[87]. The positron lifetimes are about 180 ps in TiO₂^[87], 200 ps in TiO^[88], 240 ps in Y₂O₃^[89] whereas it is 180 ps in mono- vacancy^[90]. Jun Xu et al.^[85] detected one positron lifetime of 273 ps and considered it as the signal of vacancy clusters containing four to six vacancies. But as we discussed, this positron lifetime could also be due to the nanoclusters like Y₂Ti₂O₇ which could have the lifetime around 273 ps. Thus, the authors' conclusion could be incomplete.

M.J. Alinger et al.^[87] studied ODS alloy produced by MA Fe- 14Cr- 3W- 0.4Ti and 0.25Y₂O₃ (wt.%) powders by positron annihilation lifetime and Doppler broadening spectroscopy. The characteristic annihilation momentum signatures for positrons trapped in Y₂O₃, TiO₂, Ti₂O₃ and Ti have been determined as shown in Figure I-25. It indicates that the technique which will also be used in this thesis is capable in distinguishing these clusters. But it should also be noted that the methods and qualities of preparing these samples for positron measurements have not been reported in this work. Thus, the S and W values corresponding to annihilation in these features could be discussed. In Figure I-25(b), it is remarked that the SW points for the U14YWT ODS alloy fall on a line connecting Fe and Y₂O₃. It is consistent with an increasing number density of nanofeatures that are present for all the U14YWT HIP conditions. While it is not quantified, the SW points for vacancy clusters would also fall towards the lower right side of the Figure I-25(b), mimicking to some extent Ti and Y₂O₃. Thus a fraction of annihilations at such features cannot be excluded. The positron lifetime measures in U14YWT found a short lifetime of 154- 172 ps, consistent with a mixture of annihilation at dislocations (~ 140- 170 ps^[91, 92]) and mono- vacancy (~ 180 ps^[90]), and also a long lifetime ranging from ~ 280 to 300 ps, consistent with a combination of vacancy clusters (for example, ~ 9 vacancies: ~ 290 ps^[87]) and oxide features such as in Y₂O₃ (~ 240 ps^[89]).

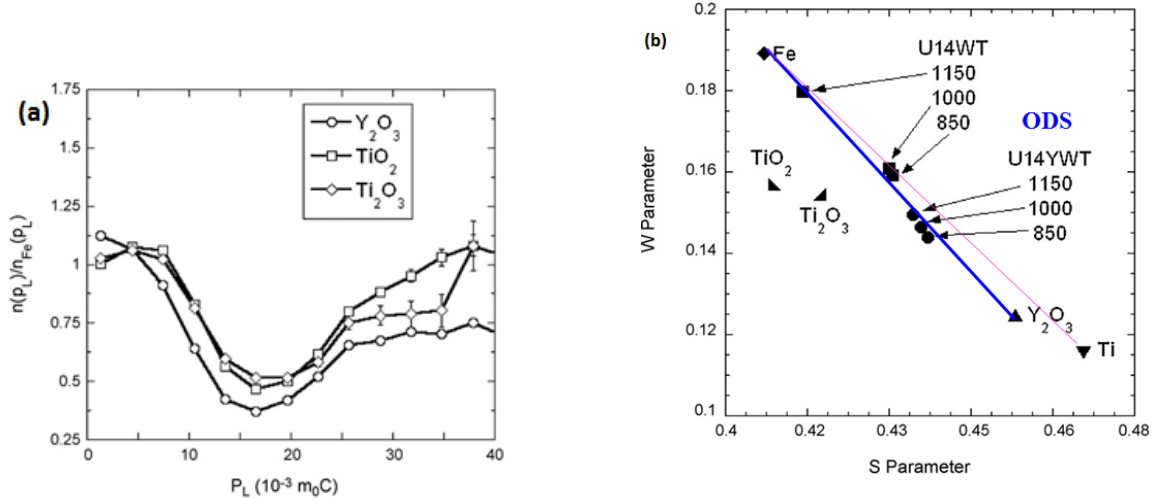


Figure I-25: (a) Measured momentum distribution of the electron-positron annihilated pairs $I(p_L)$ characteristic of oxides Y_2O_3 , Ti_2O_3 and TiO_2 normalized by dividing with the $I(p_L)$ for unalloyed Fe. (b) PAS S-W (see chapter 2 of this thesis for detailed definition) analysis of the nanofeatures (NFAs) compared to several reference materials ^[87].

A positron annihilation lifetime study has also been performed on various commercial ODS steels by V.Krsjak et al. ^[93]. A long lifetime component of 240 ps, was found. The authors assigned this value to both Y_2O_3 ^[89] nanoparticles and small clusters with the mean size of 4- 5 vacancies. Reasonable estimates for the fractions of positrons trapped in four- vacancy clusters and positrons trapped in nanofeatures have been made. The calculated densities of vacancy clusters (4 vacancies) are in the range of 6.0×10^{22} - $5.5 \times 10^{23} m^{-3}$. Thus, the presence of vacancy type defects seems to stabilize the oxide particles.

Y.Ortega et al. studied ODS EUROFER alloy by using positron lifetime, coincidence Doppler broadening (CDB) and Transmission electron microscopy ^[94, 95]. The electron-positron annihilated pairs momentum distributions for pure Fe, Y and Y_2O_3 normalized to the one of EUROFER obtained by CDB also called CDB ratios are shown in Figure I-26. Again, the qualities of preparing samples for positron measurements have not been reported in this work. Although the absolute CDB ratio could be discussed, these results show that the Yttrium environment at the positron annihilation site is clearly shown in these types of measurements. TEM observations as illustrated in Figure I-27, performed on samples of ODS- EUROFER after annealing at 1523 K, revealed the presence of voids associated with Y_2O_3 particles. One lifetime component is found to be between 240 and 340 ps. The authors attribute this value to voids containing between 3 and 15 vacancies ranges from 232 and 386 ps in α - Fe ^[96].

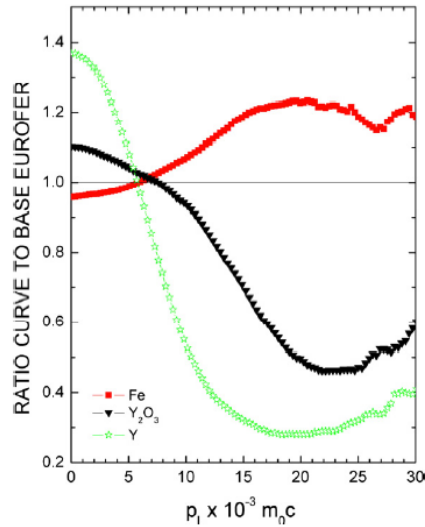


Figure I-26: CDB ratio spectra for pure Fe, Y and Y_2O_3 ^[95].

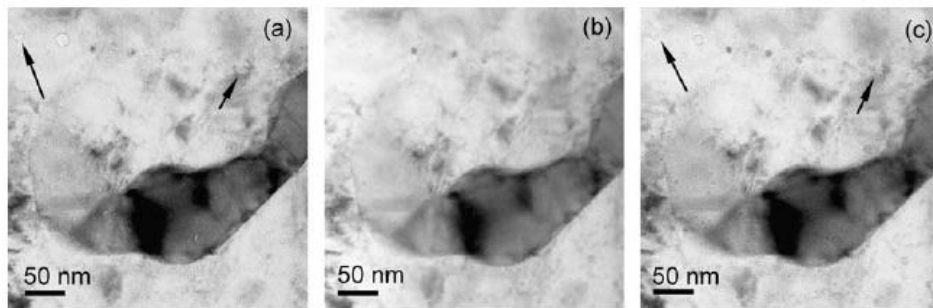


Figure I-27: TEM through- focal series of voids in the ODS EUROFER annealed at 1523 K. Some of the voids associated with Y_2O_3 particles are shown with arrows. (a) Underfocused by 1 μm , (b) in- focus and (c) overfocused by 1 μm ^[94].

All these positron studies of ODS alloys show that the positron annihilation spectroscopy is capable in characterizing the nanofeatures and vacancy clusters in ODS alloys although there are some limits. They also illustrate that vacancies have a no- ignored effect on the formation and stabilization of the nanoparticles in ODS alloys.

I.3.3. Conclusions

The nature of different types of nanoparticles in ODS steels depend on their size. Non-stoichiometric very small Y-, Ti-, O- enriched clusters are in size from ~ 2 to ~ 15 nm ($Y/Ti < 1$) and the stoichiometric $Y_2Ti_2O_7$ particles are larger from ~ 15 nm to ~ 35 nm (Y/Ti constant at ~ 1.4). The Y/Ti ratio increases with increasing particle size up to 15 nm and then saturates up to 35 nm. The diffusion of yttrium has an important role in the evolution of the oxides. However, the contradiction between experiment and calculation indicates more direct experimentation of diffusion of Y in pure bcc Fe is necessary. A core/shell structure is found for MA957 ODS alloy (nominal composition: 14Cr, 0.9Ti, 0.3Mo and 0.25 Y_2O_3 ; hot extruded at $\sim 1150^\circ C$) by APT ^[72]. The particles in MA957 with size ~ 4 nm consist of a Y, Ti,

O rich core and a Cr rich shell. The core compositions are $42.8 \pm 3.6\% \text{O}$, $37.9 \pm 3.0\% \text{Ti}$, $14.6 \pm 1.2\% \text{Y}$, $4.6 \pm 1.0\% \text{Cr}$. The studies of Hsiung et al. ^[76-78] show that this shell is amorphous.

A macroscopic three-stage mechanism has been proposed to explain the formation of oxide nanoparticles containing a core/shell structure during MA and consolidation: fragmentation, agglomeration and crystallization. The path of Fe- Y-O precipitation has been studied by using Kinetic Monte Carlo simulations and described as followed: There is an initial formation of a transient, metastable iron oxide phase Fe_2O_3 , which forms due to the rapid diffusion of O relative to Y, and due to the existence of a driving force for iron oxides precipitation. After, it is followed by the nucleation of Y_2O_3 precipitates, which occurs within the Fe_2O_3 . The phase, called $\text{Fe}_x\text{Y}_{2-x}\text{O}_3$, grows with a decrease in Fe content and an increase in Y content. Finally, these precipitates are ultimately approach the stoichiometric composition of Y_2O_3 . The Fe- Ti- O precipitation path is practically the same whereas their kinetics are not the same. This difference is ascribed to the diffusion coefficients difference between Y and Ti atoms. First-principles studies realized by C.L. Fu et al. ^[81] identify a vacancy mechanism for nucleation of stable O-enriched nanoclusters in defect- containing Fe. But Jiang et al. ^[82] consider nanoparticles formation could take place without the presence of vacancies.

The positron studies of ODS alloys show that the positron annihilation spectroscopy is capable in characterizing the nanofeatures and vacancy clusters in ODS alloys although there are some limits. They also illustrate that vacancies have a no-ignored effect on forming and stabilizing the nanoparticles of ODS alloys.

I.4. Properties of vacancy and its interaction with elements (Y, Ti, O) in Fe and FeCr matrix

In this section, the properties of point defects in bcc Fe and bcc FeCr matrix have been firstly presented. They are the basis to understand the interaction between vacancy defects and elements (Y, Ti, O) in bcc iron which is presented in the following.

I.4.1. Properties of point defects in bcc Fe matrix

The value of formation energy calculated by DFT for single vacancy in bcc Fe, E_f^V , is ranged between 1.5- 2.14 eV ^[97-102]. The formation energies for small vacancy clusters are also presented in Figure I-28 ^[103]. For interstitial, the calculations give $3 < E_f^I < 7$ eV for the value of formation energy ^[104]. This value is much higher than the one given for single vacancy. Thus, it is more difficult to introduce the interstitial than the vacancy in bcc Fe.

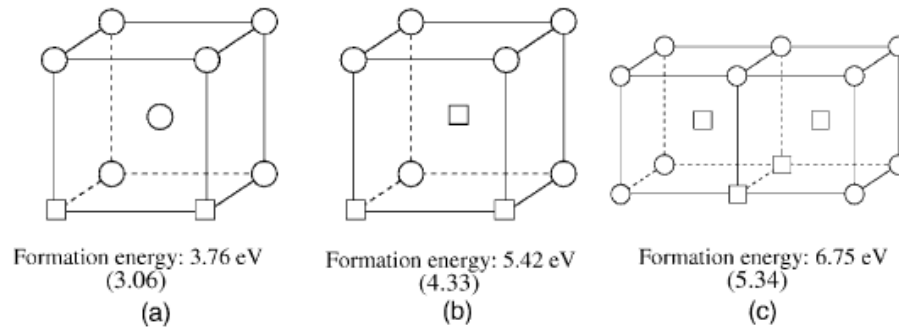


Figure I-28: Small vacancy clusters formation energies (128 atom supercells). The empty squares are vacancies; the empty circles are Fe atoms. Only the most stable configurations among the different cases studied are represented. (a) Two vacancies. (b) Three vacancies. (c) Four vacancies ^[103].

The binding energies of defect clusters are determined as illustrated in Table I-4 by ab initio calculations and for larger clusters an extrapolation law is used.

Binding energies (eV)	I_n	V_n
$n=2$	$0.80^{[105]}$	$0.30^{[105]}, 0.28^{[103]}$
$n=3$	$0.92^{[105]}$	$0.37^{[105]}, 0.36^{[103]}$
$n=4$	$1.64^{[105]}$	$0.62^{[105]}, 0.70^{[103]}$

Table I-4: The binding energy of interstitial or vacancy clusters.

The migration energies of interstitial or vacancy clusters have also been calculated by C.C.Fu et al as shown in Table I-5 ^[105, 106]. It has to be noted that the small migration energy of single vacancy and small clusters suggests that these defects should be mobile at room temperature. The lower migration energies of interstitial clusters indicate that they should migrate at lower temperature than vacancy clusters.

Migration energies (eV)	I_n	V_n
$n=1$	0.34	0.67
$n=2$	0.42	0.62
$n=3$	0.43	0.35
$n=4$	/	0.48

Table I-5: The migration energy of interstitial or vacancy clusters ^[105, 106].

These data reproduce successfully all the resistivity recovery stages after electron irradiation performed by Takaki et al. ^[107]. The experiments were made in high-purity electron irradiated iron with

irradiation doses in the range $\sim 2 \times 10^{-6}$ to $\sim 200 \times 10^{-6}$ dpa. Several stages have been revealed as illustrated in Figure I-29:

- Stage (I_{D2}), observed at 107.5 K, recombination of correlated defects, that is, of I- V pairs belonging to the same Frenkel pair by free migration of the interstitial;
- Stage (I_E), in the range 123- 144 K, recombination of I and V belonging to different Frenkel pairs, as a result of I migration;
- Stage (II), (164- 185 K), di- interstitial (I_2) migration;
- Stage (III), (220- 278 K), V migration;
- Stage (IV), (520- 550 K), dissociation of defect clusters formed at stage (III).

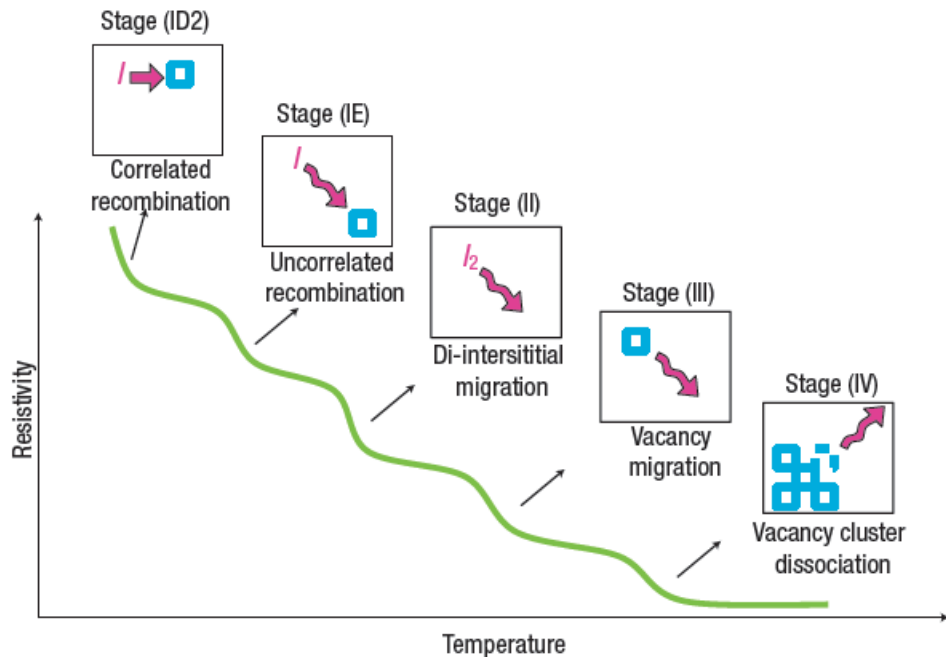


Figure I-29: Resistivity recovery stages after electron irradiation. Schematic representation of the different recovery stages as a function of increasing temperature and associated mechanisms as proposed in electron- irradiated iron by Takaki et al.^[107] The labels I, I_2 and squares represent mono- and di- interstitials and vacancies respectively^[105].

A stage (~ 423 K) between (III) and (IV) which is governed by the migration of vacancy clusters of size less than ten vacancies has been proposed by Yue Fan et al.^[108] using atomistic simulations. This stage (~ 423 K) matches quantitatively with PAS experiments on neutron irradiated single- crystal bcc Fe^[109]. It has been observed that the number of clusters with 6 or fewer vacancies undergoes a significant decrease at a temperature around 150°C , while correspondingly the number of larger vacancy clusters increases significantly. Yue Fan et al. believe that 150°C is a transition temperature for enabling the migration of vacancy clusters in a vacancy- supersaturated bcc Fe that leads to cluster accumulation. But

in the case of electron irradiation, this stage was not detected. The authors explained that it is because only a low density of vacancies is produced upon electron irradiation, making cluster formation and survival difficult. In contrast, in neutron irradiation it is possible to induce a supersaturation of vacancy defects, thus a higher probability to form clusters that can survive up to higher temperatures.

Positron annihilation spectroscopy has been used to understand defect formation in irradiated iron because of its sensitivity to the size and density of vacancy clusters in the range from mono-vacancies up to cavities containing 50-100 vacancies ^[109].

M.Eldrup et al. ^[109] studied dose dependence of defect accumulation in neutron irradiated iron. The irradiation was performed at temperatures in the range of 50°C - 70°C and at damage doses in the range of 10^{-4} to 0.23 dpa. The positron lifetime spectra were measured and the spectra were analyzed on the assumption that they were composed of five components in order to determine a multiple size distribution of the vacancy defects for different doses. Four of five components have been fixed: 200, 300, 400 and 500 ps, equivalent to three- dimensional vacancy clusters of sizes of about 0.35, 0.54, 0.73 and >1.0 nm in diameter as illustrated in Figure I-30. From the intensities of these lifetime components, the defect densities for the different cavity were estimated. The authors found that both the density and the average size increase with increasing dose.

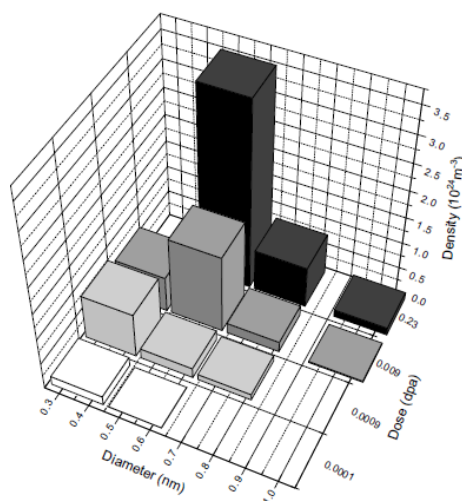


Figure I-30: Size distributions for three-dimensional vacancy clusters in Fe that was neutron irradiated to different doses (T_{irr} = 50- 70°C). The size is given by an equivalent diameter ^[109].

T. Iwai et al. ^[110, 111] studied accumulation of vacancy- type defects in iron produced by various ion irradiations (He, C, O, Fe) at room temperature, using positron beam Doppler broadening spectroscopy (see chapter 2 for detailed description of this technique). The depth profile of defect production as calculated by SRIM is presented in Figure I-31(a). The 15 keV positron beam was used so that most of implanted positrons stop in the damage region and are effectively trapped by defects. As illustrated in Figure I-31(b), S parameter increases with increasing fluence at initial stage of irradiation, and then tends to show an upper limit. The limit seems to be higher for the irradiations performed with the heavier ions. The authors conclude that the S value obtained at saturation reflects the open volume size of the

vacancy- type defects produced by each ion. The heavy ions providing greater PKA energy generate larger vacancy- type defects, very likely to be nanovoids at room temperature. Similar S parameters were obtained both in- situ and off- beam conditions as shown by solid symbols in Figure I-31(b), indicating the size of vacancy- type defects is not likely to change after irradiation and storage at room temperature. The authors explained that nanovoids which are likely to form spontaneously through cascade damage and subsequent short- range vacancy migration are thermally stable in this temperature range.

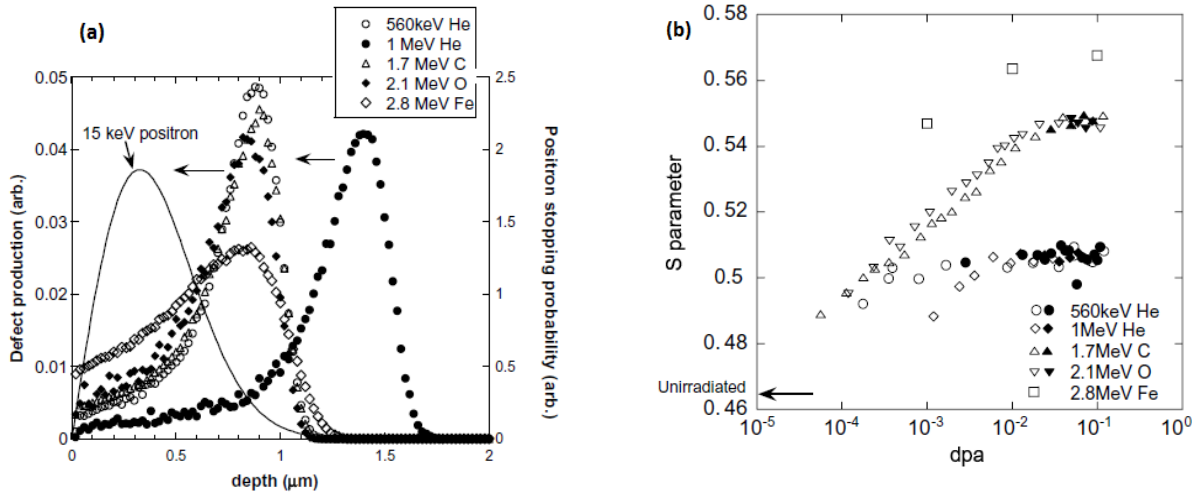


Figure I-31: (a) Depth profile of defect production and stopping probability of 15 keV positron. (b) Dose dependence of S parameter change in iron induced by various ion irradiations at room temperature. Measured with 15 keV positrons. Solid symbols express in- situ measurement^[110].

The defect accumulation was also investigated at low temperature (12 K) to reveal vacancy configurations after cascade, without any thermal migration after the cascade cooling^[111-113]. In this temperature below stage I defined by Takaki et al.^[107], vacancies and interstitials are immobile and can be suppressed by mutual annihilation and clustering after cascade processes. Under this condition where cascade structure is preserved, the ratio of vacancy concentration to NRT dpa can be treated as defect production efficiency η . Figure I-32(a) shows the dose dependence of the S parameter in iron at 12 K for H⁺ and C⁺ irradiation. The S parameter for both irradiations increased with dose then tended to saturate. This S parameter saturation likely occurs as a result of the high concentration of defects preserved without the subsequent thermal process. The increase of the S parameter with H⁺ irradiation is faster than that with C⁺ irradiation, and the saturated S value is similar for each ion. This value is much lower than the one obtained in Fe²⁺ irradiated iron at room temperature which corresponds to larger vacancy clusters as shown in Figure I-31(b). The authors assumed that almost all the trapping sites in this experiment are monovacancies and their concentrations C_v are estimated by using the specific trapping coefficient, μ value for monovacancies estimated by Vehanen et al.^[114]. As illustrated in Figure I-32(b), a linear increase of C_v with NRT dpa was observed up to 0.3 mdpa and the slopes of the lines are the defect production efficiencies. They are estimated to be 0.27 for 1 MeV H⁺ and 0.17 for 2.8 MeV C⁺. The values represent the difference in the primary knock- on atom energy spectrum of H⁺ and C⁺.

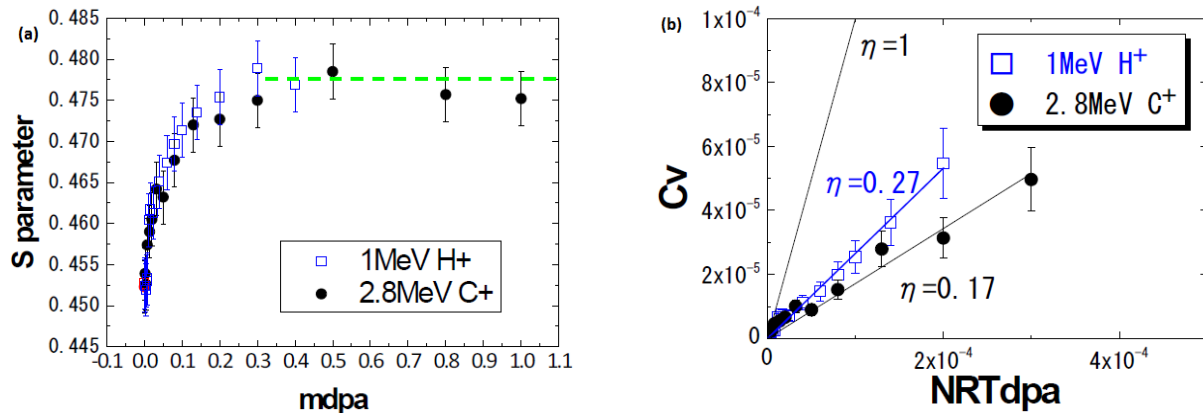


Figure I-32: (a) Dose dependence of S parameter at 12 K in iron. (b) Dose dependence of vacancy concentration calculated from measured S parameter ^[113].

An isochronal annealing of iron irradiated with 2 MeV He up to 1 mdpa at 12 K was also performed by T. Iwai et al. ^[111] and the S parameter evolution as a function of temperature is shown in Figure I-33. S parameter is almost stable from 12 to 140 K and then begins to increase from 140 to 220 K. This is interpreted as the beginning of vacancy migration and clustering around 140 K. This temperature range is much lower than the vacancy migration stage reported by Takaki et al. ^[107], 220- 278 K. T. Iwai et al. have explained that this discrepancy is attributable to the difference in defect configuration between electron and ion irradiation. While electron irradiation produces Frenkel pairs almost uniformly, ion irradiation produces cascade damage as well as simple Frenkel pairs. In the cascade region, the local concentration of Frenkel pairs is high, so that the distance between Frenkel pairs is short. This enables vacancies to aggregate easily and lowers the vacancy migration temperature range.

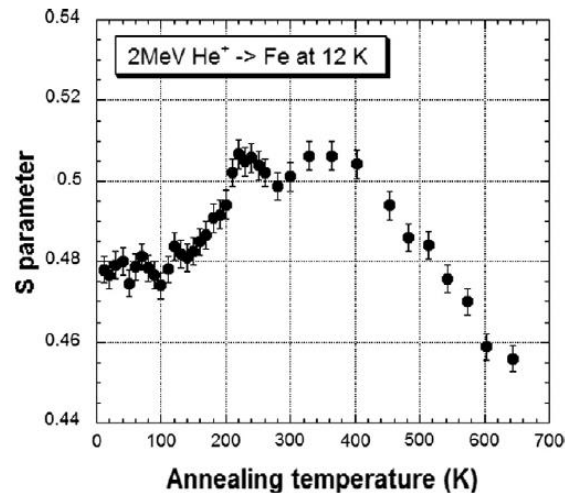


Figure I-33: S parameter change in irradiated iron with annealing temperature during isochronal annealing. 2 MeV He⁺ up to 0.1 mdpa measured by 15 keV positron. The sample was kept at 12 K throughout irradiation and measurement ^[111].

I.4.2. Properties of point defects in FeCr matrix

Emma del Rio et al. calculated formation energy of vacancies as a function of Cr concentration in FeCr alloys ^[115]. As shown in Figure I-34, for Cr concentrations above 6%, the values obtained show a linear dependence with the Cr concentration between the vacancy formation energy in iron (1.72 eV) and the vacancy formation energy in chromium (2.56 eV). However, for Cr concentrations below 6 at.% the vacancy formation energy is almost constant. The authors explained that if Cr atoms are further away than 2nd nearest neighbor position with respect to the vacancy they have a small effect on the formation energy value. This could explain the constant formation energy value for low Cr concentrations as there is a small probability of finding Cr atoms at 1nn or 2nn positions with respect to the vacancy, and the mean energy value obtained over the entire ensemble of possible configurations remains constant. In contrast, if Cr atoms are positioned at first or second nearest neighbor with respect to the vacancy, its formation energy increases as it is the case for high Cr concentration.

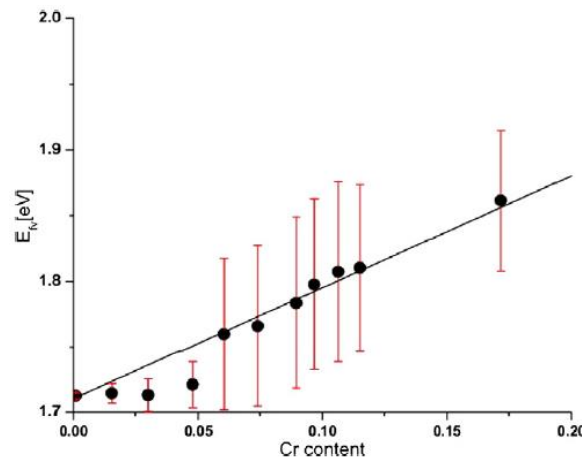


Figure I-34: Vacancy formation energy in FeCr and dispersion as a function of Cr content ^[115].

P.Olsson et al. studied Cr interactions with point defects in bcc Fe by Ab initio calculations ^[116]. The Cr-vacancy (VCr) binding energy is found to be small, about 60 meV in the first-nearest-neighbor, 7 meV in the second-nearest-neighbor and vanishes for larger separation distances. This result is in agreement with the experimental results of Möslang et al ^[117]. Using muon spectroscopy, they have estimated the VCr binding energy to be less than 105 meV. J.Kwon et al. ^[118] studied FeCr model alloys with different Cr contents irradiated with 2 MeV electrons by using positron annihilation spectroscopy and computer simulations. From Coincidence Doppler broadening measurements they showed that there was no significant difference in the high momentum region (defined by window W) of the spectrum between the irradiated pure Fe and Fe- Cr alloys as shown by the experimental results in Figure I-35. Thus, they concluded that no vacancy- Cr complexes were formed. But for the author of this thesis, this difference in the high momentum region is non- negligible. For better understanding of the results of this study, we have defined the parameters S and W. S represents the fraction of positrons annihilating with the electrons of low momentum in the range $(-2.49, 2.49) \times 10^{-3} m_0c$ defined for CEMHTI positron beam facility. W represents the fraction of positrons annihilating with the electrons of high momentum in the range $(-24.88, -9.64), (9.64, 24.88) \times 10^{-3} m_0c$. Just the positive part of the spectrum is presented in this

case. Now we note clearly that W parameter representing the high momentum region in Figure I-35 has evidently a non-negligible decrease. In fact, Nagai et al. ^[119] showed that the positrons annihilating with electrons of Cr results an increase of S and a decrease of W compared to the Fe. This corresponds well to the results of the Kwon et al study. Thus, the existence of V-Cr complexes should be discussed. In addition, the calculation shows that Cr atoms in bcc Fe have a lower barrier for vacancy (0.54 eV) assisted migration than Fe atoms do (0.71 eV). The migration energy is 0.17 eV lower for solute Cr than for the matrix atoms.

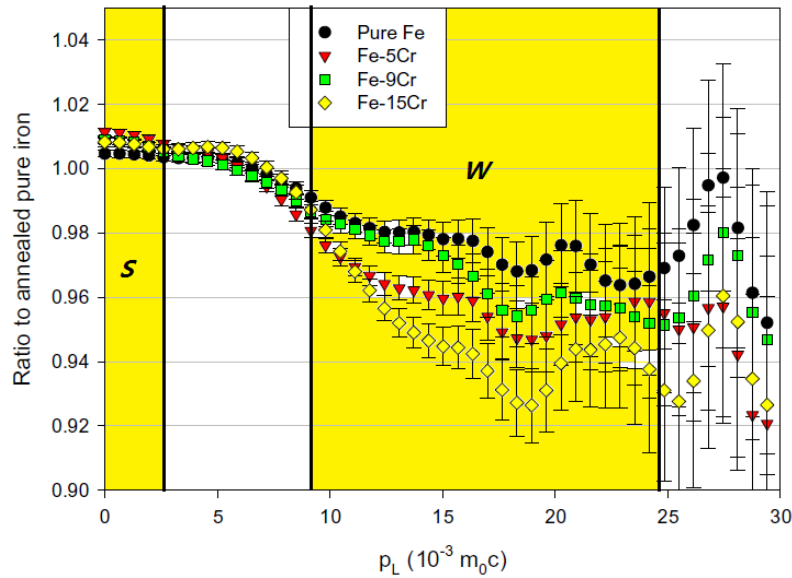


Figure I-35: Ratio curves of CBD spectra for electron- irradiated samples: pure Fe, Fe- 5Cr, Fe- 9Cr, Fe- 15Cr, normalized to the momentum distribution of well- annealed pure Fe ^[118].

The calculations of P.Olsson et al. show that Cr-Cr interactions are repulsive for all small Cr clusters considered (up to size four). The binding energies are negative and increase with the number of Cr- Cr pairs formed ^[116]. They have also studied the interactions of one and two Cr atoms with $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ self-interstitials by considering different possible configurations. It is found that $\langle 100 \rangle_{\text{Fe-Cr}}$ and $\langle 110 \rangle_{\text{Fe-Cr}}$ configurations have small binding energies (close to zero) while the $\langle 111 \rangle_{\text{Fe-Cr}}$ crowdion is more strongly bound, having binding energy 0.4 eV. The binding energies are generally found to be lower when two Cr atoms are associated with one Fe self-interstitial as compared to the case when only one single Cr atom is interacting with the Fe self-interstitial. This is coherent with the repulsion between two Cr atoms in substitutional positions. The binding interaction between $\langle 111 \rangle$ interstitials and Cr atoms will also slow down the diffusion of glissile interstitial loops. This should lead to an increased recombination with vacancies. In contrast, Cr-rich precipitates (α' phase) in Fe- Cr alloys will repel interstitial loops.

K. Arakawa et al. ^[120] studied the one- dimensional motion of interstitial- type dislocation loops in Fe- 9Cr ferritic alloy by in situ TEM. Loop motion is examined under 1000 keV high energy electron irradiation at temperatures ranging from 110 to 680 K and under thermal annealing from 295 K to 960 K after the irradiation performed at 110 K. Under high energy electron irradiation at comparatively high temperatures above around 450 K, Cr atoms are considered to suppress the motion of loops significantly

due to the segregation of Cr at the periphery of loops. In contrast, under irradiation at comparatively low temperatures below around 390 K, such segregation may not occur and the motion frequency of loops is only slightly reduced by Cr. In contrast, under thermal annealing after irradiation, the motion frequency of loops in Fe-9Cr is significantly reduced by Cr.

D. Terentyev et al. ^[121] used both ab initio and empirical potential based molecular dynamics and static calculations to parameterize a model accounting for the mobility of SIA clusters and small dislocation loops in Fe-Cr alloys depending on Cr content. They considered the interval of 5- 15% of Cr, corresponding to the typical concentration of Cr in ferritic/martensitic steels. They found a non-monotonic decrease of cluster diffusivity with the increase of Cr content: a) Small SIA clusters exhibit diffusivity minima in the 9-12% Cr range; b) with the increase of the cluster size the minima shift towards lower Cr concentrations; c) the interaction between fine Cr-rich precipitates and small dislocation loops is strongly repulsive, thus the mobility of dislocation loops increases. But where fine, dispersed α' - nuclei are formed, small dislocation loop mobility would reduce again because these clusters will get 'locked' between α' particles. By combining these three observations, they built the general picture of the swelling behavior versus Cr content as shown in Figure I-36. Effect (a) explains the swelling minimum experimentally observed at relatively low doses (1- 10 dpa) around 10% Cr, where α' formation is not expected. With increasing dose, the average size of self- interstitial clusters will also increase. As a consequence of effect (b), the swelling minimum will correspondingly shift towards lower concentration, in the range where α' precipitate cannot occur. The appearance of another swelling minimum in higher Cr-content alloys indicates that α' precipitation appears. It increases and then reduces again the mobility of dislocation loops.

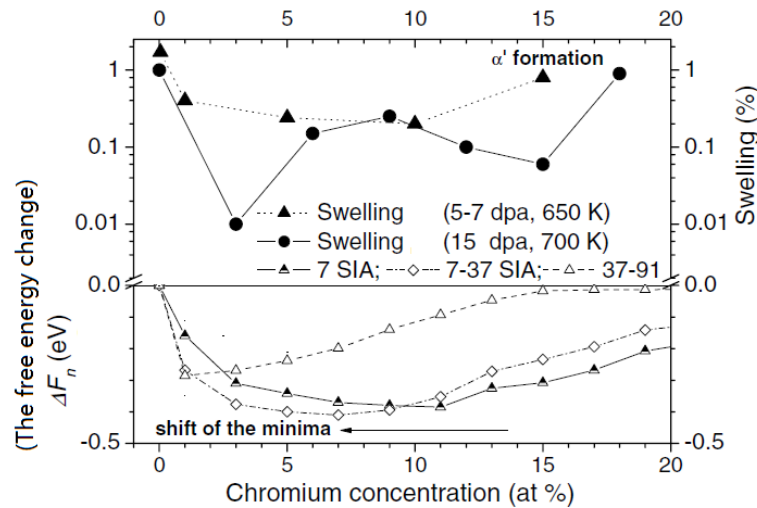


Figure I-36: Change in the free energy of clusters in an Fe-Cr alloy compared to swelling from Refs ^[122, 123] as a function of Cr concentration ^[121].

The resistivity recovery studies performed by A.L. Nikolaev ^[124] have pictured the evolution of radiation-induced defects in Fe-Cr model alloys upon annealing after low-temperature electron irradiation as follows: At temperatures of stage I (below 130 K), self-interstitial atoms (SIAs) in the form of mixed dumbbells are captured in traps which consist of two chromium atoms, and the long-

range migration of SIAs is suppressed up to 220 K. Stage III representing the migration of vacancies occurs near 205-210 K which is almost the same temperature as in pure iron. It is remarked that the onset of SIAs long-range migration takes place at 220 K which is positioned slightly above the stage III temperature.

Marlies Lambrecht et al. ^[125] studied the irradiation-induced behavior of FeCr model alloys and high Cr ferritic/martensitic steels by using both the positron lifetime and coincidence Doppler broadening techniques. The samples were irradiated by neutron in the BR2 reactor at different irradiation doses, namely 0.06, 0.6 dpa. In pure iron irradiated to a comparable dose, the positron lifetime was found much longer than that in FeCr, indicating the vacancies size reduce in FeCr. The parameters S and W extracted from the coincidence Doppler broadening (CDB) measurements for alloys irradiated at 0.06 and 0.6 dpa are given in Figure I-37, normalized to the values of pure iron. For the model alloys irradiated at 0.06 dpa, an increase in S and a decrease in W are observed with increasing Cr content. The authors indicate that more or larger defects are present with increasing Cr. But for the author of the present thesis, this conclusion should be discussed. In fact, the W parameter as function of the S parameter for the irradiated Fe–Cr alloys and for pure iron is also presented in the publication as shown in Figure I-38. It shows clearly that the slope of W(S) line changes with Cr content for 0.06 dpa irradiated FeCr, indicating the size of vacancy created by irradiation at the same damage dose decreases with Cr concentration. Irradiated Fe₃Cr sample has the biggest vacancy size with the lowest clusters concentration because the small vacancy clusters are consumed to form the bigger vacancy clusters. Thus, S parameter and W parameter difference presented in Figure I-37 reflects their vacancy clusters concentration difference but not the clusters size.

In addition, the authors observed that the S values for any FeCr alloy irradiated at 0.06 dpa remain well below the S value measured in pure Fe, irradiated to only 0.025 dpa under very similar conditions, and W values stay well above the ones obtained in the irradiated Fe. Thus, the vacancy population or size reduces by the presence of Cr compared to pure Fe.

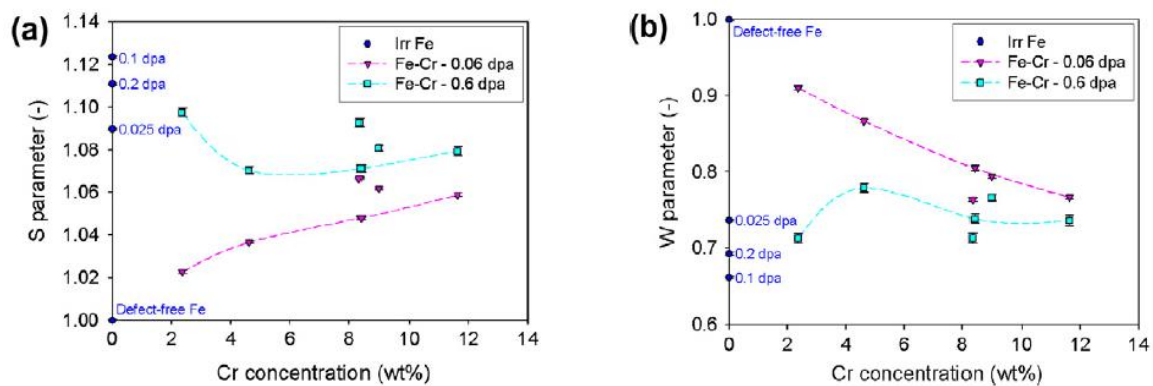


Figure I-37: The (a) S and (b) W parameters calculated from the coincidence Doppler broadening spectra for the irradiated Cr-rich alloys and some irradiated pure iron alloys. The parameter values have been normalized to those of pure, defect-free iron ^[125].

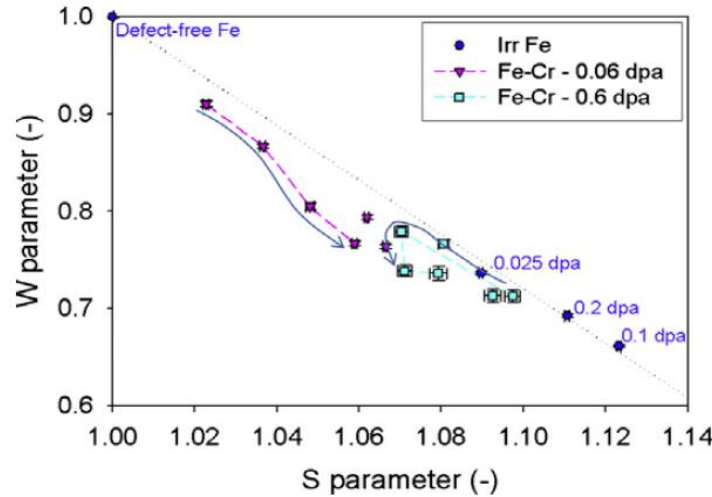


Figure I-38: The W parameter as function of the S parameter for the irradiated Fe–Cr alloys and for pure iron (as a comparison). The parameter values have been normalized to those of pure, defect-free iron. The arrows show the directions along which Cr content increases in the model alloys.

I.4.3. Interaction between vacancy and elements (Y, Ti, O) in bcc iron

Theoretical calculations suggest the stable configuration for an interstitial O atom is octahedral position whereas Y, Ti atoms are more stable in substitutional positions in bcc Fe^[83, 126, 127]. The formation energies of these solute atoms are: $E_f(O_{oct}) = 1.41 \text{ eV}$ ^[127], 1.35 eV ^[126]; $E_f(Y_{sub}) = 2.02 \text{ eV}$ ^[127], 1.86 eV ^[126], 2.01 eV ^[83]; $E_f(Ti_{sub}) = -0.80 \text{ eV}$ ^[126, 127], -0.92 eV ^[83]. The large formation energies of Y and O are consistent with the low solubility of Y (290 atomic ppm (at. ppm) in iron at 800°C)^[128] and O^[129]. The negative formation energy of Ti implies that equilibrium solubility in Fe is limited by the intermetallic Fe₂Ti phase^[127]. It has been noted that the average content of the Fe matrix for ODS alloys can reach ~1500 at. ppm for O^[81] and ~1890 at. ppm for Y^[130]. These values are significantly higher than the expected equilibrium solubility. This is explained by the high concentration of vacancies produced by MA^[131]. The formation energy of the O-vacancy pairs essentially decreases greatly if the vacancies are present as preexisting defects in Fe^[81], and it is the same for Y-vacancy case.

The interactions between these three elements (Y, Ti, O) and also with vacancy were calculated in previous study. A repulsive energy is found for Y-Ti at least up to the fifth nearest neighbor^[83] which suggests Y-Ti cannot be the driving force for the oxide cluster formation. On the contrary, the binding energies are attractive for any couple of the entities V, Y, O and Ti as shown in Table I-6. These results indicate both oxygen and vacancy could be the force keeping the clusters together.

$E_{b-1NN}(O_{int}-Ti_{sub})$	0.26 eV ^[126] 0.27 eV ^[127]	$E_{b-1NN}(V-Y_{sub})$	1.45 eV ^[65, 126]
$E_{b-2NN}(O_{int}-Ti_{sub})$	0.16 eV ^[126] 0.55 eV ^[127]	$E_{b-2NN}(V-Y_{sub})$	0.26 eV ^[65, 126]
$E_{b-2NN}(O_{int}-Y_{sub})$	0.73 eV ^[83] 0.85 eV ^[127] 1.01 eV ^[126]	$E_{b-1NN}(V-Ti_{sub})$	0.26 eV ^[65, 126]
$E_{b-1NN}(O_{int}+O_{sub})$	1.29 eV ^[127]	$E_{b-2NN}(V-Ti_{sub})$	0.16 eV ^[65, 126]
$E_{b-1NN}(O_{int}-V)$	1.65 eV ^[126] 1.45 eV ^[81]		
$E_{b-2NN}(O_{int}-V)$	0.75 eV ^[126] 0.60 eV ^[81]		

Table I-6: The binding energies between two elements of (V, Y, O and Ti).

D. Murali et al. ^[126] found that the binding energies further increase when the clusters contain more constituents as shown in Table I-7. These high binding energies will make these clusters stable and the cluster could act as nucleation sites for the growth of the nanoclusters.

$E_b(Ti-O-V)$	2.45 eV
$E_b(Y-V-O)$	3.35 eV
$E_b(Ti-Y-V-O)$	4.1 eV
$E_b(Y_2O_4V_2)$	8.7 eV
$E_b(Y_2O_4V_2Ti_4)$	12.5 eV

Table I-7: The binding energies of larger clusters ^[126].

In addition, according to D. Murali et al. ^[126], Cr has negligible interaction with vacancy ($E_{b-1NN}(Cr-V)=0.05$ eV), O ($E_{b-1NN}(Cr-O)=0.25$ eV) and repulsive interaction with Y, Ti ($E_{b-1NN}(Cr-Y)=-0.16$ eV; $E_{b-1NN}(Cr-Ti)=-0.15$ eV). It suggests as found experimentally that oxide nanoclusters could have a core/shell structure ^[76-78] in which core is enriched in Y, Ti, O and shell is enriched in Cr.

The migration energy of the solutes of ODS alloys in bcc Fe have been calculated by D. Murali et al. ^[65] and A. Claisse et al. ^[83] as shown in Table I-8. It is supposed that Fe, Cr, Ti and Y migrate thanks to the vacancy assisted mechanism, whereas O travels between two octahedral positions through a tetrahedral position without requiring help from another defect. It has to be noted that the migration energy is surprisingly low for Y. It can be attributed to the large relaxation of Y towards vacancy and the strong Y-V interaction energy.

Element	Fe	Cr	Ti	Y	O
Migration energy (eV)	0.65 ^[83]	0.52 ^[83]	0.35 ^[83] 0.42 ^[65]	0.02 ^[83] 0.03 ^[65]	0.48 ^[83]

Table I-8: The migration energy of the solutes of ODS alloys in bcc Fe.

The diffusion coefficients of Fe, Y, Ti have been calculated for various temperatures by D. Murali et al.^[65] and compared with the experimental values obtained by Hin et al.^[63] by fitting the nucleation-coarsening model to the experimental SANS data of Alinger et al.^[64]. As shown in Figure I-39, the calculated diffusion coefficient for host Fe is one order of magnitude lower than the experimental value and the calculated diffusion coefficient of Ti is three orders of magnitude lower than the experimental value. On the contrary, the calculated value for Y is much higher than that the experimental one because of the very small migration energy that has been calculated. Also, it is clear that the calculated diffusion coefficient of Y atom is higher than the calculated Ti and host Fe ones whereas the experimental results are inverse. All these great disagreements between experiment and calculation indicate that more direct experimentation of diffusion of Y, Ti is required in pure bcc.

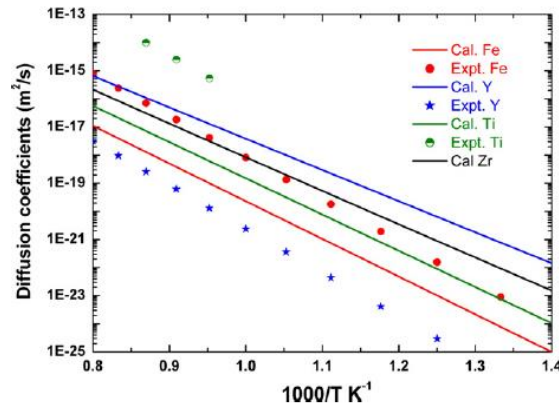


Figure I-39: The experimental diffusion coefficients compared with the ones of Fe, Ti, Y and Zr atoms in bcc Fe calculated using the Le Claire's nine frequency model^[65].

I.4.4. Conclusions

The formation, binding and migration energies of point defects in bcc matrix have been calculated. Four annealing stages of point defects have been revealed after electron irradiation by Takaki et al.^[107]. Among them, stage (III) (220- 278 K) represents V migration and stage (IV) (520- 550 K) represents dissociation of defect clusters. In addition, a stage (~ 423 K) between (III) and (IV) which is governed by the migration of vacancy clusters of size less than ten vacancies has been proposed by Yue Fan et al.^[108] using atomistic simulations. M.Eldrup et al.^[109] studied dose dependence of defect accumulation in neutron irradiated iron by PAS. They found that both the density and the average size increase with increasing dose. The PAS study of T.Iwai et al.^[110,111] shows that the heavy ions providing greater PKA energy generate larger vacancy-type defects. The defect accumulation was also investigated at low temperature (12 K) to reveal vacancy configurations after cascade, without any thermal migration after the cascade cooling^[111-113]. In this study, the defect production efficiencies are estimated to be 0.27 for 1 MeV H⁺ and 0.17 for 2.8 MeV C⁺. The values represent the difference in the primary knock-on atom energy spectrum of H⁺ and C⁺. An isochronal annealing of iron irradiated with 2 MeV He up to 1 mdpa at 12 K was also performed by T.Iwai et al.^[111]. The beginning of vacancy migration and clustering is around 140 K. This temperature range is much lower than the vacancy migration stage reported by Takaki et al.^[107], 220- 278 K. T.Iwai et al. have explained that this discrepancy is attributable to the difference in

defect configuration between electron and ion irradiation.

For Cr concentrations above 6%, the calculations show that the vacancy formation energies show a linear dependence with the concentration between the vacancy formation energy in iron (1.72 eV) and the vacancy formation energy in chromium (2.56 eV). However, for Cr concentrations below 6 at.% the vacancy formation energy is almost constant. P.Olsson et al. studied Cr interactions with point defects in bcc Fe by Ab initio study ^[116]. The Cr-vacancy (VCr) binding energy is found to be small, about 60 meV in the first-nearest-neighbor, 7 meV in the second-nearest-neighbor and vanishes for larger separation distances. This result is in agreement with the experimental results of Möslang et al ^[117]. Using muon spectroscopy, they have estimated the VCr binding energy to be less than 105 meV. Nagai et al. ^[119] showed that the positrons annihilating with electrons of Cr results an increase of S and a decrease of W compared to the Fe. The calculations of P.Olsson et al. show that Cr- Cr interactions are repulsive for all small Cr clusters considered (up to size four). They also found that $\langle 100 \rangle_{\text{Fe-Cr}}$ and $\langle 110 \rangle_{\text{Fe-Cr}}$ configurations have small binding energies (close to zero) while the $\langle 111 \rangle_{\text{Fe-Cr}}$ crowdion is more strongly bound, having binding energy 0.4 eV. In contrast, Cr-rich precipitates (α' phase) in Fe- Cr alloys will repel interstitial loops. A non- monotonic decrease of cluster diffusivity with the increase of Cr content is proposed by D.Terentyev et al. ^[121]: a) Small SIA clusters exhibit diffusivity minima in the 9-12% Cr range; b) with the increase of the cluster size the minima shift towards lower Cr concentrations; c) the interaction between fine Cr-rich precipitates and small dislocation loops is strongly repulsive, thus the mobility of dislocation loops increases. But where fine, dispersed α' - nuclei are formed, small dislocation loop mobility would reduce again because these clusters will get 'locked' between α' particles. The resistivity recovery studies performed by A.L. Nikolaev ^[124] have pictured the evolution of radiation-induced defects in Fe-Cr model alloys upon annealing after low-temperature electron irradiation. Stage III representing the migration of vacancies occurs near 205-210 K which is almost the same temperature as in pure iron. But it has been noted that the onset of SIAs long-range migration takes place at 220 K which is positioned slightly above the stage III temperature. Marlies Lambrecht et al. ^[125] studied the irradiation-induced behavior of FeCr model alloys and high Cr ferritic/martensitic steels by using both the positron lifetime and coincidence Doppler broadening techniques. The authors indicate that more or larger defects are present with increasing Cr. However, the vacancy population or size reduces by the presence of Cr compared to pure Fe.

Theoretical calculations suggest the stable configuration for an interstitial O atom is octahedral position whereas Y, Ti atoms are more stable in substitutional positions in bcc Fe ^[83, 126, 127]. The large formation energies of Y and O are consistent with the low solubility of Y (290 atomic ppm (at. ppm) in iron at 800°C) ^[128] and O ^[129]. The formation energy of the O-vacancy pairs essentially decreases greatly if the vacancies are present as preexisting defects in Fe ^[81], and it is the same for Y-vacancy case. The interactions between the three elements (Y, Ti, O) and also with vacancy were calculated and results indicated that both oxygen and vacancy could be the force keeping the clusters together. The binding energies further increase when the clusters contain more constituents. According to D. Murali et al. ^[126], Cr has negligible interaction with vacancy ($E_{b-1NN}(\text{Cr-V})= 0.05$ eV), O ($E_{b-1NN}(\text{Cr-O})= 0.25$ eV) and repulsive interaction with Y, Ti ($E_{b-1NN}(\text{Cr-Y})= -0.16$ eV; $E_{b-1NN}(\text{Cr-Ti})= -0.15$ eV). It suggests as found experimentally that these nanoclusters have a core/shell structure ^[76-78] in which core is enriched in Y, Ti, O and shell is enriched in Cr. The migration energy of the solutes of ODS alloys in bcc Fe have been calculated by D.

Murali et al.^[65] and A. Claisse et al.^[83]. It has been noted that the migration energy is surprisingly low for Y. It can be attributed to the large relaxation of Y towards vacancy and the strong Y-V interaction energy. The great disagreements between experiment and calculation for diffusion coefficients of Fe, Y, Ti require more direct experimentation of diffusion of Y, Ti in pure bcc.

1.5. Conclusions

In this chapter the scientific context has been presented and the previous studies related to the present thesis have been summarized. The different generations of nuclear reactors are firstly introduced, especially the GEN IV nuclear fission reactor. It is noted that the operating temperature of currently operating reactors (Gen II) does not exceed 400°C, whereas for Gen IV it is much higher. In addition, higher damage doses than in Gen II, are expected for some of these systems (for example, SFR). These service conditions will affect the microstructural stability and mechanical properties of structural materials. New alloys thus must be developed. Several candidate materials have been suggested, ODS materials afford many benefits among them. They afford not only negligible swelling under irradiation, owing to their ferritic bcc structure- by contrast to austenitic grades, which feature a fcc structure- but equally outstanding creep properties, owing to the nano-reinforcements present in the matrix. This material is expected to be used for claddings, targets and some other core and fuel structures of Gen- IV reactors. ODS EUROFER steel could also be used for structural applications in fusion power reactors up to about 650°C.

ODS ferritic or martensitic steels are based on Fe-Cr matrix and reinforced by nanometer scale oxide (for example, $Y_2Ti_2O_7$) particles. They are being developed and investigated for nuclear fission and fusion applications in Japan^[16-18], Europe^[19, 20], and the United States^[21]. To fabricate the ODS alloys, several steps are performed. Mechanical alloying is considered as the critical step. It results in the formation of crystal defects such as dislocations, vacancies, stacking faults, and increased number of grain boundaries in the grains. The presence of this defect structure enhances the diffusivity behavior of solute elements. The excess vacancies introduced are considered by some researchers as having the critical role in nanoparticles formation and stabilization^[24].

The ferritic or martensitic Fe-Cr matrix (bcc structure) is chosen for ODS steels to avoid the swelling under irradiation. ODS steels contain different amounts of Cr (9-18wt.%) which guarantee the good corrosion resistance and also favourable mechanical properties. The addition of Ytria (Y_2O_3) particules increases creep strength of ODS steel by solid solution hardening^[17]. Ti contributes to forming the Y-Ti-O nanoparticles in finer size resulting in an increase of creep rupture strength^[33-35].

The ODS steel has good thermal creep resistance at high operating temperatures ($T > 550^\circ\text{C}$). It also shows a much better swelling behavior than austenitic steels because of their bcc structure. In addition, very fine homogeneously distributed particles can act as sinks for helium preventing it from the formation of detrimental voids along the grain boundaries and thus reduce high- temperature helium embrittlement. The nanoclusters in ODS steels are considered stable under irradiation.

The natures of different types of nanoparticles in ODS steels depend on their size. Non-stoichiometric very small Y-, Ti-, O- enriched clusters are in size from ~2 to ~15 nm ($Y/Ti < 1$) and stoichiometric $Y_2Ti_2O_7$ particles are from ~15 nm to ~35nm (Y/Ti constant at ~1.4). The Y/Ti ratio

increases with increasing particle size in the range up to 15 nm and then saturates in the range up to 35 nm. The diffusion of yttrium has an important role in the evolution of the oxides. However, the contradiction between experiment and calculation indicates more direct experimentation of diffusion of Y in pure bcc Fe is necessary. A core/shell structure is found for MA957 ODS alloy (nominal composition: 14Cr, 0.9Ti, 0.3Mo and 0.25Y₂O₃; hot extruded at ~1150°C) by APT ^[72]. The particles in MA957 with size ~4 nm consist of a Y, Ti, O rich core and a Cr rich shell. The core compositions are 42.8±3.6%O, 37.9±3.0%Ti, 14.6±1.2%Y, 4.6±1.0%Cr. The studies of Hsiung et al. ^[76-78] show that this shell is amorphous.

A macroscopic three-stage mechanism has been proposed to explain the formation of oxide nanoparticles containing a core/shell structure during MA and consolidation: fragmentation, agglomeration and crystallization. The path of Fe- Y-O precipitation has been studied by using Kinetic Monte Carlo simulations and described as followed: There is an initial formation of a transient, metastable iron oxide phase Fe₂O₃, which forms due to the rapid diffusion of O relative to Y, and due to the existence of a driving force for iron oxides precipitation. After, it is followed by the nucleation of Y₂O₃ precipitates, which occurs within the Fe₂O₃. The phase, called Fe_xY_{2-x}O₃, grows with a decrease in Fe content and an increase in Y content. Finally, these precipitates are ultimately approach the stoichiometric composition of Y₂O₃. The Fe- Ti- O precipitation path is practically the same whereas their kinetics are not the same. This difference is ascribed to the diffusion coefficients difference between Y and Ti atoms. First-principles studies realized by C.L. Fu et al. ^[81] identify a vacancy mechanism for nucleation of stable O-enriched nanoclusters in defect- containing Fe. But Jiang et al. ^[82] consider nanoparticles formation could take place without the presence of vacancies.

The positron studies of ODS alloys show that the positron annihilation spectroscopy is capable in characterizing the nanofeatures and vacancy clusters in ODS alloys although there are some limits. They also illustrate that vacancies have a no- ignored effect on forming and stabilizing the nanoparticles of ODS alloys.

The formation, binding and migration energies of point defects in bcc matrix are calculated. Four annealing stages of point defects have been revealed after electron irradiation by Takaki et al. ^[107]. Among them, stage (III) (220- 278 K) represents V migration and stage (IV) (520- 550 K) represents dissociation of defect clusters. In addition, a stage (~ 423 K) between (III) and (IV) which is governed by the migration of vacancy clusters of size less than ten vacancies has been proposed by Yue Fan et al. ^[108] using atomistic simulations. M.Eldrup et al. ^[109] studied dose dependence of defect accumulation in neutron irradiated iron by PAS. They found that both the density and the average size increase with increasing dose. The PAS study of T.Iwai et al. ^[110, 111] shows that the heavy ions providing greater PKA energy generate larger vacancy- type defects. The defect accumulation was also investigated at low temperature (12 K) to reveal vacancy configurations after cascade, without any thermal migration after the cascade cooling ^[111-113]. In this study, the defect production efficiencies are estimated to be 0.27 for 1 MeV H⁺ and 0.17 for 2.8 MeV C⁺. The values represent the difference in the primary knock- on atom energy spectrum of H⁺ and C⁺. An isochronal annealing of iron irradiated with 2 MeV He up to 1 mdpa at 12 K was also performed by T.Iwai et al. ^[111]. The beginning of vacancy migration and clustering is around 140 K. This temperature range is much lower than the vacancy migration stage reported by Takaki et al. ^[107], 220- 278 K. T.Iwai et al. have explained that this discrepancy is attributable to the difference in

defect configuration between electron and ion irradiation.

For Cr concentrations above 6%, the calculations show that the vacancy formation energies show a linear dependence with the concentration between the vacancy formation energy in iron (1.72 eV) and the vacancy formation energy in chromium (2.56 eV). However, for Cr concentrations below 6 at.% the vacancy formation energy is almost constant. P.Olsson et al. studied Cr interactions with point defects in bcc Fe by Ab initio study ^[116]. The Cr-vacancy (V_{Cr}) binding energy is found to be small, about 60 meV in the first-nearest-neighbor, 7 meV in the second-nearest-neighbor and vanishes for larger separation distances. This result is in agreement with the experimental results of Möslang et al ^[117]. Using muon spectroscopy, they have estimated the V_{Cr} binding energy to be less than 105 meV. Nagai et al. ^[119] showed that the positrons annihilating with electrons of Cr results an increase of S and a decrease of W compared to the Fe. The calculations of P.Olsson et al. show that Cr- Cr interactions are repulsive for all small Cr clusters considered (up to size four). They also found that $\langle 100 \rangle_{\text{Fe-Cr}}$ and $\langle 110 \rangle_{\text{Fe-Cr}}$ configurations have small binding energies (close to zero) while the $\langle 111 \rangle_{\text{Fe-Cr}}$ crowdion is more strongly bound, having binding energy 0.4 eV. In contrast, Cr-rich precipitates (α' phase) in Fe- Cr alloys will repel interstitial loops. A non- monotonic decrease of cluster diffusivity with the increase of Cr content is proposed by D.Terentyev et al. ^[121]: a) Small SIA clusters exhibit diffusivity minima in the 9-12% Cr range; b) with the increase of the cluster size the minima shift towards lower Cr concentrations; c) the interaction between fine Cr-rich precipitates and small dislocation loops is strongly repulsive, thus the mobility of dislocation loops increases. But where fine, dispersed α' - nuclei are formed, small dislocation loop mobility would reduce again because these clusters will get 'locked' between α' particles. The resistivity recovery studies performed by A.L. Nikolaev ^[124] have pictured the evolution of radiation-induced defects in Fe-Cr model alloys upon annealing after low-temperature electron irradiation. Stage III representing the migration of vacancies occurs near 205-210 K which is almost the same temperature as in pure iron. But it has been noted that the onset of SIAs long-range migration takes place at 220 K which is positioned slightly above the stage III temperature. Marlies Lambrecht et al. ^[125] studied the irradiation-induced behavior of FeCr model alloys and high Cr ferritic/martensitic steels by using both the positron lifetime and coincidence Doppler broadening techniques. The authors indicate that more or larger defects are present with increasing Cr. However, the vacancy population or size reduces by the presence of Cr compared to pure Fe.

Theoretical calculations suggest the stable configuration for an interstitial O atom is octahedral position whereas Y, Ti atoms are more stable in substitutional positions in bcc Fe ^[83, 126, 127]. The large formation energies of Y and O are consistent with the low solubility of Y (290 atomic ppm (at. ppm) in iron at 800°C) ^[128] and O ^[129]. The formation energy of the O-vacancy pairs essentially decreases greatly if the vacancies are present as preexisting defects in Fe ^[81], and it is the same for Y-vacancy case. The interactions between the three elements (Y, Ti, O) and also with vacancy were calculated and results indicated that both oxygen and vacancy could be the force keeping the clusters together. The binding energies further increase when the clusters contain more constituents. According to D. Murali et al. ^[126], Cr has negligible interaction with vacancy ($E_{b-1NN}(\text{Cr-V})= 0.05$ eV), O ($E_{b-1NN}(\text{Cr-O})= 0.25$ eV) and repulsive interaction with Y, Ti ($E_{b-1NN}(\text{Cr-Y})= -0.16$ eV; $E_{b-1NN}(\text{Cr-Ti})= -0.15$ eV). It suggests as found experimentally that these nanoclusters have a core/shell structure ^[76-78] in which core is enriched in Y, Ti, O and shell is enriched in Cr. The migration energy of the solutes of ODS alloys in bcc Fe have been calculated by D.

Murali et al.^[65] and A. Claisse et al.^[83]. It has been noted that the migration energy is surprisingly low for Y. It can be attributed to the large relaxation of Y towards vacancy and the strong Y-V interaction energy. The great disagreements between experiment and calculation for diffusion coefficients of Fe, Y, Ti require more direct experimentation of diffusion of Y, Ti in pure bcc.

I.6. Thesis objectives

As explained in the previous sections, the ODS steel is a potential material for use in the future nuclear reactors because of their excellent properties induced by the fine dispersion of nanoparticles. But the atomic scale clustering mechanism of these nanoparticles is not yet cleared. Although there are some simulation works which try to shed light on the nucleation route, the lack of experimental data for fundamental properties of nanoparticle constitutions (vacancy, Y, Ti, O) makes these works difficult to be validated. For example, the lack of direct experimentation of Y diffusion in pure bcc Fe makes the Y diffusion parameter entered in these simulations suspicious.

The role of vacancies introduced by MA during the ODS fabrication is considered to be critical for forming the nanoparticles as shown in both experimental and simulation works although there are some different opinions. Thus, the experimental work in this thesis begins with studying the behaviors of vacancies in bcc Fe matrix and also FeCr matrix which serves as basis of this work. After clearing the vacancies behaviors, the interactions between V- Y, V- O and V- Ti in bcc Fe matrix are studied before passing to more complicated system like Y-O-V in Fe. The experimental approach is explained in Figure I-40.

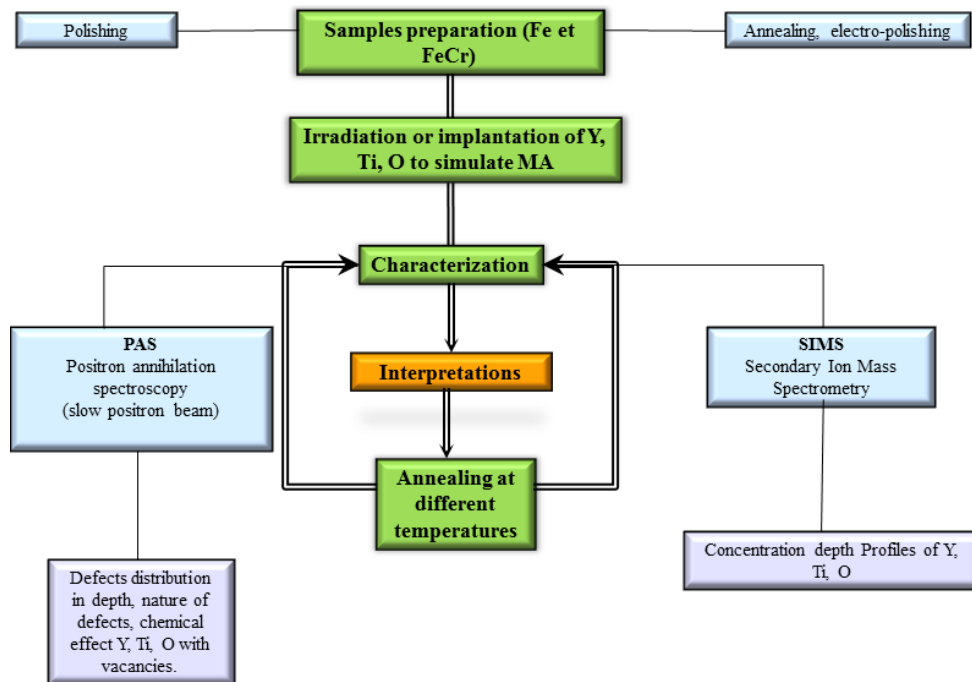


Figure I-40: The experimental approach of this thesis.

The Fe and FeCr samples are first prepared to remove the as-received defects, depending on the

nature, mechanical and electrochemical polishing combined with annealing. To study the properties of vacancy defects in Fe and FeCr without the influence of impurities, high energy (1.5 MeV in the case of Fe; 2 MeV in the case of FeCr) helium irradiation has been performed. Implantations of Y or O or Ti have been done to introduce both vacancies defects and elements for studying their interactions. After He irradiation or Y, Ti, O implantations, slow positron beam Doppler broadening (SPBDB) technique is utilized for characterizing vacancy defects. It gives the information about defects distribution in depth, defects natures and also chemical effect Y, Ti, O with vacancies. Secondary Ion Mass Spectrometry (SIMS) is used to measure the Y, Ti, O concentration profile as a function of depth and to better understand positron results. Annealing post- irradiation is performed. The samples are measured by PAS and SIMS after each annealing to study the annealing effect. In conclusion, this thesis will try to respond the following questions:

- How the solutes (Y, Ti, O, Cr) interact with vacancies in bcc Fe matrix.
- How vacancies evolve with the annealing temperatures.
- How the solutes (Y, Ti, O, Cr) diffuse in the matrix.
- What is the earliest stage of solute clustering.
- The results obtained would help to better understand how the nanoclusters nucleate and what is their kinetic precipitation path and to explain the structure of nanoclusters observed in previous studies.

Chapter II.

Materials and experimental techniques

II. Materials and experimental techniques

This chapter presents the materials and experimental techniques utilized in this thesis. In section II.1, the states of Fe and FeCr as-received samples are presented: the chemical composition, the fabrication route etc. The preparation methods of the Fe and FeCr virgin materials used for irradiation and positron annihilation spectroscopy experiments are also explained.

In section II.2, the irradiation/implantation conditions are reported for helium irradiation in Fe and FeCr samples, Y, O, Ti implantations in Fe samples. The principle of defects formation by ion irradiation/implantation is explained. Finally, the defects and solutes depth profiles as calculated using SRIM are shown.

Positron annihilation spectroscopy (PAS) allows studying a variety of phenomena and material properties on an atomic scale ^[132]. Being the anti-particle of electrons, positrons are used to probe material defects at low concentrations and with high sensitivity to the size of vacancy clusters in the range from mono-vacancies up to cavities containing 50-100 vacancies ^[109]. With the advantage of being a non-destructive materials characterization method, positron annihilation spectroscopy has been developed as a well-established tool for investigations of metals, semiconductors, polymers and porous materials. In section II.3, the interaction of positrons in condensed matter is firstly introduced: positron implantation and diffusion, positron trapping and positron annihilation. Then the slow positron beam Doppler broadening spectrometer developed in laboratory CEMHTI is presented. The defects identification and quantification are also explained.

In this thesis, the technique secondary ion mass spectrometry (SIMS) is used to analyze the solute (Y, O) depth profiles in Fe after irradiation and also after post-irradiation annealing. It is recognized as the most sensitive elemental and isotopic surface analysis technique. In section II.4, SIMS technique principle is firstly presented. The SIMS 7f installed in laboratory GEMAC is used for the measurements in this thesis. The experimental conditions, calibration and quantification of elements profiles in polycrystalline Fe are explained. Finally, SIMS technical constraints related to the work performed in this thesis are presented and thus the experiment protocol is described.

II.1. Materials preparation

The states of Fe and FeCr as-received samples are presented: their chemical composition, the fabrication route etc. The preparation methods of Fe and FeCr virgin materials used for irradiation and positron annihilation spectroscopy experiments are explained in this section.

II.1.1. Fe bcc samples

The iron samples utilized in this thesis are high purity 99.99 wt.% 7 mm×7 mm×0.5 mm sheets. The materials are provided by GoodFellow in the laminated state and their chemical composition is given in Table II.1. The major impurities are silicium (Si), carbon (C) and nickel (Ni) with the concentrations of 66.86 appm, 52 appm and 14.86 appm respectively. The concentration of oxygen (O) is not indicated in the technical document supplied by GoodFellow. But according to the communication with GoodFellow, the O concentration should be 169 appm.

Impurity	Al	As	B	C	Cr	Co	Cu	Ga	Ge	Mn	Mo
(ppm weight)	1.6	0.12	2.3	12	3.2	15	2	0.29	5.9	0.87	0.28
(atomic ppm)	3.20	0.09	11.96	52	3.47	14.44	1.79	0.24	4.79	0.90	0.17
Impurity	Ni	Nb	K	Si	Na	Ta	Ti	W	V	Zn	Fe
(ppm weight)	16	<0.1	0.23	36	0.25	<10	0.41	0.18	0.49	0.19	bal.
(atomic ppm)	14.86	0.06	0.31	66.86	0.59	3.56	0.48	0.06	0.55	0.16	bal.

Table II.1: Chemical composition of pure Fe samples provided by GoodFellow.

The first step is to develop a procedure to obtain a homogenous non-defective surface and bulk of pure Fe samples, qualified as 'virgin samples' or 'reference samples'.

In order to obtain a homogenous irradiation, the surface of samples should present the least roughness as possible. Mechanical polishing is applied to reach this objective. The procedures are the following:

- 2 minutes polishing with an abrasive disk of 600 grains/cm² (diameter of grain ~ 408 µm), then 2 minutes with an abrasive disk with 1200 grains/cm² (diameter of grain ~ 289 µm). These two polishings are lubricated with water.
- Then the samples are polished with diamond paste pasted on felts. 5 minutes polishing with felts FD6 with diamond grains of 6 µm; then 5 minutes with felts FD3 with diamond grains of 3 µm and finally 10 minutes with felts FD1 with diamond grains of 1 µm.

The final state of samples surfaces is mirrored. And a surface roughness of ~ 10 nm (measured by AFM) has been obtained after polishing.

The samples provided by GoodFellow are in the laminated state and includes many defects. In addition, the mechanical polishing introduces also strain and defects near the surface of samples. It is important to remove these initial defects to ensure that they are not present in the sample before irradiation to prevent misinterpretation of the irradiation results. In the case of pure Fe, annealing is used to provide enough thermal energy for the crystalline reorganization. The annealing temperature is fixed at the value of 750°C for the Fe samples. This temperature is effective to remove initial defects and keep α phase of samples (as indicated in Figure II-1(b)). Annealing was carried out for one hour under vacuum. The furnace used is an electron-bombardment furnace developed in laboratory CNRS-Orleans/CEMHTI as presented in Annex A1. As shown in Figure II-1(a), the heating rate selected to reach the desired temperature is about 30°C/min. Samples were cooled down from the annealing temperature to room temperature in the furnace by turning off the heating when annealing temperature is below 320°C and with a cooling slope of 30°C/min when annealing temperature is above 320°C. The temperature and electric current are stable during the one hour annealing. The electric current is ~ 8A

for 750°C. The measurement accuracy is of 2°C for temperatures up to 400°C, and 0.3% of the measured value for measurements beyond 400°C.

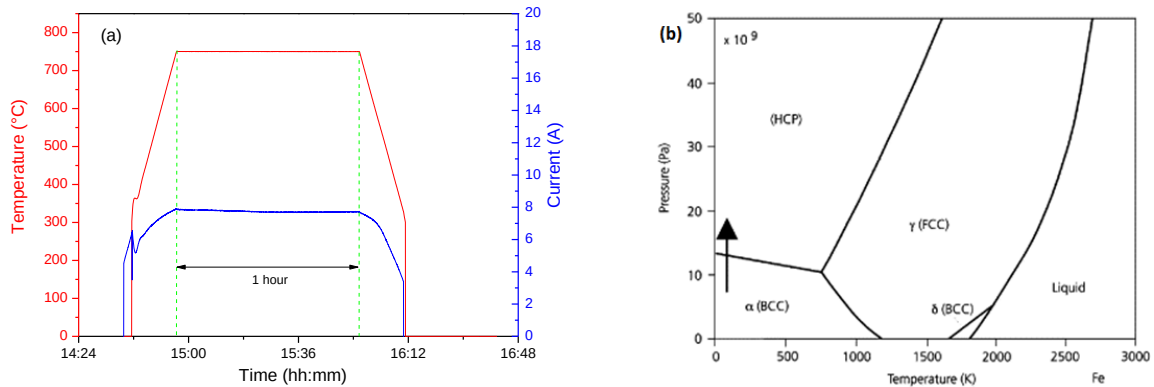


Figure II-1: (a) Temperature and electric current evolutions during one hour's annealing under vacuum. (b) Pure iron phases in terms of pressure and temperature.

After preparation, the Fe samples show a polycrystalline structure with mean grain sizes of 20-100 μm . Electron backscatter diffraction (EBSD) image shows that the grains of the sample do not have a preferential orientation as shown in Figure II-2. Different colors in EBSD image represents different grain orientations which are defined by the color coded map. The axes of the specimen are selected in order to express important surfaces or direction of the specimen. RD represents rolling direction and TD is transversal direction. Thus, the color coded map gives the planes directions parallel to the sample surface, for example the red representing (001) planes.

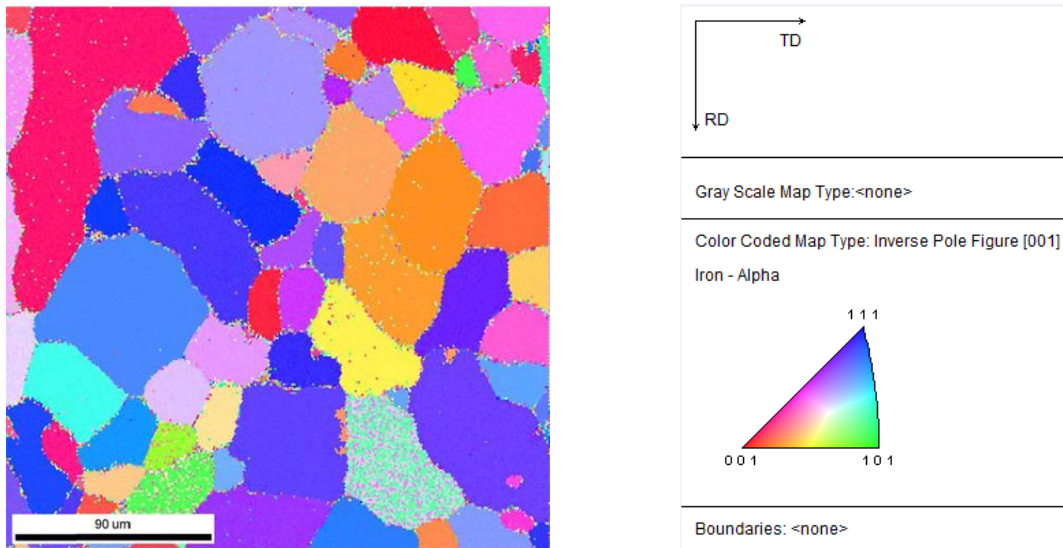


Figure II-2: 250 μm × 250 μm EBSD image of polycrystalline Fe sample.

In addition, after helium irradiations in Fe and FeCr, or Y implantation in Fe, the samples are also annealed in this furnace in order to study their post- irradiation annealing behavior.

II.1.2. FeCr model alloy samples

The FeCr based model alloys of industrial purity, namely, Fe-3Cr (2.36 at.%Cr), Fe-5Cr (4.93 at.%Cr), Fe-9Cr (8.93 at.%Cr) and Fe-12Cr (12.33 at.%Cr), have also been used in this study. They were fabricated at Ghent University Belgium within the PhD thesis of Milena Matijasevic ^[133] by furnace melting of industrial pure Fe and Cr. After casting, the obtained ingots were cold worked under protective atmosphere to fabricate plates of 9mm thickness. These plates were then annealed for 3 hours at 1050°C in high vacuum for austenization and stabilization. The duration of the heat treatment was chosen in order to get rid of any possible precipitation or phase transformation that might have been occurred during hot rolling and also to allow a maximum degassing of the alloys. This treatment was then followed by air cooling to room temperature. Finally, the tempering procedure has been performed by heating the alloys up to 730°C for 4h and air cooling to room temperature. After the elaboration, the materials have been cut mechanically at SCK.CEN (Mol, Belgium) ^[134].

The nominal chemical composition of the model alloys Fe-5Cr, Fe-9Cr and Fe-12Cr has been measured during the PhD Thesis of M. Matijasevic using induced coupled plasma mass spectrometry and the combustion technique at OCAS (Zelzate, Belgium), and is reported in Table II.2. The chemical composition of the Fe- 3Cr model alloys was measured at SCK.CEN.

Impurity (at%)	Fe	Cr	Si	P	Mn	Ni	V	C	N	O	S	Al	Ti
Fe- 3Cr	Bal.	2.36	0.002	0.013	0.009	0.044	0.001	0.008	0.017	0.03	?	0.003	0.004
Fe- 5Cr	Bal.	4.93	0.08	0.02	0.02	0.06	0.001	0.09	0.05	0.21	0.01	0.01	0.003
Fe- 9Cr	Bal.	8.93	0.18	0.02	0.03	0.07	0.002	0.09	0.06	0.23	0.001	0.014	0.004
Fe- 12Cr	Bal.	12.33	0.22	0.09	0.03	0.085	0.002	0.129	0.09	0.22	0.012	0.006	0.004

Table II.2: Nominal chemical composition (at.%) of the model alloys Fe-3Cr, Fe-5Cr, Fe-9Cr, Fe-12Cr.

Tomographic atom probe was used to check the randomness of the spatial distribution of the alloying elements inside the grains at the nanoscale in the Fe-5Cr, Fe-9Cr and Fe-12Cr model alloys by V. KUKSENKO ^[134] who used the same lots of FeCr samples in his thesis as in this work. The measured chromium concentrations in the overall analyzed volume for Fe-5Cr, Fe-9Cr model alloys are respectively, (4.7±0.1)at.% and (9.3±0.3)at.% in both alloys. They are in good agreement with the reference data. But the non-homogeneity of chromium distribution is revealed in the Fe-12Cr alloy with a variation of Cr content in the range 9.9-13.2at.% with the mean value equal to (11.7±1.2)at.%. In addition, the broad distribution of grain-size and the non-homogeneity of dislocation distribution are revealed in the Fe-9Cr and Fe-12Cr model alloys. Cr enriched clusters segregation is observed by SEM, TEM- EDS experiments along the grain boundaries as shown in **Figure II-3(a)** and chromium atoms appear to be homogeneously distributed at the nanometric scale inside grains (neglecting the Cr enriched segregations) as shown in the 3D APT image in **Figure II-3(b)** for Fe- 5Cr, Fe- 9Cr and Fe- 12Cr alloys.

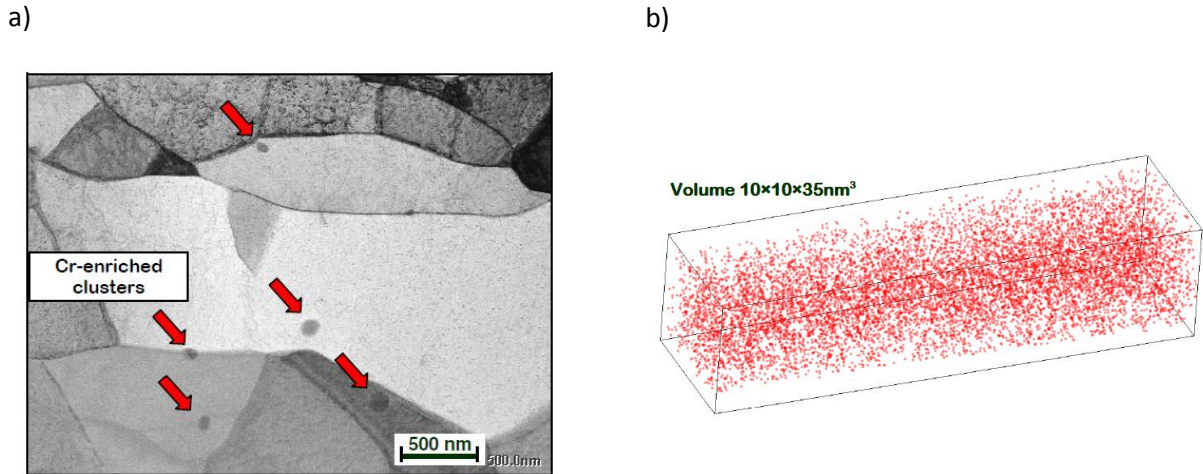


Figure II-3: a) The presence of large Cr enriched clusters mainly along grain boundaries revealed by TEM- EDS experiments b) 3D distribution of Cr atoms reveals that Cr atoms are homogeneously distributed in as-received Fe- 12Cr model alloy.

As in the case of Fe sample, the mechanical polishing is also applied for FeCr samples to reduce the surface roughness. The polishing procedures are the same as for Fe sample. But compared to the Fe samples, the annealing has not been performed after mechanical polishing for FeCr samples because this treatment could change the phase, preventing the comparison with results of other research groups. Another technique named electrochemical polishing has been used to remove the deformed surface layer as presented in Annex A2. This technique allows removing a thin surface layer of conductive material, like FeCr, without introducing a work hardening layer onto the sample. The time of electrochemical polishing is controlled to remove $\sim 10 \mu\text{m}$ layer on sample surface.

II.1.3. Conclusion

The iron samples utilized in this thesis are high purity 99.99 wt.% 7 mm×7 mm×0.5 mm sheets with the major impurities silicon (Si), carbon (C), nickel (Ni) and oxygen (O). Before the irradiation and positron annihilation spectroscopy experiments, the Fe samples are mechanically polished to reach a surface roughness of $\sim 10 \text{ nm}$. An annealing at 750°C is performed after polishing to get the Fe virgin samples without defects. After preparation, the Fe samples show a polycrystalline structure with mean grain sizes of 20 - 100 μm . Electron backscatter diffraction (EBSD) image shows that the grains of the sample do not have a preferential grain orientation.

The FeCr model alloys utilized in this thesis namely, Fe-3Cr (2.36 at.%Cr), Fe-5Cr (4.93 at.%Cr), Fe-9Cr (8.93 at.%Cr) and Fe-12Cr (12.33 at.%Cr) are of industrial purity,. The major impurities are silicon (Si), carbon (c) and oxygen (O). Cr enriched clusters segregation is observed along the grain boundaries by SEM, TEM- EDS and Cr atoms appear to be homogeneously distributed at the nanometric scale inside grains (neglecting the Cr enriched segregations) in the 3D APT image for Fe- 5Cr, Fe- 9Cr and Fe- 12Cr alloys. The FeCr virgin samples are first mechanically polished to get a smooth surface and electrochemical polishing is used to remove the deformed $\sim 10 \mu\text{m}$ layer on the sample surface.

II.2. Defects and solutes introduction: irradiation and implantation

Ion irradiations or implantations are used to introduce defects and solutes. The conditions are presented in this section, for helium irradiation in Fe and FeCr samples, and Y, O, Ti implantations in Fe samples. The principle of defects formation by ion irradiation/implantation is explained. Finally, the defects and solutes depth profiles as calculated using SRIM are shown.

II.2.1. Irradiation/ Implantation conditions

a) Helium irradiation in Fe and FeCr samples

The high energy helium 4 ($^4\text{He}^+$) irradiations, at 1.5 MeV in Fe and at 2 MeV in FeCr, have been carried out with the 3.5 MeV Van der Graaff electrostatic accelerator at CEMHTI laboratory in Orleans, France. Several ion beams, H^+ , D^+ , $^3\text{He}^+$ and $^4\text{He}^+$, are available with this machine. The $^4\text{He}^+$ irradiations have been performed by scanning the ion beam on the sample holder where the Fe or FeCr samples are fixed. The samples are fixed by screwed metal washers. Three samples are fixed on the same sample holder for each implantation. The sample holder is cooled by water circulation. One collimator is placed before the sampler holder. The collimator is polarized by a -400 V voltage in order to collect the secondary electrons ejected during beam impacting on sample holder. The beam surface is 0.25 cm^2 and the scanned surface by beam is 7.07 cm^2 . The implantation current is measured by intercepting the implantation beam intermittently with a rotating finger. The ratio between the measured current and the effective current received by the target is checked during all the experimental campaign. The charge Q received by the surface S implanted is integral of the implantation current during all the implantation time. The implantation fluence F (at/cm^2) is given by the equation as followed:

$$F = \frac{Q}{S \times e}$$

In this equation, ' e ' is the electron charge ($1.6 \times 10^{-19} \text{ C}$) and S is the scanned surface area. For example, to obtain a fluence of $10^{16} \text{ at}/\text{cm}^2$ $^4\text{He}^+$ in our case, the received charge should be $11312 \text{ }\mu\text{C}$ for a surface of 7.07 cm^2 . The implantation flux is chosen to be limited. In addition, the implantation current gives the implantation flux f ($\text{at}/(\text{cm}^2.\text{s})$) through the followed equation. Thus, for an implantation flux of $1.447 \times 10^{12} \text{ at}/\text{cm}^2/\text{t}$, the current is $1.637 \text{ }\mu\text{A}$. With this current, the implantation time should be 6909 seconds to reach the fluence. The impreciseness of the charge measure is $\sim 5\%$.

$$f = \frac{I}{S \times e}$$

b) Y, O, Ti implantations in Fe samples

The 1.2 MeV Y, 700 keV Ti, 650 keV O and 285 keV O implantations were carried out with the 3 MV Tandetron accelerator at the HZDR laboratory in Dresden, Germany. The 3 MV Tandetron is used both as high current MeV implanter and for various ions beam analytical works.

The ion beam is obtained by sputtering of the source material using 7 keV Cs ions. Source material is FeO for 16O^+ , TiH for 48Ti^+ and YO for 89Y^+ . The ions obtained are separated by the analyzing magnet.

The purity of the ion sources are good and the impurity level is much lower than 1 ppm in every case. The Fe samples are glued onto the round sample holder of 5 cm diameter by silver solution. Four Fe samples of 7 mm× 7 mm are glued on the same sample holder for each implantation. The samples are scanned by the ion beam and the implanted area is about 2.5 cm in diameter. The current was measured by 4 corner Faraday cups. During the implantations, the sample holder is cooled by water circulation to keep the room temperature.

II.2.2. Damage induced by ion irradiation/implantation

During ion irradiations or implantations, the energetic incident particles transfer one part of the energy to the lattice atoms, by elastic collisions or inelastic collisions. In the metallic materials like Fe and FeCr irradiated with ions with limited energies, the main mechanism is due to elastic collisions which induce direct displacement of lattice atoms. As shown in Figure II-4(a), the incident particles of M_1 mass with energy E_i transfers kinetic energy T (calculated by the followed equation) to the lattice atom of M_2 mass giving birth to a primary knock-on atom (PKA).

$$T = 4 \frac{M_1 M_2}{(M_1 + M_2)^2} \cdot \cos\varphi \cdot E_i$$

If the transferred kinetic energy T is higher than the displacement energy threshold E_d defined as the minimum required energy to permanently displace the atom from its regular position, the PKA will be displaced from its site. As shown in Figure II-4(b); if the energy T of PKA is high enough, the PKA becomes itself a projectile generating additional knock-on atoms leading to the production of a displacement cascade in which point defects are accumulated.

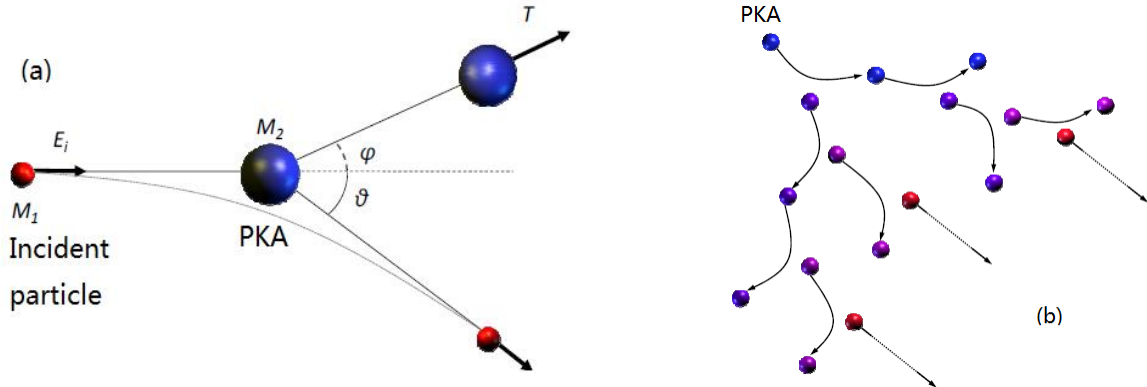


Figure II-4: (a) Elastic collision between the incident particle and primary knock-on atom (PKA). (b) The cascade formation by collection of point defects created by PKA.

The PKA generates vacancies (V) and the ejected atoms could be placed into interstitial (I) positions. V and I point defects are in equal numbers. Each pair of V- I is called a Frenkel pair. Many Frenkel pairs are thus created in displacement cascade. According to MD simulations ^[135], cascades evolve in several stages: collision phase, where the new sub cascades are created (duration ~ 1 ps); thermal spike phase, with a large increase of displaced atoms, without a new sub cascade formation (duration ~ 1 ps) and a

lattice restoration phase (few ps) where 99.5% of atoms find its lattice positions and only few stable defects remain. These residual defects are in the form of mono- vacancies and self- interstitial atoms (SIA) as well as SIA and vacancy clusters. These defects could migrate within the material. If an interstitial meets a vacancy, there is a recombination and both defects disappear. On the other hand, when two defects of the same nature meet, they can gather together to form a dimer. The arriving of a third defect of the same nature can lead to a trimer and so on. Thus defect clusters with a size of few tens of nanometers can be formed by agglomeration of mobile point defects and their clusters. L. Malerba reviewed the molecular dynamics (MD) simulations of displacement cascades in α - Fe that have been performed using different interatomic potentials^[136]. **Figure II-5** (a) strives to condense as much information as possible from the literature data concerning the defect production efficiency (η), defined as the ratio between the number of Frenkel pairs (FP) that survived in cascade recombination at the end of the simulations and the number of NRT displacements. It has to be noted that all interatomic potentials (used till 2003- 2004) with only one exception provide essentially the same defect production efficiency for cascade energies above 2 keV, with a value of 0.3 ± 0.1 , in agreement with experimental assessments. **Figure II-5(b)** presents the fraction of the vacancy in clusters defined as the ratio of the number of vacancy defects found in clusters (of size ≥ 2) to the total number of FP. The three potentials provide similar results, with the fraction ~ 0.2 - 0.3 . Concerning the cluster size, the author indicates that there is general agreement on the fact that it is difficult to find more than 4 - 5 vacancies in the same cascade produced cluster, the average size being 2- 3. However, there are too few data to draw definitive conclusions.

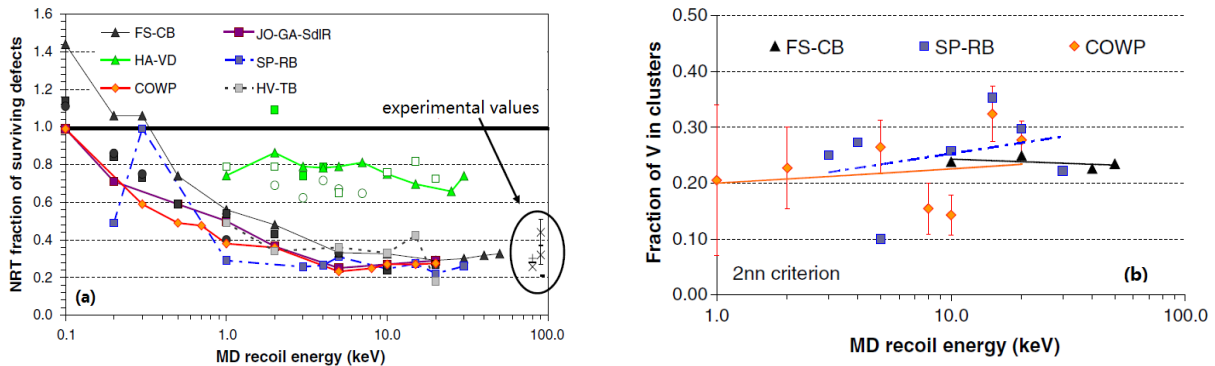


Figure II-5: a) Defect production efficiency versus cascade energy according to the six potentials. Full symbols are averages; empty symbols are single cascades. Triangles, diamonds and squares correspond to simulations at, respectively, 100, 300 and 600 K. Efficiency values obtained from combinations of experimental and calculation data for α - Fe are given for comparison on the right side of the figure. b) Vacancy clustered fraction obtained from different potentials using 2 nn criterion for the analysis. The same relationship between simulation temperature and symbol as in a).^[136]

It should also be noted that the foreigner atoms, for example the energetic incident ions (Y, Ti, O in this thesis), are also introduced into the materials and enter in the substitutional or interstitial positions during implantations. Their presence could change the mobility and agglomeration of point defects. There are also other defects like dislocation, dislocation loops etc. introduced during implantation/irradiation. But in this thesis, the authors focus on the properties of vacancy defects.

II.2.3. Defects and solutes depth profiles calculated using SRIM

a) He irradiation in bcc Fe and FeCr

The Figure II-6 shows the depth profiles of He concentrations and the corresponding induced damage calculated by using SRIM 2008^[137] for pure Fe irradiated with 1.5 MeV ^4He for fluence of $5 \times 10^{15} \text{ cm}^{-2}$ and for Fe-12Cr irradiated with 2 MeV ^4He for fluence of 10^{16} cm^{-2} . The 'K- P quick calculation of damage' mode has been utilized as suggested by R.E. Stoller et al.^[138] because the number of displacements obtained from this model is more comparable to the NRT model than the one obtained by the full cascade mode. The value of the displacement energy threshold E_d for bcc Fe is ranged between 22- 54.5 eV^[139-145]. The most plausible and the one used in this thesis is 40 eV^[139, 146]. For FeCr model alloys, an average displacement energy of 40 eV^[147, 148] has been widely accepted in the previous studies. The radiation damage exposure is quantified by unit known as atomic displacement per atom (dpa). The effect of defects recombination in the cascades is not considered in SRIM calculation. Thus, for the same type of irradiated ions with the same energies, the damage dose in dpa is proportional to the fluence. In the same figure, the slow positron implantation profile is also illustrated for different energies (see chapter 2 section II.3 for details)^[149].

Eight different fluences have been performed in the range from 1×10^{13} to $1 \times 10^{17} \text{ cm}^{-2}$ for 1.5 MeV He irradiated Fe. As shown in Figure II-6(a), in the track region of ^4He ions located between surface and $2 \mu\text{m}$ which is probed by the slow positron beam, the damage dose is 0.1 dpa and the helium concentration is 4 atomic ppm for the highest fluence of 10^{17} cm^{-2} . This concentration is quite low, thus the effect of helium on vacancy defects could be ignored in the following.

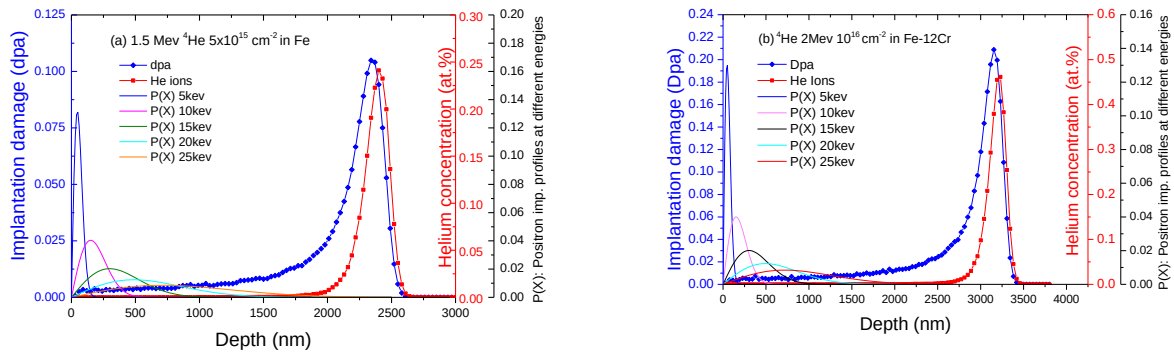


Figure II-6: Depth profile of defect production and atomic concentration (a) for 1.5 MeV ^4He irradiation at the fluence of $5 \times 10^{15} \text{ cm}^{-2}$ in Fe (b) for 2 MeV ^4He at the fluence of 10^{16} cm^{-2} in Fe12Cr compared to positron implantation profiles calculated for various energies P(X).

For 2 MeV He irradiated FeCr, five fluences have been carried out in the range from 10^{14} to $1.3 \times 10^{17} \text{ cm}^{-2}$. The densities of Fe-Cr model alloys with 3-12 at.%Cr content are very similar: 7.845 g/cm^3 for Fe-3 at.%; 7.832 g/cm^3 for Fe-5 at.%; 7.805 g/cm^3 for Fe-9 at.% and 7.785 g/cm^3 for Fe-12 at.%. And Fe and Cr displacement threshold energies are the same, 40 eV, as suggested by the references^[147, 148]. For these reasons, the defects and solutes profiles of the four model alloys are similar. Only the profiles calculated

for Fe-12 at.%Cr are shown in Figure II-6(b). The other three cases are considered the same as this one. Like in irradiated Fe, the positrons with energy from 0.5keV to 25keV probe the region from 0 to 2 μm in FeCr where helium atomic concentration remains relatively low and damage is relatively homogenous. The damage dose at depth ~ 720 nm is used to represent damage level in the sample because positrons with 25keV have a mean implantation depth of 720 nm. For the highest fluence, $1.3 \times 10^{17} \text{ cm}^{-2}$, the damage dose is 0.078 dpa and helium atomic concentration is 3.11×10^{-5} at.% (0.3 appm). This concentration is quite low, moreover the NRA (nuclear reaction analysis) results ^[150] have shown that helium profile spread little during the irradiation, thus the effect of helium to vacancy defects could also be ignored in irradiated FeCr.

The irradiation conditions for 1.5 MeV He in Fe and 2 MeV He in Fe-12 Cr are reported in Table II.3. The irradiation conditions for Fe-3Cr, Fe-5Cr and Fe-9Cr are considered the same as for Fe-12Cr.

Matrix	Irradiation type	Fluence (at.cm ⁻²)	Probed region	Damage dose at $\sim 720\text{nm}$ (dpa)	He atomic concentration at $\sim 720\text{nm}$ (appm)
Fe	1.5 MeV ⁴ He	10^{13}	0- 2 μm	1×10^{-5}	0.0004
		2×10^{13}	0- 2 μm	2×10^{-5}	0.0008
		10^{14}	0- 2 μm	1×10^{-4}	0.004
		2×10^{14}	0- 2 μm	2×10^{-4}	0.008
		5×10^{14}	0- 2 μm	5×10^{-4}	0.02
		10^{15}	0- 2 μm	1×10^{-3}	0.04
		10^{16}	0- 2 μm	1×10^{-2}	0.4
		10^{17}	0- 2 μm	1×10^{-1}	4
Fe-12Cr	2 MeV ⁴ He	10^{14}	0- 2 μm	6×10^{-5}	0.00023
		2×10^{14}	0- 2 μm	1.2×10^{-4}	0.00046
		10^{15}	0- 2 μm	6×10^{-4}	0.0023
		10^{16}	0- 2 μm	6×10^{-3}	0.023
		1.3×10^{17}	0- 2 μm	7.8×10^{-2}	0.3

Table II.3: 1.5 MeV He irradiation conditions in Fe and 2 MeV He irradiation conditions in Fe-12Cr samples.

b) Y, Ti and O implantations in Fe

The Figure II-7 shows the atomic concentration profiles of 1.2 MeV Y, 700 keV Ti and 285 keV O in Fe and of their corresponding damage dose given in dpa calculated by the 'K- P quick calculation of damage' mode in SRIM 2008. The implantation energies are fixed in order to have the same average projection ranges ($R_p = 262$ nm in these cases) for all these three types of ions as indicated in Table II.4. With regard to the slow positron implantation profiles in pure Fe, the positrons with energy from 0.5keV to 25keV could detect the entire implanted region. Those of 10keV to 25keV enter in the non-implanted region, which is called 'lattice', so the information of the lattice (without vacancy defect) should be obtained. The implantations have been performed at various fluences and at the room temperature. For Y implantations, the low temperature implantations have also been realized to study the effect of irradiation temperature. These experiments were performed by using liquid nitrogen flow to cool the sample holder. The concentrations of Y, Ti and O at R_p were fixed at the same values, 1170 appm and 1760 appm, for the two highest fluences. These concentrations are already higher than the low solubility of Y (290 at. ppm in iron at 800°C) ^[128] and of O ^[129]. Thus, they should have a non-negligible influence on the vacancy. It has been noted that the implantation energies increase with the mass of the ions O, Ti, Y, to have the same projection ranges. Higher energy is required to implant the heavier ion. And for the same number of ions implanted into the Fe sample, the Y implantation induces higher damage dose than Ti and O as shown in Table II.4. It has to be noted that Y, Ti, O ion implantations have damage doses much higher than that of He irradiation.

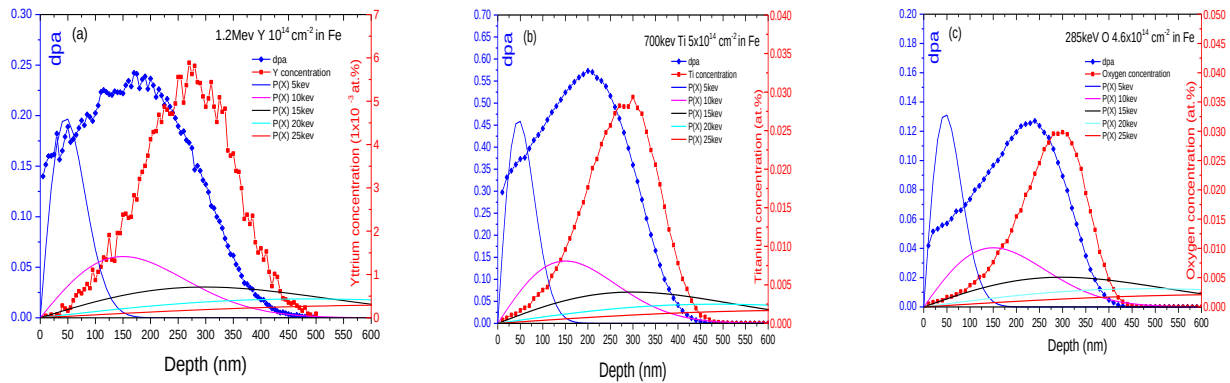


Figure II-7: Depth profile of defect production and atomic concentration for (a) 1.2 MeV Y in Fe (b) 700 keV Ti in Fe (c) 285 keV O in Fe compared to positron implantation profiles calculated for various energies P(X).

The implantations conditions, damage dose and solute concentrations, are summarized in the following table.

Ions	Implantation T (°C)	Implantation Energy	Ions range Rp (nm)	Fluence (cm ⁻²)	Max. damage dose (dpa)	Max. Concentration (appm)
Y	RT and low temperature (LN ₂)	1.2 MeV	262 nm	10 ¹⁴	0.24	60
				2x10 ¹⁵	4.85	1170
				3x10 ¹⁵	7.27	1760
Ti	RT	700 keV	262 nm	5x10 ¹⁴	0.57	300
				2x10 ¹⁵	2.28	1170
				3x10 ¹⁵	3.42	1760
O	RT	285 keV	262 nm	4.6x10 ¹⁴	0.13	300
				1.8x10 ¹⁵	0.5	1170
				2.7x10 ¹⁵	0.75	1760

Table II.4: 1.2 MeV Y, 700keV Ti and 285keV O irradiation conditions in Fe samples.

In addition, 650 keV O implantations are also performed. This implantation energy gives a projection range of 510 nm much deeper than the one of the 285 keV O implantation (262 nm). This deeper range has been chosen to facilitate the observation of O diffusion towards the sample surface if the diffusion occurs. Two fluences have been carried out at room temperature and the O concentrations are fixed as the same for 285 keV O implantations. The damage doses of these two energy implantations are very close. The damage dose and O concentration depth profiles calculated using SRIM are shown in Figure II-8 and Table II.5.

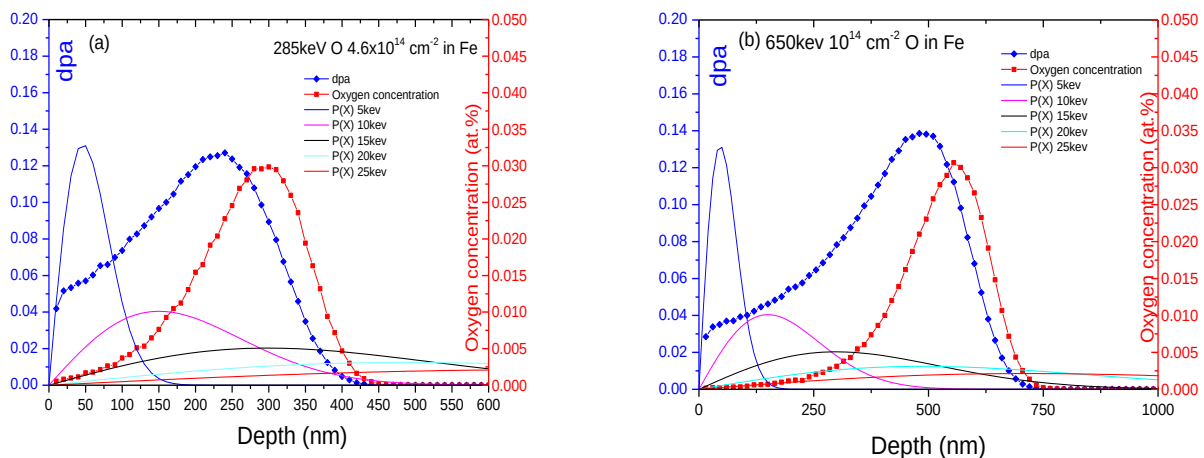


Figure II-8: Depth profile of defect production and atomic concentration (a) for 285 keV O implantation in Fe (b) for 650 keV O implantation in Fe compared to positron implantation profiles calculated for various energies P(X).

Ions	Implantation T (°C)	Implantation Energy	Ions range Rp (nm)	Fluence (cm ⁻²)	Max. damage dose (dpa)	Concentration (appm)
O	RT	285 keV	262nm	4.6x10 ¹⁴	0.13	300
				1.8x10 ¹⁵	0.5	1170
				2.7x10 ¹⁵	0.75	1760
O	RT	650 keV	510 nm	5.8 x10 ¹⁴	0.14	300
				2.2x10 ¹⁵	0.52	1160

Table II.5: 650 keV O and 285keV O implantation conditions in Fe samples.

II.2.4. Conclusions

The high energy helium 4 (⁴He+) irradiations, 1.5 MeV in Fe and 2 MeV in FeCr, have been carried out to study the pure vacancy defects in Fe and FeCr matrix. The 1.2 MeV Y, 700 keV Ti, 650 keV O and 285 keV O implantations in Fe were carried out to study the interactions between Y, Ti, O atoms and vacancy in Fe matrix.

Irradiation in Fe and FeCr introduces in the material defects and the foreigner atoms as the incident ions (Y, Ti, O in this thesis), which stop in the substitutional or interstitial positions. L. Malerba reviewed the molecular dynamics (MD) simulation of displacement cascades in α -Fe^[136]. In MD simulation of displacement cascades induced in α -Fe the defect production efficiency, defined as the ratio between the number of Frenkel pairs (FP) that survived in- cascade recombination at the end of the simulations and the number of NRT displacements, has been found, at the value of 0.3 ± 0.1 for cascade energies above 2 keV, in agreement with experimental assessments. The fraction of the vacancy in clusters defined as the ratio of the number of vacancy defects found in clusters (of size ≥ 2) to the total number of FP is ~ 0.2 - 0.3 and the average size of these clusters is 2- 3 vacancies..

SRIM code has been used to calculate the damage and solutes depth profiles iduced in the different irradiation/implantation conditions: He irradiations in Fe and FeCr samples, Y, Ti, O implantations in Fe samples. Eight different fluences have been performed in the range from 1×10^{13} to 1×10^{17} cm⁻², it corresponds to a damage dose ranging from 1×10^{-5} to 1×10^{-1} dpa for 1.5 MeV He irradiated Fe. For 2 MeV He irradiated FeCr, five fluences have been carried out in the range from 10^{14} to 1.3×10^{17} cm⁻² corresponding to the damage dose in the range from 6×10^{-5} to 7.8×10^{-2} dpa. The Y, Ti and O implantations have been performed at various fluences. The concentrations of Y, Ti and O at Rp were fixed at the same values, 1170 appm and 1760 appm, for the two highest fluences. They should have a non-negligible influence on the vacancy.

II.3. Positron annihilation spectroscopy (PAS)

Positron annihilation spectroscopy (PAS) allows studying a variety of phenomena and material properties on an atomic scale^[132]. Being the anti-particle of electrons, positrons annihilate with electrons and allow probing the electronic structure of the solids. Due to their capacity to get trapped in defects, positrons are used to probe defects at low concentrations and with high sensitivity to the size of the vacancy defects in the range from single vacancies up to cavities containing 50-100 vacancies^[109]. With the advantage of being a non-destructive material characterization method, positron annihilation has

been developed as a well-established tool for investigations of metals, semiconductors, polymers and porous materials.

Three different techniques are available for PAS: 1) angular correlation spectroscopy 2) Doppler broadening spectroscopy 3) positron lifetime spectroscopy. The first two techniques give information on the electron momentum distribution at the positron annihilation state while the third exploits the sensitivity of positrons to the electron density. In this thesis, Doppler broadening spectroscopy is used. Coupled to a slow positron beam facility developed in the CEMHTI laboratory at Orleans, it allows studying thin layers. Slow positron beam Doppler broadening (SPBDB) technique and its theoretical basis will be detailed in this section. For more details about PAS analysis and slow positron beam technique, readers can refer to the references ^[132, 151] devoted to these topics.

In this section, the interaction of positrons in condensed matter is firstly introduced: positrons implantation and diffusion, their trapping and annihilation. Then the slow positron beam Doppler broadening spectrometer developed in CEMHTI laboratory is presented. The defects identification and quantification have been explained.

II.3.1. The interaction of positrons in condensed matter

This section summarizes the basic processes which occur to positrons entering condensed matter. The implantation and diffusion of positrons are presented. After, the main features of positron trapping and detrapping from bulk and surface defects are summarized. Finally, the positron annihilations in different states are discussed.

a) Positrons implantation and diffusion in matter

Once positrons with a kinetic energy enter into the sample, they lose rapidly their energy by interaction with electrons and are thermalized. For the fast positrons emitted by a radioactive source such as ²²Na, these positrons have a fairly wide energy distribution and their implantation depth is described by the following equation ^[152]:

$$P(z) = e^{-\alpha z} \text{ and } \alpha(\text{cm}^{-1}) = 16 \times \frac{\rho(\text{g.cm}^{-3})}{E_{\text{max}}^{1.4}(\text{MeV})}$$

Where z is the implantation depth and α is the attenuation coefficient in the solid. α depends on the material density and the maximum kinetic energy E_{max} of positrons which is 540 keV in the case of ²²Na source. In the pure Fe, they could penetrate into samples up to a maximum depth of about 200 μm . The implantation profile of the fast positrons in Fe is illustrated in the Figure II-9(a).

For the mono-kinetic positrons as supplied by the slow positrons beam in CEMHTI laboratory, these positrons have low kinetic energy in the range from 0.5 keV to 25 keV and their implantation depth profile is makhovian and given by the following equation ^[153]:

$$P(z) = -\frac{d}{dz} \left(e^{-\left(\frac{z}{z_0}\right)^m} \right) \text{ where } z_0 = \frac{z_m}{0.886} \text{ and } z_m = \frac{A}{\rho} E^n$$

Where z_m is the mean implantation depth of positrons (in cm). ρ is the material density (in $\mu\text{g.cm}^{-3}$). E is the implanting energy of positrons (in keV). And A , m and n are constants which depend slightly on the materials and their values are presented in Table II.6. With these parameters, the implantation profiles of the mono-kinetic positrons in Fe are illustrated in the Figure II-9(b). It has to be noted that the implantation profiles broaden with the increasing implantation energy. It means that higher energy positrons detect deeper region of samples but correspondingly the depth resolution decreases.

$A (\mu\text{g.cm}^{-3}.\text{keV}^{1.7})$	M	n
2.95	2	1.7

Table II.6: A , m and n constants for determining the monochromatic positrons implantation profiles^[154].

During positron implantations, the annihilation probability in the solid is very low. This probability increases once positrons are thermalized and start to diffuse in the solid. In fact, the cross section of positron annihilation is the inverse function of positron speed. The most fraction of positrons annihilate when their kinetic energy is lower than that of electrons in the solid.

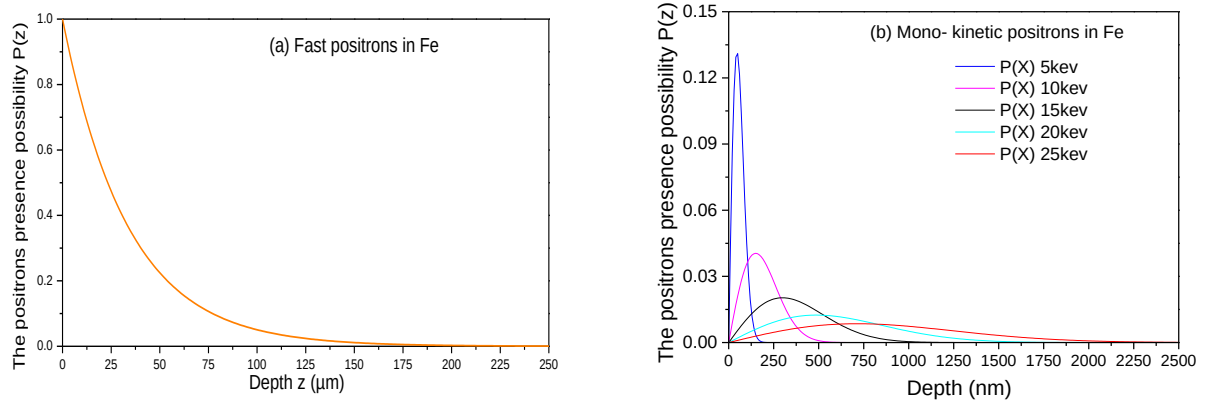


Figure II-9: The positrons implantations profiles in Fe. (a) The fast positrons emitted by an intense radioactive source $\beta^+ {}^{22}\text{Na}$. (b) The mono- kinetic slow positrons with energy fixed in the range from 0.5 keV to 25 keV in the case of slow positrons beam in CEMHTI laboratory.

In the absence of point defects in the material lattice, the intrinsic diffusion length L^+ of positrons before annihilation is given by the following equation^[153]:

$$L^+ = \sqrt{\frac{D_+}{\lambda_L}}$$

Where D_+ is the diffusion coefficient of positrons and λ_L is the positron annihilation rate in the material lattice. The positron diffusion lengths reported for defect-free metals are $\sim 100 \text{ nm}$ ^[155]. Higher L^+ value of 184 nm, has been obtained by Iwai and *al.*, for pure Ni (99,997 wt.%) annealed at 800°C in vacuum for one hour^[156]. Diffusion length decreases when the point defects concentration increases and the positron trapping increases. The effective diffusion length is defined as:

$$L_{eff}^+ = \sqrt{\frac{D_+}{\lambda_L + K_d}}$$

Where K_d is the trapping rate of positrons in defects. The trapping of positron in the material could occur in vacancies, dislocations, solute- vacancy complexes or precipitates (positron trapping will be discussed in the next section). It has been noted that the effective diffusion length of positrons decreases when the trapping rate K_d increases.

b) Positron trapping

Positron trapping is a quantum- mechanical transition between a delocalized propagating state of positron in lattice when it diffuses and a localized one, at an open- volume defect, around a negatively charged impurity or at a surface. Trapping in defects could be described by the specific trapping coefficient μ_d and the defect concentration c_d . It is described by the following equation:

$$k_d = \mu_d c_d$$

And the effective diffusion length is then transformed into the following form:

$$L_{eff}^+ = \sqrt{\frac{D_+}{\lambda_L + \mu_d c_d}}$$

Thus, it is concluded that the effective diffusion length of positrons is the inverse function of the square root of defect concentration.

According to the size and charge of defect, the trapping could be classified into two types: deep and shallow trapping. The binding energy of positrons in the deep traps is high and their escape from the trapping is negligible at room temperature. It is not the case for the shallow traps which have a low binding energy for positrons and the positrons could escape only by thermally activated process even at room temperature. For example, the vacancy type defects are deep traps and the dislocations are shallow traps in metals. There is no charged defect in metals.

The specific trapping coefficient μ_d is calculated as the following equation:

$$\mu_d = \frac{\mu_d^{at}}{N^{at}}$$

Where N^{at} is the atomic density of material, $8.49 \times 10^{22} \text{ at.cm}^{-3}$ for the Fe. In the metal, the atomic specific trapping coefficient μ_d^{at} for the vacancy defect varies from 10^{14} to 10^{15} s^{-1} [157]. For the single vacancy V in Fe, the atomic specific trapping coefficient μ_V^{at} has been determined to be $1.1 \pm 0.2 \times 10^{15} \text{ s}^{-1}$ [158]. Thus, the specific trapping coefficient μ_V is $1.296 \times 10^{-8} \text{ cm}^3 \cdot \text{s}^{-1}$. For the vacancy clusters nV in the metal, the trapping coefficient could be estimated as directly proportional to the number of vacancies n [159].

$$\mu_{nv} = n \times \mu_V$$

To increase the trapping rate of positrons for dislocation, the measure of positrons at low temperature (below room temperature) could be performed. The trapping coefficient in dislocation depends on temperature and increases at low temperature^[160]. A cryocooler is available in CEMHTI laboratory which could be linked to the sample holder of positron machine. It is used to cool the samples to cryogenic temperatures; helium liquid is used in this case.

The positrons could also be sensitive to the presence of the precipitates in the matrix. The trapping criterion of the positrons in the precipitate is defined by its affinity, A^+ , with the given elements. The positron will be trapped in the spherical precipitate of the P element in the M element matrix, if the affinity difference $\Delta A^+ = |A_P^+| - |A_M^+|$ is positive and the radius of the precipitate exceed the critical radius r_c calculated as followed^[161]:

$$r_c = \frac{0.31}{\sqrt{\Delta A^+}}$$

Where r_c is in nm and the ΔA^+ is in eV. The positron affinities for elements in ODS steel are: Fe= -3.84 eV, Cr= -2.62 eV, Y= -5.31 eV, Ti= -4.06 eV^[86]. For example, ΔA^+ between Y and Fe is 1.47 eV. The critical radius r_c for Y precipitates is 0.2557 nm and thus the critical volume of precipitate is 0.07 nm³. Taking the atomic radius of one Y atom at 0.18 nm and its volume at 0.024 nm³, the Y precipitates containing three or more Y atoms could be detected by the positrons. For the Ti precipitates, this number is 12 Ti atoms.

c) Positron annihilation

The positron is the antiparticle of the electron. Their meeting led to the annihilation and is followed by the emission of electromagnetic radiation. The annihilation mode of e^+/e^- pair depends strongly on the spin state of the pair. For a pair in the spin state $S=0$ (para), the number of photons γ emitted is even and it is odd for a pair in the spin state $S=1$ (ortho).

- Annihilation emitting 1 γ photon occurs for high kinetic energy positron (> 1 MeV) which is able to approach a nucleus. This annihilation state is quasi non-existent in our experimental conditions.
- Annihilation emitting 2 γ photons has the largest cross section.
- Annihilation emitting 3 or more γ photons has a low cross section. The value of cross section decreases when the number of photons increases.

Thus, the annihilation emitting 2 γ photons is dominant when the positrons enter in the solid. Two configurations of e^+/e^- pair exist before their annihilation.

- Free configuration: the positron interacts with the medium without to be linked to an electron.
- Bound configuration: the positron forms a hydrogen-type atom with an electron. This configuration is called positronium and it is formed mainly at the sample surface and in the large free volume defects (cavities, nanopores...).

In the free configuration, the positron could freely annihilate with electrons in a delocalized state. It could also annihilate with electrons in a highly localized trapping sites in the matrix, especially in the vacancy type defect. These two states are detailed in the following.

Delocalized state

In a crystalline solid, the positron is subject to periodic potential network due to the nucleus of atoms. Its wave function is thus a function of Bloch in the form:

$$\Psi(r) = e^{ikr} u_k(r)$$

$U_k(r)$ is a periodic function with the same periodicity as the crystal lattice.

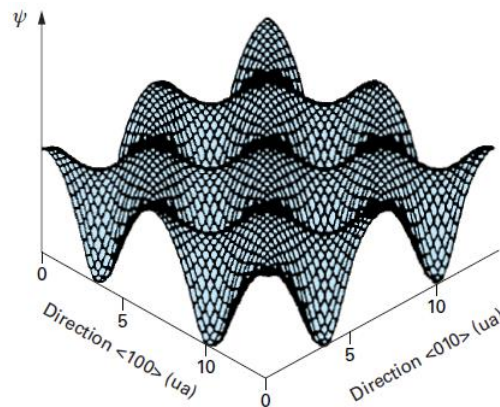


Figure II-10: Three- dimensional representation of the probability density of the positron presence in the delocalized state calculated for nickel ^[132]. The zones of the minimum probability are the places where the atomic nuclei are located.

As shown in Figure II-10, the repulsive interaction between the atomic nuclei and positrons makes the probability of positron presence in the interstitial regions maximum. The annihilation rate in the lattice is defined by λ_L which is the inverse of the positron lifetime in the lattice τ_L . The positron annihilation characteristics in delocalized state define the positron annihilation in the lattice without positron trapping.

Localized state

The positron is positively charged and the Coulomb energy decreases in regions poor in nucleus. The vacancy type defects are the atomic site where lacks nucleus. The positrons fall in these free volumes whose energy states are lower than that of lattice and remain trapped in these defects. Once trapped, the positron explores the local electron density which decreases with the increase of vacancy defects free volume. The wave function of a positron in the localized state is shown in Figure II-11.

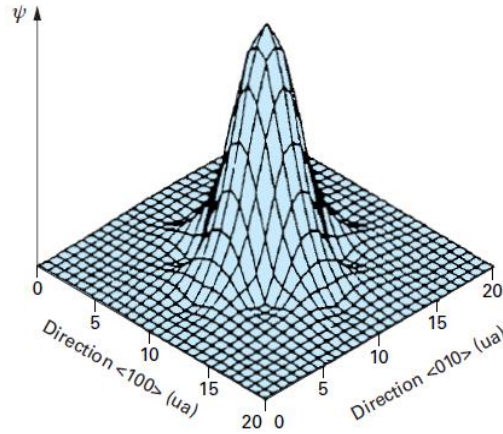


Figure II-11: The wave function of a positron in the localized state calculated for nickel.^[132]

The positron annihilation characteristics are utilized to study the defects present in the solid. Slow positron beam Doppler broadening (SPBDB) technique is used in this thesis and its theoretical basis will be detailed in next section.

II.3.2. Slow positron beam Doppler broadening

a) Slow positron beam in CEMHTI

It took about twenty years to develop the implanter of mono- kinetic slow positron beam. They were developed in some U.S. laboratories in the early 1980 and operate in the following principle as shown in Figure II-12. A fraction of positrons emitted in the high vacuum (under a pressure of about 10^{-7} Pa) by a high intensity radioactive source β^+ (50 mCi that to say 1.85 GBq) are converted into a straight- line positron beam of a few eV, quasi mono- energetic, being slowed by a moderator. The positrons thermalized near the surface of the moderator are emitted spontaneously and all leave with a narrow and low energy distribution centered around 3 eV with a narrow angular distribution perpendicular to the moderator surface. The positron beam is then guided and accelerated to a target by the magnetic and electric fields.

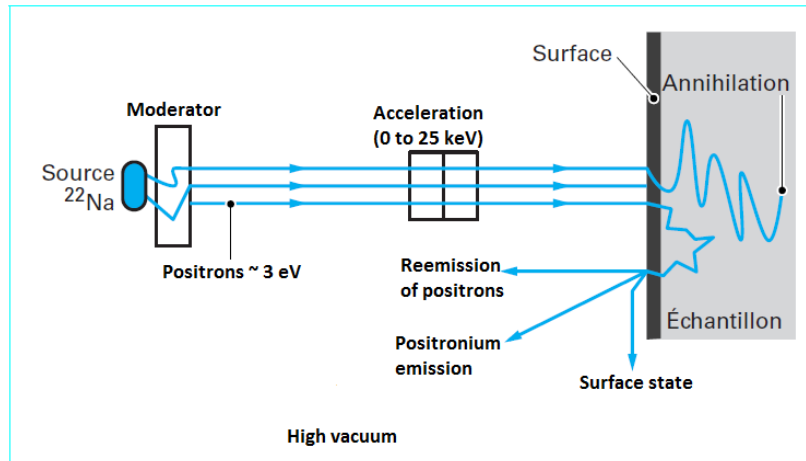


Figure II-12: Schematic principle of a slow positrons beam ^[132].

The slow positron flux obtained is only $\sim 10^5 \text{ cm}^{-2} \cdot \text{s}^{-1}$ due to the low moderation efficiency. Several attempts have been made to produce intense slow positron beam and allow further technical developments such as the microbeam. The sources could be replaced in this case by electron accelerators or nuclear reactors. In the last case, the production process of positrons consists in creating the e^+/e^- pairs by bombarding heavy targets with the gamma photons. It allows getting the intense flux of slow positrons about $10^8 \text{ cm}^{-2} \cdot \text{s}^{-1}$. For example, one target of tungsten placed in the gamma photons flux of one nuclear reactor (Munich in German ^[162] and Delft in Holland ^[163]) allows to get this intense positrons flux.

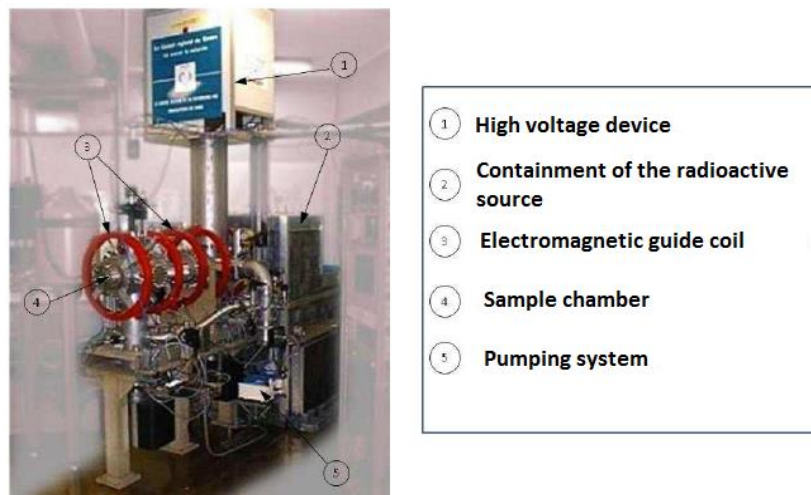


Figure II-13: The main components of slow positron beam in laboratory CEMHTI, Orleans.

The main components of slow positron beam in CEMHTI laboratory are illustrated in Figure II-13. The slow positrons beam with variable energy (0.1 to 25 keV) allows to characterize thin layers. This accelerator is coupled to a Doppler broadening spectrometer which allows measuring the energy of the

gamma photon emitted by e⁺/e⁻ annihilation. It gives the momentum distribution of the annihilated e⁺/e⁻ pair. This enables the characterization of vacancy- type defects or free volumes in solids.

In addition, an in- situ heating system has been developed in this positron machine. The sample is fixed on the copper sample holder which is heated by the voltage generator. During the heating, the sample chamber is always in high vacuum. The heating temperatures measured by thermocouple are in the range from 50°C to 550°C. After being heated, the sample is cooled in the sample chamber until returning to the room temperature. The positron measurement is launched after sample cooling.

b) Doppler broadening spectroscopy

In this section, the principle of Doppler Broadening Positron Annihilation Spectroscopy and its analysis are presented.

When a pair of e⁺/e⁻ annihilates, the momentum of the pair depends mainly on that of electron because the positron is most probably thermalized. Two gamma photons are emitted during the pair's annihilation and the energy of each gamma photon in the coordinate of mass center is expressed as followed:

$$E = m_0 c^2$$

C is the light speed and m₀ is the electron or positron mass. Thus, the energy obtained is 511 keV.

In the laboratory coordinate, the energy of gamma photon differs from 511 keV because of the Doppler broadening effect owing to the e⁺/e⁻ pair momentum. The energy of each photon becomes 511keV ± ΔE and the two photons are emitted in quasi- opposite directions at an angle of 180° ±θ as shown in Figure II-14. The energy deviation ΔE and angular θ deviation depend on the e⁺/e⁻ pair momentum P as followed:

$$\Delta E = \frac{c p_L}{2} \text{ and } \theta = \frac{p_T}{m_0 c}$$

p_L (p_T, respectively) is the longitudinal component (transversal, respectively) of the e⁺/e⁻ pair momentum.

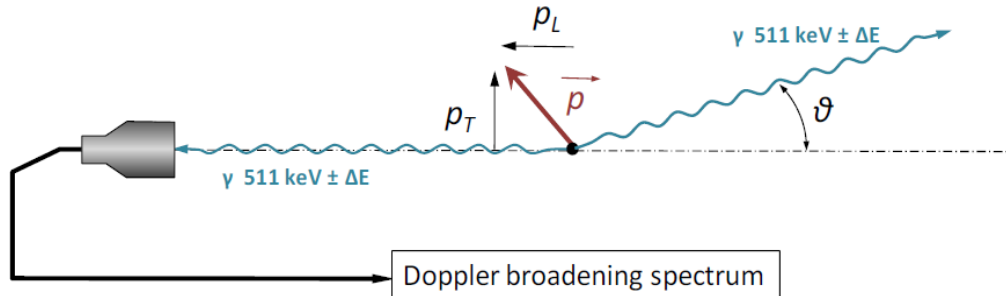


Figure II-14: Schematic demonstration of Doppler broadening spectrum measurement.

The Doppler broadening spectroscopy (DBS) consists in measuring the broadening of the annihilation line at 511 keV by using a high resolution gamma spectrometer. The DBS in CEMHTI laboratory uses a

high purity germanium (Ge) detector with a good resolution (<1.3 keV at 511 keV) and a high efficiency (>25% at 1.33 MeV). The Ge detector is functioning under the liquid N₂ temperature and polarized under the voltage of +3500 V. The signals emitted by the detector go through a series of analogic devices (amplification, anti-stack system...). The data are then converted into digital forms by one analogic digital converter. These collected data then form one Doppler spectrum which counts the number of each gamma photon's energy. In general, one Doppler spectrum includes 2×10^6 counts.

Once one spectrum is obtained, its treatment consists of subtracting the background noise. For the slow positron beam, this background noise is mainly due to the Compton scattering of 511 keV annihilation gamma rays. Thus as shown in Figure II-16(a), the noise of left side of 511 keV is higher than that of right side. The background noise depends on photon energy and is expressed as followed:

$$BF(E) = A + (B - A) \frac{F(E)}{F_{\text{totale}}}$$

Where $BF(E)$ is the background noise at energy E , A is the average noise on right side of the peak ($E > 523$ keV), B is the average noise on left side of the peak ($E < 504$ keV), $F(E)$ is the spectrum area between the energy E and E_r ($E_r = 523$ keV) and F_{totale} is the total spectrum area between E_l and E_r .

The symmetric spectrum is obtained as illustrated in Figure II-16(b) after subtracting the background noise. The spectrum is characterized by two parameters named S and W . S integrates the counts of the area around the centroid. S represents the fraction of e^+/e^- annihilations with low momentum which are mainly annihilations valence electron. The momentum window is defined in the range $(-2.49, 2.49) \times 10^{-3} m_0c$ for CEMHTI positron beam facility. W integrates the counts of the area in the wings of the spectrum. W represents the fraction of e^+/e^- annihilations with high momentum which are mainly annihilations with core electrons. The momentum window is in the range $(-24.88, -9.64), (9.64, 24.88) \times 10^{-3} m_0c$.

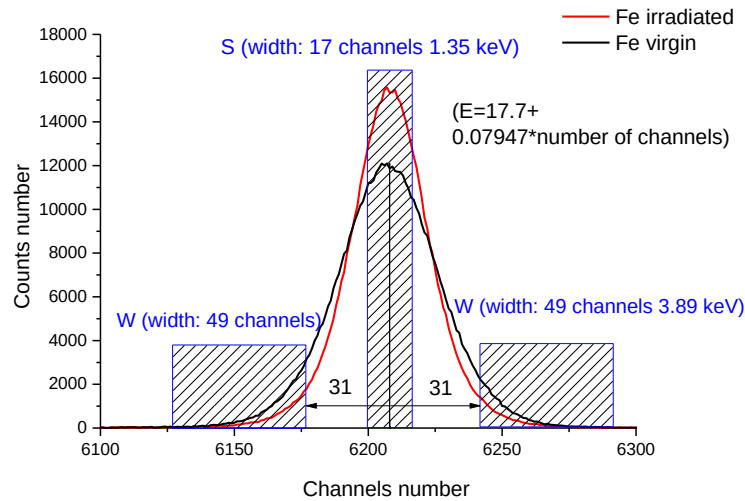


Figure II-15: The choice of S , W window width. The black curve represents the Fe virgin sample measured by positron with 25 keV. The red curve represents the Fe irradiated with 1.5 MeV He measured by positron with 25 keV.

Figure II-15 shows the curves representing the Fe virgin sample and the Fe sample irradiated with 1.5 MeV He respectively measured by positron with 25 keV. Comparing to the S, W window width choosed for CEMHTI positron beam facility as presented before, it is noted that the changements of S and W values could be well reflected.

When the vacancy defects are present in the sample, the parameter S (W) increases (decreases) because the possibility of positron annihilating with the valence electron (core electron) increases (decreases). Thus, the parameters S, W are sensitive to the presence of defects in material.

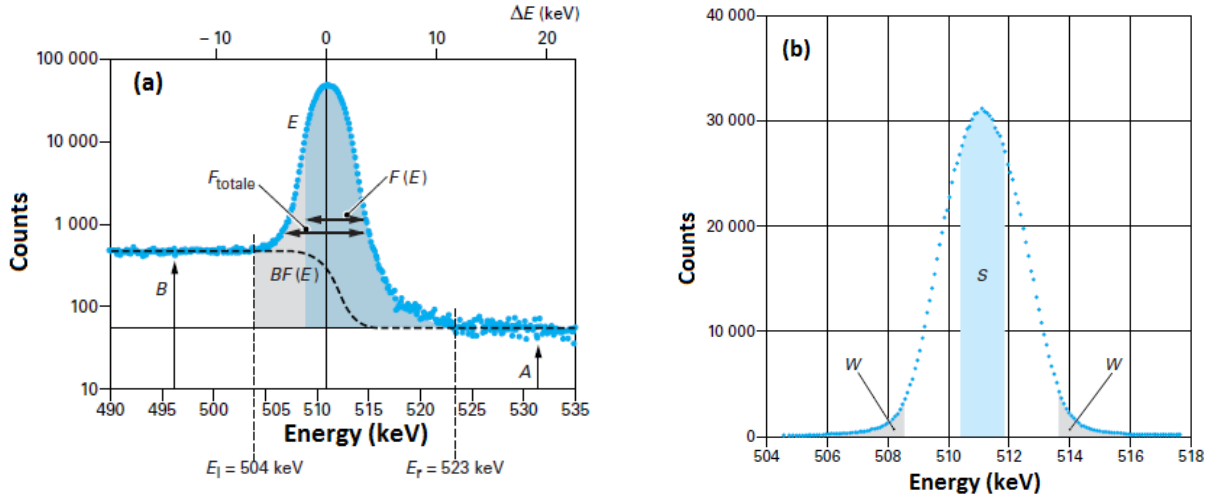


Figure II-16: (a) raw Doppler spectrum (b) spectrum obtained after subtraction of background noise. [132]

c) Defects identification and quantification

The interpretations of Doppler broadening results are mainly based on the diagram S in function of W. The S/W diagram provides the information about the different annihilation states in the sample. When the defects are present in the solid, the energy distribution of electrons is locally modified. The vacancy- type defects are the trapping sites where the number density of core electrons decreases much more than that of valence electrons. Thus, the presence of vacancy- type defects induces the increase of S and decrease of W compared to S, W values of the lattice without defects named as S_L and W_L . The lattice positron-electron annihilation characteristics correspond to a crystal lattice without defects. For the positrons annihilation in one distribution of traps, the S, W values are the sum of each type trap contribution with its characteristic S_i and W_i weighted by the annihilation fraction f_i in each type of defect i.

$$S = \sum_i f_i S_i \text{ and } W = \sum_i f_i W_i \text{ and } \sum_i f_i = 1$$

With the slow positron beam, the annihilation characteristics could be represented as the function of incident positrons energy E . When there are two annihilation states present in the sample, the annihilation fractions $S(E)$ and $W(E)$ are expressed as followed:

$$S(E) = f_1 S_1 + f_2 S_2 \text{ and } W(E) = f_1 W_1 + f_2 W_2 \text{ and } f_1 + f_2 = 1$$

Where f_1 and f_2 are the annihilation fractions in state 1 and 2. The function between $S(E)$ and $W(E)$ could thus be obtained by eliminating f_1 and f_2 :

$$S(E) = A \times W(E) + B \text{ where } A = -\frac{S_2 - S_1}{W_1 - W_2} \text{ and } B = \frac{S_2 W_1 - S_1 W_2}{W_1 - W_2}$$

The $S(W)$ points measured in a sample with two annihilation states thus align into one line with negative slope. The slope of the line depends on the defect nature and increases in absolute value with the increase of vacancy defect size. Figure II-17 illustrates the points S as function of W for different types of defects, the single vacancy V_1 , the di-vacancy V_2 and etc. and also lattice without defects as calculated in Silicon^[164]. The lines linking the lattice point and the defects ones have been plotted. If V_1 is the only one defect in the samples, the pair (S, W) measured will be located on the line defined by the points (S_L, W_L) and (S_{V_1}, W_{V_1}) which is characteristic of annihilation in V_1 . When the V_1 concentration increases, the annihilation fraction of positron in V_1 increases and the point (S, W) measured will approach to the point (S_{V_1}, W_{V_1}) . In addition, the slope of the characteristic line increases with the increase of the volume of the vacancy defect, from V_1 to V_5 .

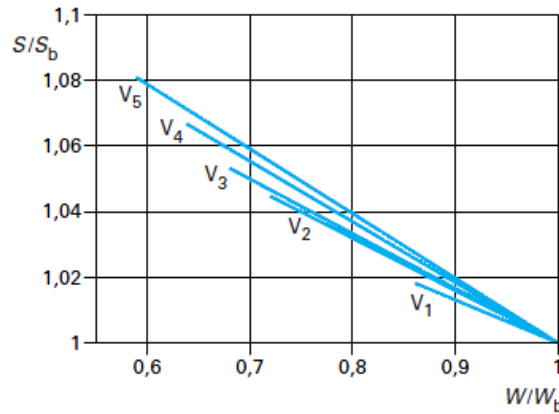


Figure II-17: Theoretical evolution of low momentum annihilation fraction S and high momentum annihilation fraction W as function of vacancy defect size in lattice silicon^[164]

The positron annihilation characteristics S , W could also allow giving information in the local chemical environment probed by positron. Y.Nagai et al. apply two-detector coincidence Doppler broadening (CDB) method of positron annihilation radiation to measure many kinds of elements^[165]. Figure II-18 shows the examples of the CDB spectrum for elements Ti, V, Cr and Mn. The pure Fe is chosen as the reference element and thus the CDB spectrums are normalized as the ratio curve. As illustrated in the figure, S and W are also sensitive to the chemical environment probed by positron. The

S values of these elements are higher than that of Fe and W values are lower. The S, W differences could be used to distinguish these elements from Fe.

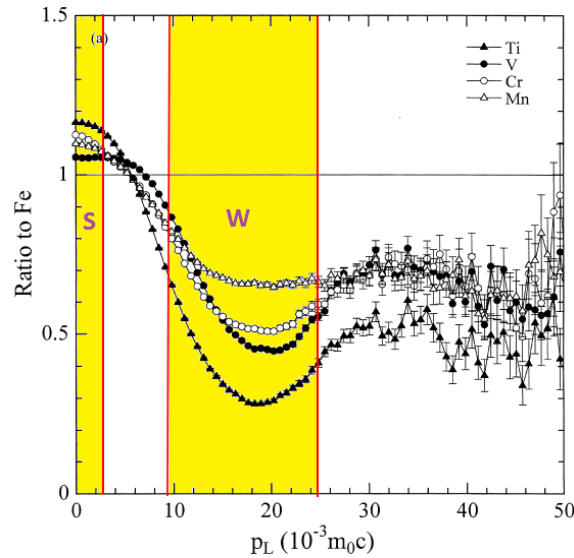


Figure II-18: The coincidence Doppler broadening (CDB) spectra for different elements after normalizing relative to Fe. ^[119]

Two forms of these foreign elements presence in the matrix could be detected by positrons. The first form is the element precipitate. As explained in the previous section, the precipitate could only be detected when the precipitate element has a higher binding energy than matrix element with positrons and the radius of the precipitate exceed the critical radius. For example, the positron affinity for Fe is -3.84 eV and for Cr is -2.62 eV ^[86]. Thus, the Cr precipitate in Fe matrix could not be detected because of Cr lower positron affinity in absolute value. The second form is the foreign element combining with a vacancy- type defect. In this case, the positrons could be trapped in this complex without considering the foreign element's positron affinity. For example, the positrons are sensitive to Helium- V complex in Fe matrix and the positron annihilation characteristics of vacancy are changed according to helium electron momentum distribution.

The concentration of detected defects could be determined by using the positron trapping model. The simplest model named the "one deep trap model" is presented. The deep trap could be vacancy-type defect as shown in Figure II-19. In this case, one part of positrons annihilates in the delocalized state, the lattice. Other part annihilates in localized state, the vacancy-type defect. In this model, it is assumed that the detrapping rate of positrons from the vacancy defect is zero at room temperature.

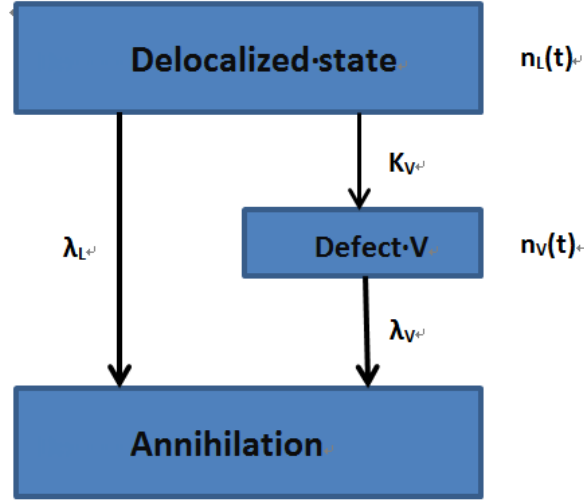


Figure II-19: Schematic illustration of one deep trap model of positron in solid.

The positrons populations in each of these two states at instant t could be expressed with the following equations:

$$\frac{dn_L(t)}{dt} + (\lambda_L + K_V)n_L(t) = 0$$

$$\frac{dn_V(t)}{dt} + \lambda_V n_V(t) = K_V n_L(t)$$

Where $n_L(t)$ is the positrons population delocalized in the lattice at instant t and $n_V(t)$ is the one trapped in the vacancy defect. λ_L is the positron annihilation rate in the material lattice and λ_V is the one in the vacancy defect. K_V is the trapping rate of positrons by vacancy.

The initial conditions assume that the positrons are not trapped during the period of thermalization and they are expressed as followed.

$$n_L(t = 0) = n_0$$

$$n_V(t = 0) = 0$$

And n_0 is the positons population in lattice at instant $t = 0$. With these conditions, the equations become:

$$n_L(t) = n_0 e^{-(\lambda_L + K_V)t}$$

$$n_V(t) = n_0 \frac{K_V}{\lambda_L - \lambda_V + K_V} (e^{-\lambda_V t} - e^{-(\lambda_L + K_V)t})$$

The total population of positrons in sample at instant t could be written as:

$$n(t) = n_L(t) + n_V(t) \text{ thus } n(t) = n_0 \sum_i I_i e^{-\frac{t}{\tau_i}}$$

$$\text{In this case } n(t) = n_0(I_1 e^{-\frac{t}{\tau_1}} + I_2 e^{-\frac{t}{\tau_2}}).$$

Where τ_1, τ_2 are the components of positron lifetime and I_1, I_2 are their intensities which could be obtained by positron lifetime measurement. Thus, they are calculated as followed:

$$\tau_1 = \frac{1}{\lambda_L + K_V} \text{ with } I_1 = \frac{\lambda_L - \lambda_V}{\lambda_L - \lambda_V + K_V}$$

$$\tau_2 = \frac{1}{\lambda_V} \text{ with } I_2 = \frac{K_V}{\lambda_L - \lambda_V + K_V}$$

The average positron lifetime could be defined as followed:

$$\tau_{average} = \int_0^{\infty} t \left(-\frac{dn(t)}{dt} \right) dt = I_1 \tau_1 + I_2 \tau_2 = f_L \tau_L + f_V \tau_V$$

With these equations, the f_L and f_V could be calculated:

$$f_L = \frac{\lambda_L}{\lambda_L + K_V}$$

$$f_V = \frac{K_V}{\lambda_L + K_V}$$

Where f_L and f_V represent the fractions of positrons annihilated in the lattice and vacancy respectively and $K_V = \mu_V \times C_V$ (voir section II.3.1II.3.1.b). Thus, the S, W parameters could be expressed in function of vacancy concentration C_V .

$$S = \frac{\lambda_L}{\lambda_L + \mu_V C_V} S_L + \frac{\mu_V C_V}{\lambda_L + \mu_V C_V} S_V$$

$$W = \frac{\lambda_L}{\lambda_L + \mu_V C_V} W_L + \frac{\mu_V C_V}{\lambda_L + \mu_V C_V} W_V$$

In the case of Fe, the positron annihilation characteristics of Fe lattice without defects (S_L, W_L) are determined as (0.35720, 0.11130) ^[166]. The characteristics of single vacancy in Fe (S_V, W_V) are (0.41644, 0.07053) which are determined in the study of 316L alloy (in the base of Fe) irradiated by 1.5 MeV 1×10^{16} Helium ^[167]. The annihilation rate in Fe lattice $\lambda_L = 1/\tau_L$ is determined by positron lifetime in Fe lattice τ_L which is 106- 110 ps ^[90, 168-170]. For the single vacancy in Fe, the atomic specific trapping coefficient μ_V^{at} is determined to be $1.1 \pm 0.2 \times 10^{15} \text{ s}^{-1}$ ^[158]. Thus, the specific trapping coefficient μ_V is $1.296 \times 10^{-8} \text{ cm}^3 \cdot \text{s}^{-1}$. With these parameters, the theoretical evolution of S and W as function of single vacancy concentration in Fe calculated with the one deep trap model is obtained and shown in Figure II-20. From this figure, it

has to be noted that the positrons could distinguish the concentration of single vacancy from 10^{16} cm^{-3} to 10^{20} cm^{-3} (0.118 appm to 1180 appm). The single vacancies with concentration higher than 10^{20} cm^{-3} will not change the values of S and W any more. This means that the saturation of positron trapping occurs in this type of defect. As explained in the previous section 3.1 of this chapter, the trapping coefficient could be estimated as directly proportional to the number of vacancies n . Thus, the positrons could distinguish the concentration of vacancy clusters with n vacancies from approximately $(1/n) 10^{16} \text{ cm}^{-3}$ to $(1/n) 10^{20} \text{ cm}^{-3}$, for example 10^{15} cm^{-3} to 10^{19} cm^{-3} (0.0118 appm to 118 appm) for vacancy clusters with size of 10 vacancies.

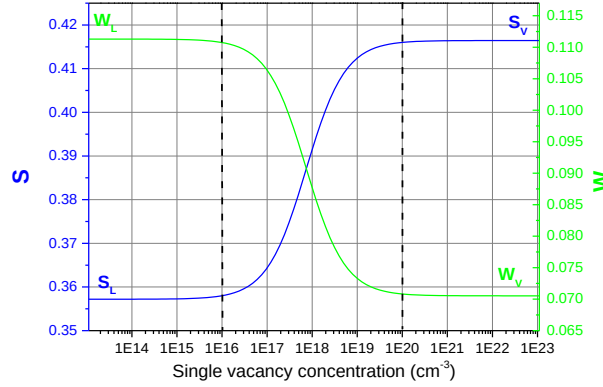


Figure II-20: Theoretical evolution of S , W as function of single vacancy concentration of Fe calculated by the one deep trapping model.

d) Defects depth profiles

The advantage of using slow positron beam is their capability to probe thin layers in sample as a function of depth. Due to the implantation depth profiles and diffusion of positrons in the sample the information of S as function of depth cannot be obtained directly from S as function of positron energy. The program Vepfit^[171] is used to obtain this information. It allows to fit experimental data $S(E)$ and $W(E)$ and to get the S and W depth profiles by considering that the sample is made of one or several homogenous characteristic layers of material. It fits these curves by considering the implantation and also diffusion profile of positrons. Each layer could be defined as a sum of successive slices of a given thickness $\Delta Z = Z_{i+1} - Z_i$ where the W_i and S_i are constant. The surface is a special positron annihilation state because positrons could be trapped and annihilate at the surface and positronium could also form and annihilates with specific annihilation characteristics. Therefore, Vepfit considers the surface as one additional annihilation state for fitting the curves. The theoretical relations used by Vepfit are the following:

$$W(E) = \sum_{i=1}^n f_i(E)W_i + f_{sf}(E)W_{sf}$$

$$S(E) = \sum_{i=1}^n f_i(E)S_i + f_{sf}(E)S_{sf}$$

Where $f_i(E)$ is the annihilation fraction in each slice i for the incident energy E and $f_{sf}(E)$ is the probability of surface annihilation. It should be noted that S_i , W_i could also represent a set of annihilation states. Vepfit supplies information about S_i , W_i , depth, thickness and the positron effective diffusion length L_{eff}^+ of each slice. The fitting model is illustrated in Figure II-21.

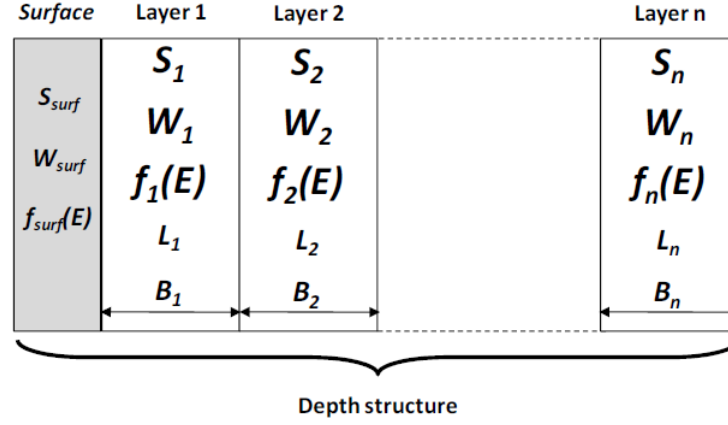


Figure II-21: The structure of homogenous layers simulated by Vepfit.

It should be noted that the objective of Vepfit adjustment is to minimize the difference between the experimental and the calculated spectrum. Several combinations of parameters shown in Figure II-21 could be obtained to achieve this objective. Thus, the results obtained should be examined to check their physical pertinence. For example, the positron intrinsic diffusion length L^+ in metal without defects is $\sim$ (100- 200) nm and the one in irradiated metal is shorter. Thus, L^+ values longer than 200 nm should not be adopted.

In addition, increasing numbers of parameters, for example the number of layers needed to fit experimental data, could induce error conclusions. Therefore, a minimum correlation must be done to explain the use of several layers. Typically for a perfect material, there is only one layer. While for pure Fe and Fe-Cr model alloys, the oxide layer is identified by positrons in addition to bulk signal.

In the fourth chapter of this thesis, the $S(E)$ and $W(E)$ values obtained for Fe sample implanted by 1.2 MeV Y with fluence of $3 \times 10^{15} \text{ cm}^{-2}$ have complex shapes shown as the points in the following figures. A Vepfit model of three layers with all free parameters has been tried to fit the curve as illustrated in Figure II-22. It is noted that it is not well fitted for the high positron energy part of the curve. In this case, one part of the positron with high energy should already detect the Fe lattice. Thus, in Figure II-23, we have given the positron annihilation characteristic of the Fe lattice to the third layer. But this time the low positron energy part of the curve is badly fitted. These results indicate that the model of three layers is not sufficient to fit the curve. The model of four layers is thus utilized as demonstrated in Figure II-24. Firstly it is known that the fourth layer is the Fe lattice layer. In addition, we have to fix the positron diffusion lengths of the second and the third layer to decrease the parameters number. It is noted that the curve is well fitted this time. After we have tried to change the positron diffusion lengths to check how the Vepfit results would change. As shown in Figure II-25, the cuves are also well fitted and the chagement of the other obtained parameters is minimal.

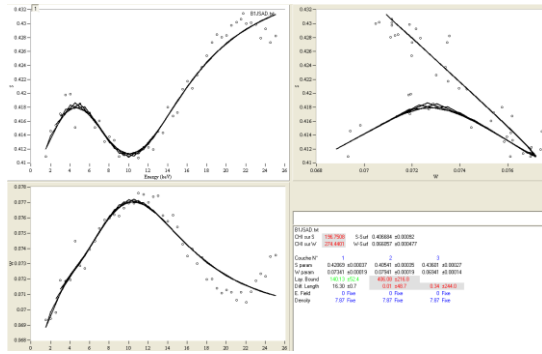


Figure II-22: One Vepfit model of three layers for fitting the positron results of Fe implanted by 1.2 MeV Y with fluence of $3 \times 10^{15} \text{ cm}^{-2}$.

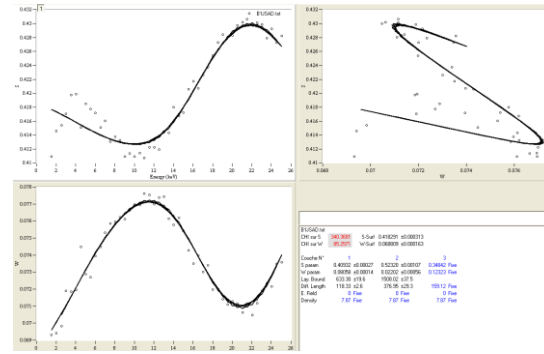


Figure II-23: One Vepfit model of three layers for fitting the positron results of Fe implanted by 1.2 MeV Y with fluence of $3 \times 10^{15} \text{ cm}^{-2}$.

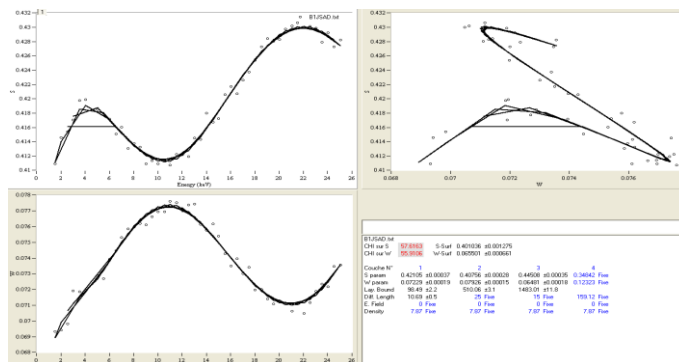


Figure II-24: One Vepfit model of four layers for fitting the positron results of Fe implanted by 1.2 MeV Y with fluence of $3 \times 10^{15} \text{ cm}^{-2}$.

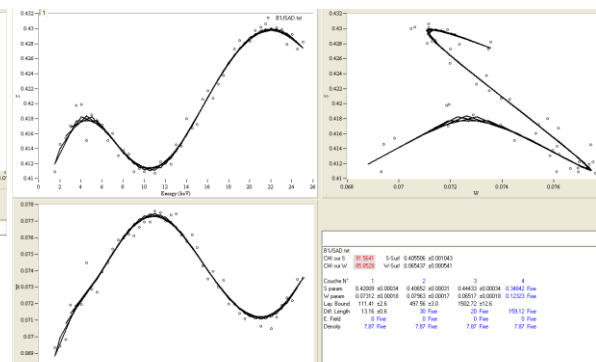


Figure II-25: One Vepfit model of four layers for fitting the positron results of Fe implanted by 1.2 MeV Y with fluence of $3 \times 10^{15} \text{ cm}^{-2}$.

II.3.3. Conclusions

Positron annihilation spectroscopy (PAS) has been presented in this section.

The slow mono- kinetic positrons with 25 keV could probe in Fe up to 2 μm . The positron diffusion lengths reported for defect-free metals are $\sim 100 \text{ nm}$ ^[155]. The vacancy type defects are deep traps and the dislocations are shallow traps in metals. There is no charged defect in metals. The trapping coefficient in dislocation depends on temperature and increases at low temperature. The positrons could also be sensitive to the presence of the precipitates if the affinity difference $\Delta A^+ = |A_P^+| - |A_M^+|$ is positive and the radius of the precipitate exceed the critical radius r_c . For example, ΔA^+ between Y and Fe is 1.47 eV. The critical radius r_c of Y precipitate is 0.2557 nm which corresponds to three or more Y atoms. For the Ti precipitates, this number is 12 Ti atoms.

The slow positrons beam with variable energy (0.1 to 25 keV) allows measuring the thin layer of samples. This accelerator is coupled to a Doppler broadening spectrometer which allows measuring the energy of the gamma photon emitted by e^+/e^- annihilation. It gives the momentum distribution of the e^+/e^- pairs during annihilation. This enables the characterization of vacancy- type defects or free volumes in solids. The spectrum obtained by positron experiments is characterized by two parameters named S and W. S represents the fraction of e^+/e^- annihilations with electrons of low momentum which are mainly valence electron. W represents the fraction of e^+/e^- annihilations with electrons of high momentum which are mainly core electrons. When the vacancy defects are present in the sample, the parameter S (W) increases (decreases) because the possibility of positron annihilating with the valence electron (core electron) increases (decreases). The S(W) points measured in a sample with two annihilation states align into one line with negative slope. The slope of the line depends on the defect nature and increases in absolute value with the increase of vacancy defect size. The positron annihilation characteristics S, W could also allow giving information in the local chemical environment probed by positron. For example, Cr has a higher S value than that of Fe but W value is lower. Two forms of these foreign elements presence in the matrix could be detected by positrons. The first form is the element precipitate. The second form is the foreign element combining with a vacancy- type defect. The concentration of detected defects could be determined by using the positron trapping model. The simplest model named one deep trap model allows to determine the concentration of defects and for single vacancy the quantification is possible from 10^{16} cm^{-3} to 10^{20} cm^{-3} in Fe. The advantage of using slow positron beam is their capability to detect the thin layers of sample in function of depth. The program Vepfit ^[171] is used to obtain this information. It allows to fit experimental data S(E) and W(E) and to get the S and W depth profiles by considering that the sample is made of one or several homogenous characteristic layers of material.

II.4. Secondary ion mass spectrometry (SIMS)

In this thesis, the technique secondary ion mass spectrometry (SIMS) is used to analyze the solute (Y, O) depth profiles in Fe after irradiation and also after post-irradiation annealing. It is recognized as the most sensitive elemental and isotopic surface analysis technique. In this section, SIMS technique principle is firstly presented. The SIMS 7f installed in laboratory GEMAC used for the measurements performed in this thesis is briefly described. The experimental conditions, calibration and quantification

of elements profiles in polycrystalline Fe are explained. Finally, SIMS technical constraints relative to the experiments performed in this thesis are presented and thus the experiment protocol is defined.

II.4.1. Technique principle

As shown in Figure II-26(a), when a solid sample is bombarded by primary ions of few keV energy, a fraction of the particles emitted from the target is ionized. Secondary Ion Mass Spectrometry consists of analyzing these secondary ions with a mass spectrometer. Secondary ion emission by a solid surface under ion bombardment supplies information about the elemental, isotopic and molecular composition of its uppermost atomic layers. It is recognized as the most sensitive elemental and isotopic surface analysis technique.

As illustrated in Figure II-26(b), a basic SIMS instrument consists of:

- A high-energy primary beam source (usually O_2^+ , O^- , Cs^+ , Ar^+ , Ga^+ or neutrals) to supply the bombarding species. The kinetic energy is transferred to the solid causing a collision cascade in the sample. Some of the collisions return to the surface, resulting in the ejection of atoms and clusters from the sample. Some of these ejected particles are ionized when they leave the surface. The type of secondary ions (SI) formed strongly depends on the properties of the primary ion including its composition, current density and energy. Since ionization and emission of ions occurs from the top layers of the sample, the SI yield is strongly influenced by the electronic state of the substrate. In addition, the chemical nature, crystallinity, and topography of the sample also affect the SI yield.
- These secondary ions are extracted from the sample as they are produced. If large mass spectrometer components are held at ground potential, the sample must be held at high voltage, the accelerating potential. The secondary ions accelerate toward the ground plate of an electrostatic lens. The first lens is called the immersion or ion extraction lens. The second one focuses the ion beam onto the mass spectrometer entrance slits or aperture. This two lens system constitutes an ion microscope.
- A mass analyzer is used to isolate the ion of interest. There are three types of mass analyzer commonly used: Time of flight (TOF), quadrupole (QMA/QMS), and double focusing mass sector. Magnetic sector instruments are widely used because they have very high-mass resolving power and SI transmission. Double- focusing magnetic sector mass analyzers are commercially available in the Cameca series of microprobes (lateral resolution: < 50- 150 nm) and microscopes (lateral resolution: $\sim 1 \mu m$).
- An ion detection system is used to record the magnitude of the secondary ion signal. Most modern mass spectrometers have more than one detector. For example, the Cameca ims-4f has four secondary ion detectors: an electron multiplier, a Faraday cup, an image plate and a resistive anode encoder. In this instrument, only one detector can be used at any time. But in the Cameca ims-1270 the instrument is equipped with eleven detectors some of which can be used simultaneously to give higher precision and rapid acquisition.

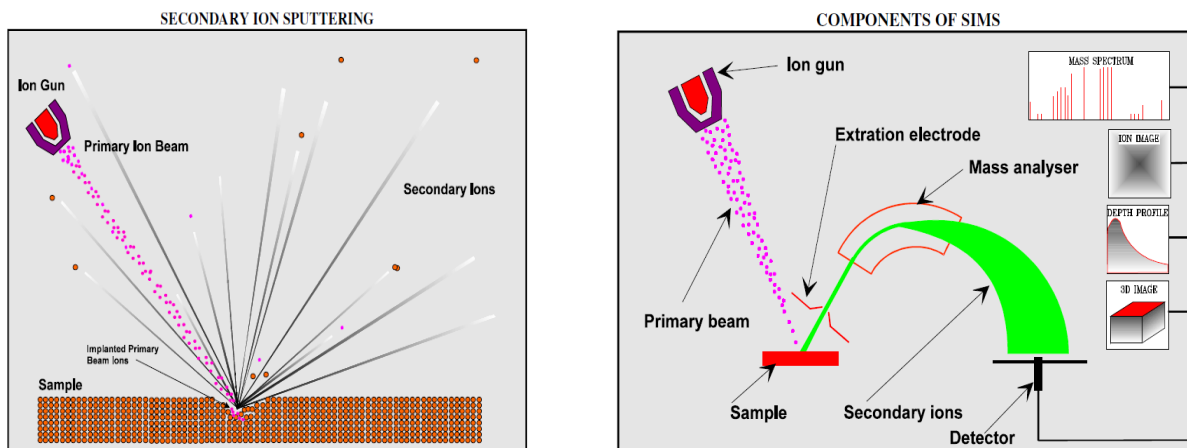


Figure II-26: (a) Schematic of secondary ion sputtering (b) Components of SIMS.

For many years, SIMS has been used to obtain accurate atomic distributions as a function of depth in a sample commonly termed 'depth profiles'. SIMS is also capable to realize the chemical images of samples by using ion microscope and ion microprobe. More details about SIMS could be found in reference ^[172].

II.4.2. SIMS 7f in GEMAC

The SIMS experiments in this thesis are performed in the laboratory GEMaC (Le Groupe d'Etude de la Matière Condensée) of Versailles University equipped with the latest generation of SIMS machine (IMS7f CAMECA).

The CAMECA IMS 7f is a double- focusing magnetic sector SIMS with well-established analytical performances. The IMS 7f offers unparalleled depth profiling capabilities with high depth resolution (a few nm) and high dynamic range. A high efficiency optical gate is used to eliminate crater edge effects, and the high mass resolution ($M/\Delta M = 10000$) ensures true elemental analysis by eliminating the numerous interfering ions. The high transmission mass spectrometer is combined with two reactive, high density ion sources, O_2^+ and Cs^+ , thus providing high sputtering rate and excellent detection limits ($1 \times 10^{14} \text{ at.cm}^{-3}$). All these performances are suitable for elements concentrations profile analysis in this thesis.

Thanks to a unique stigmatic optical system, the IMS 7f performs both direct ion microscopy and scanning microprobe imaging. Besides, its electron flood gun provides a unique self- compensation mode that makes it possible to measure depth profiles on complex insulating structures.

Therefore, the IMS 7f proves extremely useful for addressing the most diverse issues in materials analysis: doping concentration and distribution, impurity control, layer interface quality (junction impurities, diffusion of contaminants ...).

In addition, the CAMECA IMS7f machine in GEMaC laboratory has an optional add- on software packages which is named 'Checkerboard' mode ^[173]. It allows the operator to modify the shape, size and position of the gate after the initial measurement has been performed, thus optimizing the rejection of

crater edge effects and dust particles (if any) present at the crater bottom. In fact, as SIMS is a destructive technique: once the analysis is performed; it is no longer possible to re-measure on the same analysis spot. And even if the size of the sample allows repeating the analysis, having to perform different runs has a direct cost in terms of instrument throughput. In standard depth profiling, the analyzed area is fixed in the analysis recipe by defining the gating size, which may be optical (by a mechanical aperture), electronic (blanking of the secondary ions coming from an area outside the gate), or a combination of both. Ions coming from the crater bottom inside the area defined by the gating are collected and recorded, whereas the others are rejected. In scanning ion imaging mode, signal is collected from the whole rastered surface for each data point and it is possible to extract the information from specific regions of interest. However, this mode is mostly suited for dedicated applications such as small area analyses, as it generates image files of considerable size (image definition of 256×256 pixels minimum). The Checkerboard option combines the advantages of both modes (depth profiling and scanning ion imaging) in order to store a maximum of information while sputtering the sample. This is achieved by recording the information volume as a sequence of compact ion images (from 8×8 up to 128×128 pixels), thus simplifying data handling. This gives the operator the chance to optimize the profile dynamic range for a given measurement, since the analyzed area can be modified in the data post-treatment. As shown in Figure II-27, the red line represents the element profile without optimized gating. After optimizing gating as shown in bottom left, dramatic improvements in depth resolution are realized as illustrated by the white line. Thus, checkerboard greatly improves the quality of the depth profiling data and the throughput of the instrument.

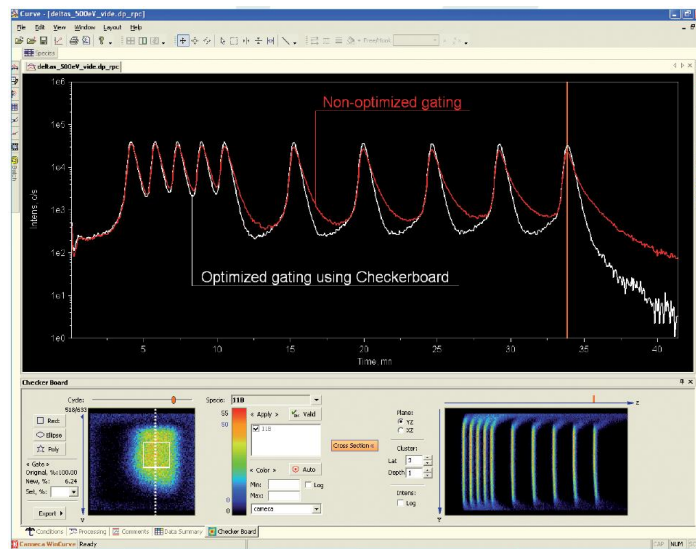


Figure II-27: Comparison of ions depth profiles without (red) and with (white) optimized gating –size and position of the gate- using Checkerboard mode in SIMS software. Bottom left: 2D crater view and gate; bottom right: crater cross- section ^[173].

II.4.3. Elements profiles detections in polycrystalline Fe

a) Experimental conditions

In this section, the SIMS experimental conditions used in this thesis are presented.

Primary beam source: To get the best SI yield, a primary beam source of O_2^+ is used for getting the Y profiles in Fe implanted with Y. Cs^+ is used for getting the O profiles in Fe implanted with O. For the Y, O double beams implanted Fe samples, the Cs^+ is also used to get only O profiles which will allow as reference for the quantification of the O profiles in the O implanted samples (see chapter 4 section 2.2 for explanations).

Primary beam current: The higher primary beam current reduces the measurement time for the crater of the same size. But higher current degrades the resolution. Thus, a compromise should be found. 200 nA O_2^+ beam is chosen for Y measurement with a crater of $250 \times 250 \mu m^2$. 40 nA Cs^+ beam is chosen for O measurement with a crater of $150 \times 150 \mu m^2$.

Primary beam angle: For a primary beam source of O_2^+ used for getting the Y profiles, the angle between the primary beam and the spectrometer axis is 46.2 degree. For a primary beam source of Cs^+ used for getting the O profiles, this angle is 23.6 degree.

Secondary ion choice: The SI representing the element X presence could be simply the $X^{+/-}$ or the combinations with matrix atom or primary beam atom. For the sample Fe implanted with Y, the $^{56}Fe^{16}O$ signal is recorded for representing the Fe matrix and the ^{89}Y , $^{89}Y^{16}O$ signals are recorded for representing the element Y. The secondary ion polarity is chosen to be positive. When the ^{89}Y are ejected from the surface of sample, one fraction of SI is combined with primary beam atom ^{16}O . It is noted that the profiles shapes of ^{89}Y and $^{89}Y^{16}O$ should be the same although their magnitudes are different. For the sample Fe implanted with O, the ^{56}Fe and ^{16}O signals are recorded for the Fe matrix and O elements respectively. The secondary ion polarity is chosen to be negative to obtain the largest O signals.

b) Calibration and quantification

Mass interferences occur whenever another ion has the same nominal mass as the analyzed ion. Such interferences are called isobaric. Oxides are common interferences since oxygen-metal bonds are particularly stable. Primary ions often combine with sample elements to produce interferences. Thus, during the analysis of Y in Fe by primary beam O_2^+ , $^{57}Fe^{16}O_2$ interferes because it has a very close mass compared to ^{89}Y ($^{57}Fe^{16}O_2$: $56.9354 + 15.9949 \times 2 = 88.9252$; ^{89}Y : 88.9058). Mass spectrometers with sufficient mass resolution can separate atomic ions from molecular ion interferences. Mass resolution is usually specified in terms of $m/\Delta m$ where m is the exact mass of the atomic ion and Δm is the difference between atomic ion and molecular ion mass. For example, ^{89}Y and $^{57}Fe^{16}O_2$ require $m/\Delta m \sim 4600$ for separation. CAMECA IMS 7f has a high mass resolution ~ 10000 . Thus, ^{89}Y and $^{57}Fe^{16}O_2$ could be separated with this machine.

As shown in Figure II-28(a), the raw data provided by a SIMS measurement is the secondary ion count rate as a function of time. The data should be converted into concentration as a function of depth as illustrated in Figure II-28(b). To convert the time axis into depth, the SIMS analyst uses a profilometer

to measure the sputter crater depth. A profilometer is a separate instrument that determines depth by dragging a stylus across the crater and noting vertical deflections. Total crater depth divided by total sputter time provides the average sputter rate. Depth is the product of sputter rate and analysis time.

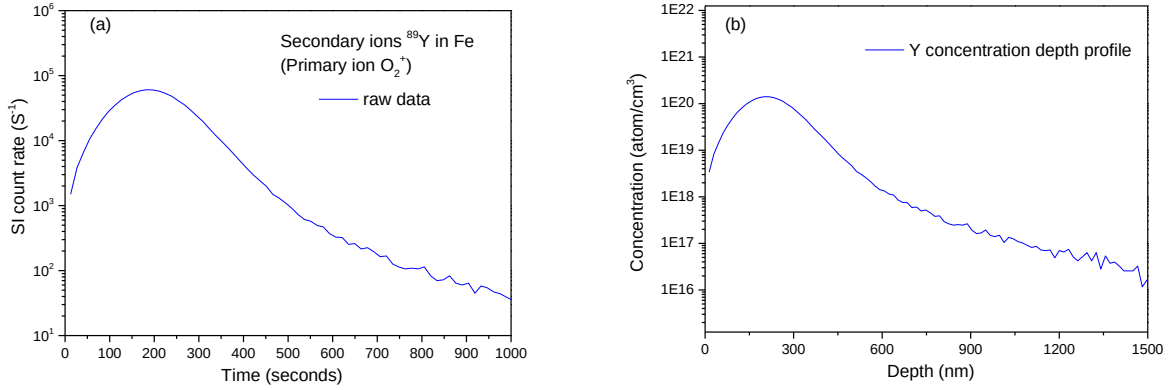


Figure II-28: (a) Raw data for a measurement of Y in Fe matrix. (b) Y concentration in Fe as a function of depth.

Relative sensitivity factors (RSFs) convert the vertical axis from ion counts into concentration. RSF_E is defined according to the following equation 1.

$$\frac{I_R}{C_R} = RSF_E \cdot \frac{I_E}{C_E} \quad (1)$$

RSF_E represents relative sensitivity factor for element E; I_E is secondary ion intensity (counts number) for element E; I_R is the secondary ion intensity for reference element R; C_E represents concentration of E; C_R is concentration of R. The matrix element is usually chosen as the reference, for example Fe in our case. Substituting M (matrix) for R (reference) and rearranging gives the equation 2.

$$C_E = RSF_E \cdot \frac{I_E C_M}{I_M} \quad (2)$$

In trace element analysis, we can assume that the matrix elemental concentration remains constant. The matrix concentration can be combined with the elemental RSF_E to give a more convenient constant, RSF as illustrated by the equation 3.

$$RSF = C_M \cdot RSF_E \quad (3)$$

Thus, this RSF is a function of the element of interest and the sample matrix. Equation 4 is the most common form of the RSF equation.

$$C_E = RSF \cdot \frac{I_E}{I_M} \quad (4)$$

To obtain RSF for samples Fe implanted by Y, it is assumed that the desired Y fluence is exactly completed and all ions stay in the sample after implantation. The RSF is calculated by the equation 5.

$$RSF = \frac{Dose \times I_M}{\int_a^b I_E dt \times V} \quad (5)$$

Dose is the Y fluence of the implantation; $\int_a^b I_E dt$ is the total signal of the Y element during the measurement time; V is the sputter rate. This RSF value is used to calculate the Y concentration after post- irradiation annealing.

For determining the O fluence in O implanted sample, one Y, O double beams implanted Fe sample has been used as the reference sample. The RSF obtained for the O fluence in the reference sample is used to determine the O fluence in O implanted sample.

c) Grain effect on irradiation and sputtering

As presented in section II.1.1, the Fe samples used in this thesis are polycrystalline with the mean grain sizes of 20- 100 μm . It has to be noted that this polycrystalline microstructure arises the technical constraint for SIMS measurements in the name of ion sputtering. The sputtering yield of sample surface by primary beam depends on grain orientation. Figure II-29(b) illustrates the optical image of SIMS crater analyzed by primary beam O_2^+ for 1.2 MeV Y implanted Fe at fluence $3 \times 10^{15} \text{ cm}^{-2}$. The surface topography at the bottom of the crater shows different level of roughness after ion sputtering by O_2^+ . The dark part of topography means that this part of crater is deep and the white part means shallow depth. Compared to the EBSD image for the crater as shown in Figure II-29(a), it has been noted that different grains have different sputtering yields. For example, the grain 1 has been much more sputtered than the grain 4. This phenomenon has also been observed in polycrystalline tungsten under a 30 keV focused Ga^+ ion beam investigated by in situ scanning electron microscopy and electron backscatter diffraction. Crystal orientation significantly influences the erosion behavior of tungsten surface ^[174]. The sputter- roughened surface of polycrystalline Fe will largely degrade the depth resolution when converting the raw data to concentration depth profile.

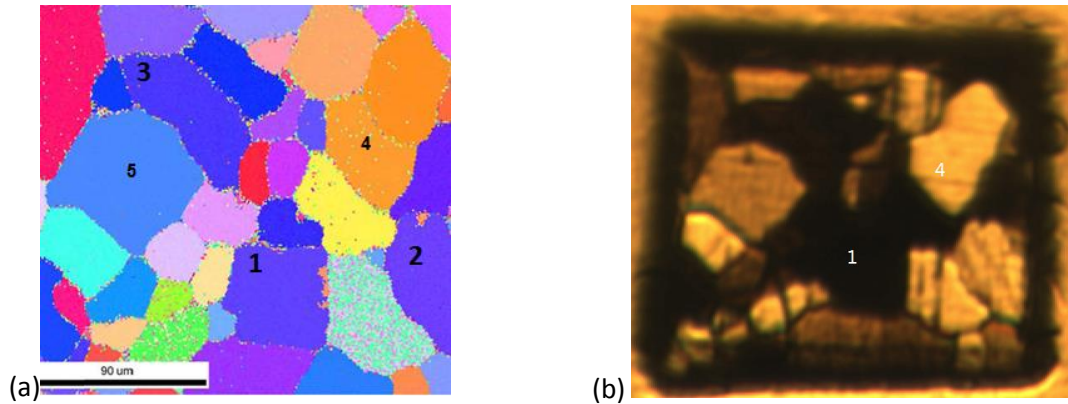


Figure II-29: (a) 250 $\mu\text{m} \times 250 \mu\text{m}$ EBSD image of SIMS crater. (b) Optical image of SIMS crater analyzed by primary beam O_2^+ for 1.2 MeV Y implanted Fe at fluence $3 \times 10^{15} \text{ cm}^{-2}$.

In addition, the ion implanted profiles are different in grains with different orientations. Many physical phenomena occur when a charged particle is incident upon a solid target, for example elastic

scattering, inelastic energy- loss processes, secondary- electron emission, electromagnetic radiation, nuclear reactions, etc. The yields of physical processes are very strongly dependent on the orientation of the momentum of the particle relative to the crystalline axes or planes. The stopping power of the particle is much lower in certain directions than others. This phenomenon will be illustrated in the following.

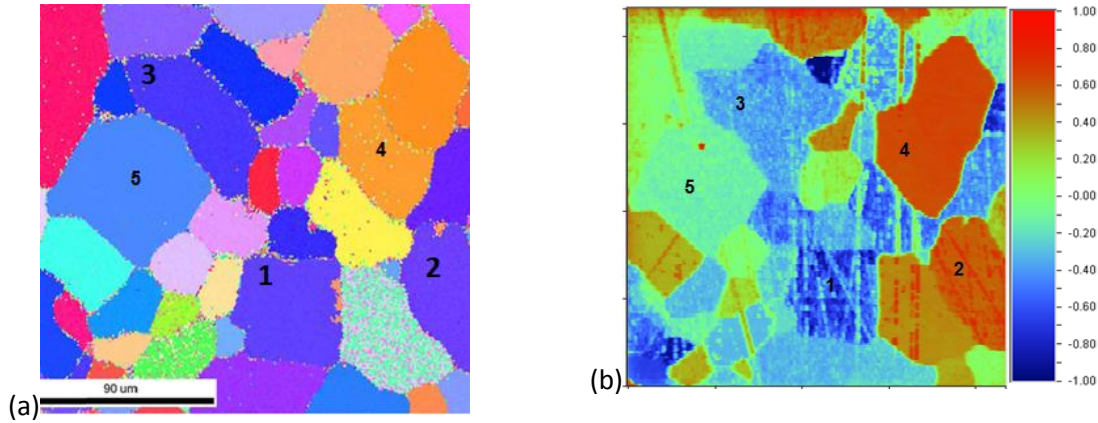


Figure II-30: (a) 250 $\mu\text{m} \times 250 \mu\text{m}$ EBSD image of SIMS crater. (b) Profilometer image of SIMS crater analyzed by primary beam O_2^+ for 1.2 MeV Y implanted Fe at fluence $3 \times 10^{15} \text{ cm}^{-2}$.

In order to get the Y profiles of different grains and increase the depth resolution, the integrated profilometer of SIMS crater analyzed by primary beam O_2^+ for 1.2 MeV Y implanted Fe at fluence $3 \times 10^{15} \text{ cm}^{-2}$ has been performed. In Figure II-30(b), the different colors in the image represents the different depth levels within the crater. The positive values mean the shallow depth and the negative ones mean the deep depth. It is found that the grains in the profilometer image corresponds to their respective grains in the EBSD image as shown in Figure II-30.

Five grains numbered in the Figure II.25 have been chosen to be measured to get their Y profiles. The depths of each grain after ions sputtering are obtained by profilometer and thus the sputtering speeds have been calculated with SIMS analyze time. As shown in Table II.7, the grain 1 has the deepest depth and its sputtering speed is the fastest.

Grain number	Crater depth (nm)	SIMS analyze time (s)	Sputtering speed (nm/s)
1	2981	5007	0.60
3	2816	5007	0.56
5	2576	5007	0.51
2	1830	5007	0.37
4	1812	5007	0.36

Table II.7: Depth and sputtering speed of five grains numbered within the crater.

The SIMS data have been obtained for each grain with 'Checkerboard' mode by adjusting the shape, size and position of the gate to the different grains. With the sputtering speeds, the data of five grains are converted into Y concentration as a function of depth as shown in Figure II-31. It is clear that the profiles in different grains are totally different which proves that the ion implanted profiles are different

in grains with different orientations. The ion projected range (R_p) in each grain is also obtained as shown in Table II.8.

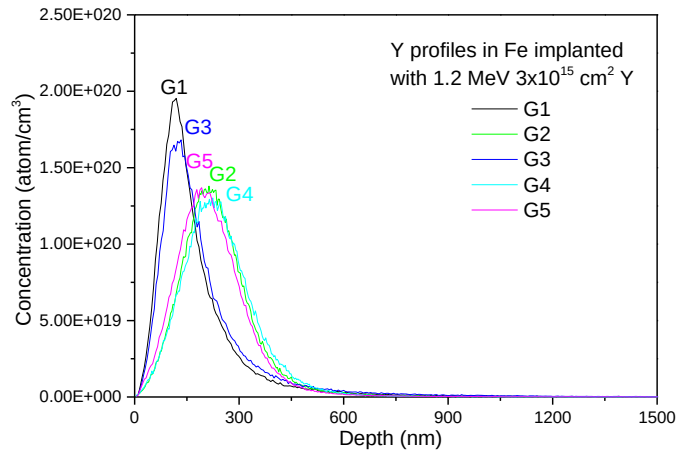


Figure II-31: Y profiles of five grains in Fe sample implanted with $1.2 \text{ MeV } 3 \times 10^{15} \text{ cm}^{-2} \text{ Y}$.

Grain number	Crater depth (nm)	Sputtering speed (nm/s)	Peak time (s)	R_p depth (nm)
1	2981	0.60	210	125
3	2816	0.56	237	133
5	2576	0.51	392	202
2	1830	0.37	584	213
4	1812	0.36	620	224

Table II.8: Ion projected range (R_p) depth of five grains numbered within the crater.

It has to be noted that the grains with the deeper crater have the ion projected range closer to the surface. It means that the grains sustaining high yield of ion sputtering during SIMS measurement have the shallow Y profiles after Y implantation. It could be explained that the grains sustaining the high sputtering yield have the surface direction which locates the high atomic density. The plane of high atomic density facilitates the ion sputtering by SIMS. In contrary, this plane has the high stopping power for the incident particles. Thus, the Y profiles in this type of grains are closer to the sample surface, it has been observed in grain 1.

d) SIMS technical constraints and experiment protocol

As explained in the last section, the implanted ions profiles in different oriented grains of polycrystalline Fe are different. This arises the difficulty to study the ion diffusion after the post-irradiation annealing. If the grains with different orientations are analyzed before and after post-irradiation annealing, the conclusion on ion diffusion after annealing could be incorrect because their ion

profiles after irradiation are already different. In addition, the beam diameter of slow positron experiments performed in this thesis is ~ 1 mm. It means that ~ 20 grains are analyzed in the same time and thus the information obtained is average. For this reason, the averaged ion profile is desired for being better compared to the positron results. To reach this objective, the problem of the difference in the sputtering yields of grains in polycrystalline Fe should be resolved. Sample rotation technique has been used in some SIMS experiments to provide the constant secondary ion yield and improve depth resolution ^[175]. Sample rotation prevents ion- beam- induced surface roughness during sputtering by averaging the ion beam direction azimuthally and reducing the inhomogeneity of low energy ion beams. But GEMaC laboratory does not possess this device.

Instead, another technique named oxygen blowing which is also able to resolve this problem is available in GEMaC. When the sample is bombarded by primary ion beam, the oxygen is blown onto the sample in the same time. It allows the sample surface to be saturated on oxygen and thus provide the constant secondary ion yield. The oxygen blowing pressure is set to be $\sim 2.1 \times 10^{-6}$ mbar. The optical image of SIMS craters with and without oxygen blowing are compared in Figure II-32. It is clear that the crater analyzed with oxygen blowing is much more flat.

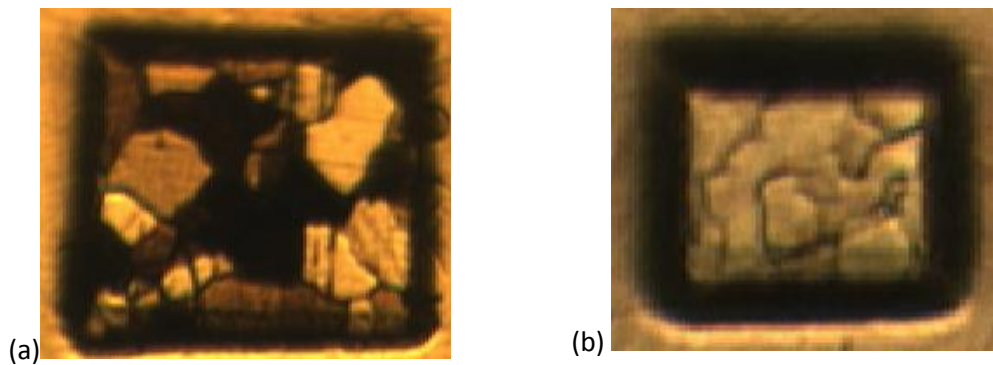


Figure II-32: Optical image of SIMS crater (a) without oxygen blowing (b) with oxygen blowing.

Thus, the Y profiles in Fe are analyzed by SIMS with oxygen blowing technique in this thesis.

However, the oxygen blowing technique could not be performed to analyze the oxygen depth profiles in Fe because the additional oxygen content introduced by this technique could make the misinterpretation of the oxygen depth profiles. But it is noted that the effect of grains on oxygen implantation in Fe should be limited because of oxygen lighter mass compared to Y. In order to confirm this hypothesis, the O profiles in different grains of polycrystalline Fe have been measured and compared.

Figure II-33 shows the profilometer image of SIMS crater analyzed by primary beam Cs^+ for 650 keV O implanted Fe at the fluence of $2.2 \times 10^{15} \text{ cm}^{-2}$. Four grains numbered in the image have been chosen to be measured to get their O profiles. The depths of each grain after ions sputtering are obtained by profilometer. The SIMS data have been obtained for each grain with 'Checkerboard' mode by adjusting the shape, size and position of the gate to the different grains. Thus, the O profiles in each grain are

obtained as shown in Figure II-34. The implanted O profiles in different grains of polycrystalline Fe are very similar. In conclusion, O depth profile in one grain could represent the average information.

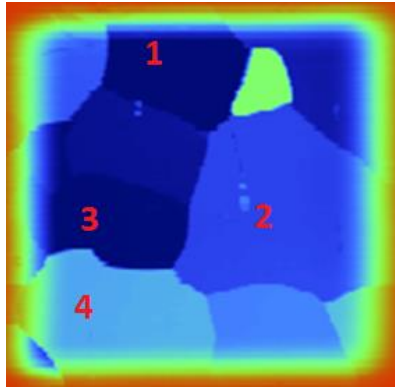


Figure II-33: Profilometer image of SIMS crater analyzed by primary beam Cs^+ for 650 keV O implanted Fe at fluence $2.2 \times 10^{15} \text{ cm}^{-2}$.

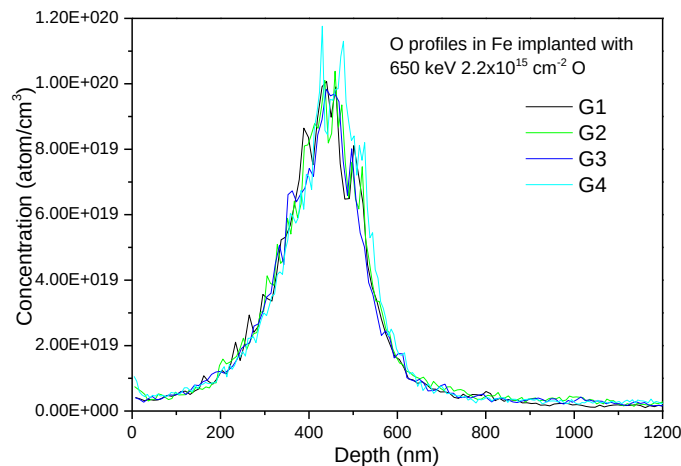


Figure II-34: O profiles of four grains in Fe sample implanted with 650 keV $2.2 \times 10^{15} \text{ cm}^{-2}$ O.

It is noted that there is a tail for the O depth profile which could be the O concentration in the virgin sample. It is ~ 20 appm lower than 169 appm reported by Goodfellow.

The mode 'checkerboard' without oxygen blowing technique is used to obtain the O depth profile in one grain which will represent the averaged profile.

II.4.4. Conclusions

The Secondary Ion Mass Spectrometry (SIMS) is used to analyze the solute (Y, O) depth profiles in Fe after irradiation and also after post-irradiation annealing. The SIMS experiments in this thesis are performed in the laboratory GEMaC (Le Groupe d'Etude de la Matière Condensée) of Versailles University equipped with the latest generation of SIMS machine (IMS7f CAMECA). The IMS 7f offers unparalleled depth profiling capabilities with high depth resolution (a few nm) and high dynamic range. A high efficiency optical gate is used to eliminate crater edge effects, and the high mass resolution

($M/\Delta M = 10000$) ensures true elemental analysis by eliminating the numerous interfering ions. The high transmission mass spectrometer is combined with two reactive, high-density ion sources, O_2^+ and Cs^+ , thus providing high sputter rate and excellent detection limits (1×10^{14} at.cm⁻³). In addition, the CAMECA IMS7f machine in GEMaC laboratory has an optional add-on software packages which is named 'Checkerboard' mode [173]. It allows the operator to modify the shape, size and position of the gate after the initial measurement has been performed, thus optimizing the rejection of crater edge effects and dust particles (if any) present at the crater bottom.

To get the best SI yield, a primary beam source of O_2^+ is used for getting the Y profiles in Fe implanted with Y. Cs^+ is used for getting the O profiles in Fe implanted with O. The depth calibration is performed by measuring the sputter crater depth. Relative sensitivity factors (RSFs) convert the ion count number into concentration. To obtain RSF for samples Fe implanted by Y, it is assumed that the desired Y fluence is exactly completed and all ions rest in the sample. One reference sample, Y, O double beams implanted sample, has been used to obtain RSF for Fe sample implanted with O.

The sputtering yield of sample surface by primary beam depends on grain orientation, inducing the sputter-roughened surface of polycrystalline Fe. It will largely degrade the depth resolution. Using oxygen blowing is used provide the constant secondary ion yield for measuring the Y profiles in Fe. In the case of O profiling, the mode 'checkerboard' without oxygen blowing is used to obtain the O depth profile in one grain which will represent the averaged profile.

II.5. Conclusions

This chapter presents the materials and experimental techniques have been described.

The iron samples utilized in this thesis are high purity 99.99 wt.% with the major impurities silicon (Si), carbon (C), nickel (Ni) and oxygen (O). Before the irradiation and positron annihilation spectroscopy experiments, the Fe samples are prepared by mechanical polishing and 750°C annealing to remove native defects. After preparation, the Fe samples show a polycrystalline structure with mean grain sizes of 20-100 μm without preferential grain orientation.

The FeCr model alloys utilized in this thesis are of industrial purity, namely, Fe-3Cr (2.36 at.%Cr), Fe-5Cr (4.93 at.%Cr), Fe-9Cr (8.93 at.%Cr) and Fe-12Cr (12.33 at.%Cr). The major impurities are silicon (Si), carbon (c) and oxygen (O). Cr enriched clusters segregation is observed at the grain boundaries and Cr atoms appear to be homogeneously distributed at the nanometric scale inside grains for Fe- 5Cr, Fe- 9Cr and Fe- 12Cr alloys. The FeCr virgin samples have been mechanically and electrochemically polished to remove the deformed $\sim 10 \mu m$ layer on sample surface.

The high energy helium 4 ($^4He^+$) irradiations, 1.5 MeV in Fe and 2 MeV in FeCr, have been carried out to study the pure vacancy defects in Fe and FeCr matrix. The 1.2 MeV Y, 700 keV Ti, 650 keV O and 285 keV O implantations in Fe were carried out to study the interactions between Y, Ti, O atoms and vacancy in Fe matrix.

Irradiation in Fe and FeCr introduces in the material defects and the foreigner atoms as the incident ions (Y, Ti, O in this thesis), which stop in the substitutional or interstitial positions. L. Malerba reviewed the molecular dynamics (MD) simulation of displacement cascades in α - Fe [136]. In MD simulation of

displacement cascades induced in α -Fe the defect production efficiency, defined as the ratio between the number of Frenkel pairs (FP) that survived in- cascade recombination at the end of the simulations and the number of NRT displacements, has been found, at the value of 0.3 ± 0.1 for cascade energies above 2 keV, in agreement with experimental assessments. The fraction of the vacancy in clusters defined as the ratio of the number of vacancy defects found in clusters (of size ≥ 2) to the total number of FP is ~ 0.2 - 0.3 and the average size of these clusters is 2- 3 vacancies.

SRIM code has been used to calculate the damage and solutes depth profiles induced in the different irradiation/implantation conditions: He irradiations in Fe and FeCr samples, Y, Ti, O implantations in Fe samples. Eight different fluences have been performed in the range from 1×10^{13} to 1×10^{17} cm⁻², it corresponds to a damage dose ranging from 1×10^{-5} to 1×10^{-1} dpa for 1.5 MeV He irradiated Fe. For 2 MeV He irradiated FeCr, five fluences have been carried out in the range from 10^{14} to 1.3×10^{17} cm⁻² corresponding to the damage dose in the range from 6×10^{-5} to 7.8×10^{-2} dpa. The Y, Ti and O implantations have been performed at various fluences. The concentrations of Y, Ti and O at Rp were fixed at the same values, 1170 appm and 1760 appm, for the two highest fluences. They should have a non-negligible influence on the vacancy.

The slow positron beam will allow to probe defects in Fe up to 2 μ m. Different defects can be detected by positrons: vacancy type defects are deep traps and dislocations are shallow traps in metals with a trapping coefficient which increases at low temperature. The positrons could also be sensitive to the presence of precipitates if the affinity difference $\Delta A^+ = |A_P^+| - |A_M^+|$ is positive and the radius of the precipitate exceed the critical radius r_c .

The slow positrons beam with variable energy (0.1 to 25 keV) is coupled to a Doppler broadening spectrometer which allows measuring the energy of the gamma photon emitted by e⁺/e⁻ annihilation. It gives the momentum distribution of the e⁺/e⁻ pairs during annihilation. This enables the characterization of vacancy- type defects or free volumes in solids. The spectrum obtained by positron experiments is characterized by two parameters named S and W. S represents the fraction of e⁺/e⁻ annihilations with electrons of low momentum which are mainly valence electron. W represents the fraction of e⁺/e⁻ annihilations with electrons of high momentum which are mainly core electrons. When the vacancy defects are present in the sample, the parameter S (W) increases (decreases) because the possibility of positron annihilating with the valence electron (core electron) increases (decreases). The S(W) points measured in a sample with two annihilation states align onto one line with negative slope. The slope of the line depends on the defect nature and increases in absolute value with the increase of vacancy defect size. The positron annihilation characteristics S, W could also allow giving information in the local chemical environment probed by positron. For example, Cr has a higher S value than that of Fe but W value is lower. Two forms of these foreign elements presence in the matrix could be detected by positrons. The first form is the element precipitate. The second form is the foreign element combining with a vacancy- type defect. The concentration of detected defects could be determined by using the positron trapping model. The simplest model named one deep trap model allows to determine the concentration of defects and for single vacancy the quantification is possible from 10^{16} cm⁻³ to 10^{20} cm⁻³ in Fe. The advantage of using slow positron beam is their capability to detect the thin layers of sample in function of depth. The program Vepfit^[171] is used to obtain this information. It allows to fit experimental

data $S(E)$ and $W(E)$ and to get the S and W depth profiles by considering that the sample is made of one or several homogenous characteristic layers of material.

The Secondary Ion Mass Spectrometry (SIMS) is used to analyze the solute (Y, O) depth profiles in Fe after irradiation and also after post-irradiation annealing. The SIMS experiments in this thesis are performed in the laboratory GEMaC (Le Groupe d'Etude de la Matière Condensée) of Versailles University equipped with the latest generation of SIMS machine (IMS7f CAMECA). The IMS 7f offers unparalleled depth profiling capabilities with high depth resolution (a few nm) and high dynamic range. A high efficiency optical gate is used to eliminate crater edge effects, and the high mass resolution ($M/\Delta M = 10000$) ensures true elemental analysis by eliminating the numerous interfering ions. The high transmission mass spectrometer is combined with two reactive, high-density ion sources, O_2^+ and Cs^+ , thus providing high sputter rate and excellent detection limits ($1 \times 10^{14} \text{ at.cm}^{-3}$). In addition, the CAMECA IMS7f machine in GEMaC laboratory has an optional add-on software packages which is named 'Checkerboard' mode^[173]. It allows the operator to modify the shape, size and position of the gate after the initial measurement has been performed, thus optimizing the rejection of crater edge effects and dust particles (if any) present at the crater bottom.

To get the best SI yield, a primary beam source of O_2^+ is used for getting the Y profiles in Fe implanted with Y. Cs^+ is used for getting the O profiles in Fe implanted with O. The depth calibration is performed by measuring the sputter crater depth. Relative sensitivity factors (RSFs) convert the ion count number into concentration. To obtain RSF for samples Fe implanted by Y, it is assumed that the desired Y fluence is exactly completed and all ions rest in the sample. One reference sample, Y, O double beams implanted sample, has been used to obtain RSF for Fe sample implanted with O.

The sputtering yield of sample surface by primary beam depends on grain orientation, inducing the sputter-roughened surface of polycrystalline Fe. It will largely degrade the depth resolution. Using oxygen blowing is used provide the constant secondary ion yield for measuring the Y profiles in Fe. In the case of O profiling, the mode 'checkerboard' without oxygen blowing is used to obtain the O depth profile in one grain which will represent the averaged profile.

Chapter III.

The properties of vacancy defects in bcc Fe and FeCr matrix

III. The properties of vacancy defects in bcc Fe and FeCr matrix

The properties of vacancy defects induced in bcc Fe and FeCr matrix are studied in this chapter. The Fe and FeCr virgin samples qualities after preparations are firstly checked by positron annihilation spectroscopy. Then, the nature of the vacancy defects induced by He irradiation in Fe and FeCr matrix is characterized as a function of the ion fluence. Finally, their evolution as a function of annealing performed after irradiation is reported depending on the ion fluence and on the composition of the material.

III.1. The quality of virgin samples

Before irradiation, the quality of the Fe and FeCr virgin samples is checked by using positron annihilation spectroscopy.

III.1.1. Fe bcc virgin samples

After mechanical polishing and annealing at 750°C, the Fe virgin samples are characterized by using slow positron beam Doppler Broadening spectroscopy.

a) PAS results

As presented in the previous section II.1.1, the received Fe samples in the laminated state are mechanically polished and then annealed at 750°C under vacuum for 1 hour in order to obtain homogenous non-defective surface and bulk. The quality of these 'virgin samples' or 'reference samples' is examined by slow positron beam Doppler broadening (SPBDB) technique in the CEMHTI laboratory.

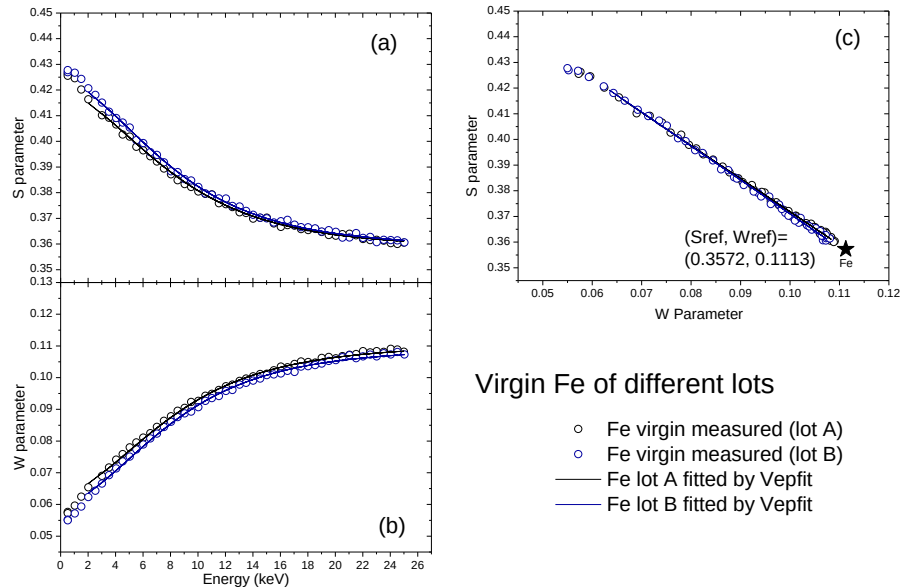


Figure III-1: Low (S) (a) and high (W) (b) momentum annihilation fraction as a function of positron energy and S as a function of W (c) for the virgin pure Fe samples. VEPFIT is used to fit the $S(E)$, $W(E)$ and $S(W)$ curves with a model of one homogeneous layer^[176].

All as-received polished and annealed Fe samples have given reproducible SPBDB results and a typical representation is illustrated for two samples in Figure III-1. Three types of curves are presented. $S(E)$ (fig III.1.a) represents the low momentum annihilation fraction S as a function of positron energy E in the range from 0.1 to 25 keV and $W(E)$ (fig III.1.b) represents the high momentum annihilation fraction W as a function of E in the same range. The $S(W)$ points (fig III.1.c) give the information about the positron annihilation characteristic of the lattice and defects with different sizes or concentrations as explained in section II.3.2(C).

It has to be noted that S (respectively, W) decreases slowly (increases) as a function of positron energy E which corresponds to the positron implantation depth. It is known from the slow positrons implantations profiles presented in Figure II.7(a) that positrons with low energy stop close to the surface and the ones with high energy stop mainly in the sample bulk. In the case of Fe virgin sample, S_{bulk} value is lower than S_{surface} and W_{bulk} value is higher than W_{surface} . The slow evolutions of $S(E)$ and $W(E)$ indicate that a large fraction of positrons diffuses back to the sample surface at intermediate positron energy and annihilation occurs both at the surface and in the bulk of sample. The $S(W)$ points align on one straight line which indicates two annihilation states are detected, surface and bulk states in this case. The experimental results are adjusted with VEPFIT^[171] program using the simple assumption that the sample is homogeneous. It has been noted that the fitted curves are well adjusted compared to the experimental ones and the annihilation characteristics of this homogeneous layer are reported in Table III-1.

S_{bulk}	W_{bulk}	$L_{\text{bulk}}^+ \text{ (nm)}$	S_{surface}	W_{surface}
0.357(2)	0.111(3)	160±2	0.419(7)	0.062(8)

Table III-1: The annihilation characteristics of the homogeneous layer for Fe virgin sample.

b) Discussion

The effective positron diffusion length in the virgin sample is $L^+ = 160 \pm 2$ nm. The positron diffusion lengths reported for defect-free metals are ~ 100 nm^[155]. Higher L^+ value of 184 nm, has been obtained by Iwai and *al.*, for pure Ni (99,997 wt.%) annealed at 800°C in vacuum for one hour^[156]. All these results reveal that the quantity of open-volume defects in the bulk of the virgin samples is low. In addition, the results are reproducible and thus the quality of these Fe samples prepared by the same procedures is considered as good. The annihilation characteristics S and W obtained in the virgin sample are considered as the reference ones and can be defined as the annihilation characteristics of the Fe lattice: $S_{\text{ref}} = 0.357(2)$ and $W_{\text{ref}} = 0.111(3)$.

III.1.2. FeCr bcc virgin samples

After mechanical and electrochemical polishing, the quality of FeCr virgin samples is examined by positrons.

a) PAS results

The received Fe-Cr model samples are mechanically polished and then electrochemical polished as described in Chapter 2 section II.1.2 to remove the deformed surface layer. The qualities of samples have also been checked by SPBDB as shown in Figure III-2.

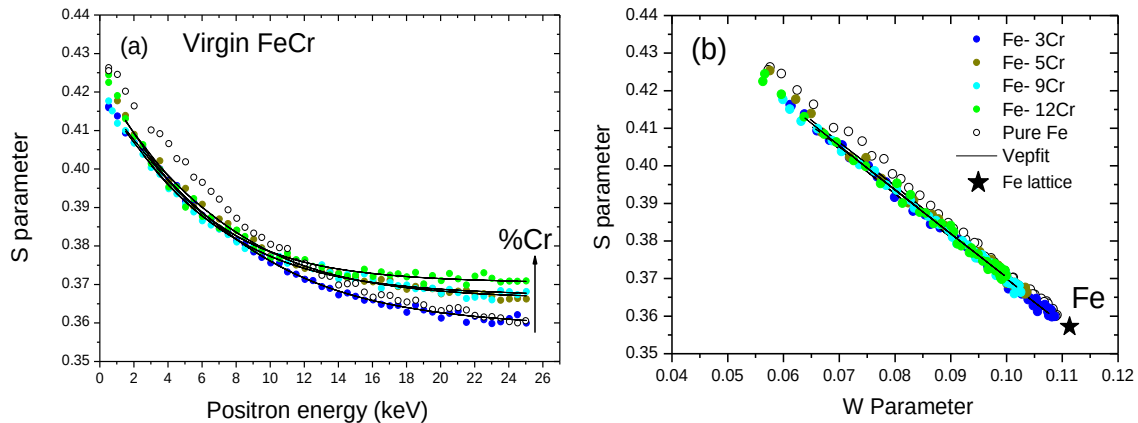


Figure III-2: Low (S) annihilation momentum fraction versus (a) positron energy for the FeCr virgin model samples (Fe- 3Cr, Fe- 5Cr, Fe- 9Cr, and Fe- 12Cr) and (b) high (W) annihilation momentum fraction of Vepfit results.

Only two curves, $S(E)$ and $S(W)$, are presented in this figure. $W(E)$ curve has evidently an inverse form compared to $S(E)$ curve as for the case of Fe and thus it is not illustrated here. All the results of measurements obtained for several samples of the same set give reproducible data. Thus, the Figure III-2 shows the PAS results for one virgin FeCr sample of each type of model alloys (Fe- 3Cr, Fe- 5Cr, Fe- 9Cr and Fe- 12Cr).

$S(E)$ curves of these four FeCr model alloys are similar to those of the pure Fe samples. S for all alloys decreases slowly as a function of positron energy E and S values become approximately constant at the high positron energies (~ 22 keV to ~ 25 keV). It has to be noted that these steady S values increase with the increase of Cr concentration as shown by the arrow in the figure but are very close for Fe- 5Cr and Fe- 9Cr. All $S(W)$ curves of four FeCr alloys align on their respective straight lines. The experimental results are not well adjusted using a simple model of one homogenous layer indicating that a layer with specific annihilation characteristic exists close to the surface. The adjustment using a model of 2 homogenous layers is suitable as it could be observed in Figure III-2 and the annihilation characteristics corresponding to these 2 layers are reported in Table III-2. The first layer exists in all the samples with a thickness in the range from 20 to 120 nm. The second layer gives the positron annihilation characteristics in the bulk of the FeCr samples. It has to be noted that their characteristics L^+ , S and W depend on the composition of the model alloy. The $S(W)$ values obtained for each type of FeCr model alloy are plotted in Figure III-3 with the lattice annihilation characteristics of pure Fe and pure Cr. Their $S(W)$ points align on the same line named DX. It has been observed that they are further from the Fe lattice point defined in the previous section when Cr concentration increases.

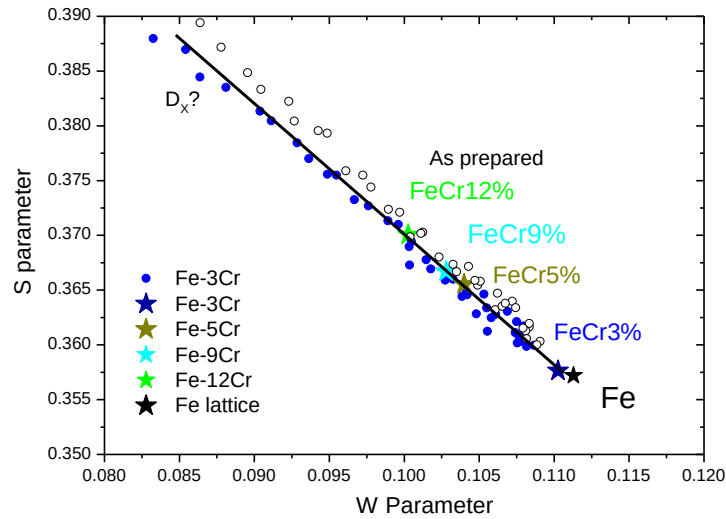


Figure III-3: SW annihilation characteristics of as prepared Fe-3Cr, Fe-5Cr, Fe-9Cr and Fe-12Cr samples and of Fe lattice.

Material	Layer 1				Layer 2		
	S	W	L^+ (nm)	Thickness (nm)	S_{bulk}	W_{bulk}	L^+ (nm)
Fe	/	/	/	/	0.3572	0.1113	160
Fe- 3Cr	0.3757	0.0992	38	20	0.3576	0.1103	135
Fe- 5Cr	0.3863	0.0872	37	120	0.3655	0.1040	125
Fe- 9Cr	0.3823	0.0908	38	57	0.3667	0.1028	120
Fe- 12Cr	0.3635	0.1043	47	43	0.3701	0.1003	98

Table III-2: Positron annihilation characteristics obtained by Vepfit for the FeCr model alloys.

b) Discussion

The results show that the positron annihilation characteristics differ from one FeCr alloy to another. The S_{bulk} (W_{bulk}) increases (decreases) with the increase of Cr concentration.

- Firstly it has to be noted that the increasing presence of Cr atoms in the matrix would lead to the increase of annihilation probability with Cr electrons. The annihilation characteristics in Cr have been obtained as followed. The Cr samples have been prepared by mechanical polishing and annealing at 1100°C under vacuum during 10 h. The SPBDB results show that S (respectively, W) decreases slowly (increases) as a function of positron energy E as shown in Figure III-4. The fitting of the experimental data by using the Vepfit program and a model of one homogeneous layer gives a positron diffusion length L^+ of $\sim 200 \pm 1$ nm and the annihilation characteristics $S = 0.3625$ and $W = 0.0980$. Thus, the quantity of open-volume defects in the bulk of the Cr virgin samples is

low. We propose that the annihilation characteristics determined for the bulk in this sample are equal to the characteristics of annihilation of positrons in the lattice and these values $S_L(\text{Cr}) = 0.3625$ and $W_L(\text{Cr}) = 0.0980$ are used in the following to evaluate the theoretical characteristics in the FeCr model alloys. Thus, $S_{\text{lattice}}(\text{Cr}) > S_{\text{lattice}}(\text{Fe})$ and $W_{\text{lattice}}(\text{Cr}) < W_{\text{lattice}}(\text{Fe})$ and the annihilation characteristics in the FeCr alloys should correspond to the increase of S and the decrease of W when the Cr concentration increases. Nagai et al. have also reported the same observations^[119]. Thus, in the case where FeCr samples would not contain positron traps, the (S, W) points of the different alloys should follow the straight line between $(S_L(\text{Fe}), W_L(\text{Fe}))$ and $(S_L(\text{Cr}), W_L(\text{Cr}))$ lattice points.

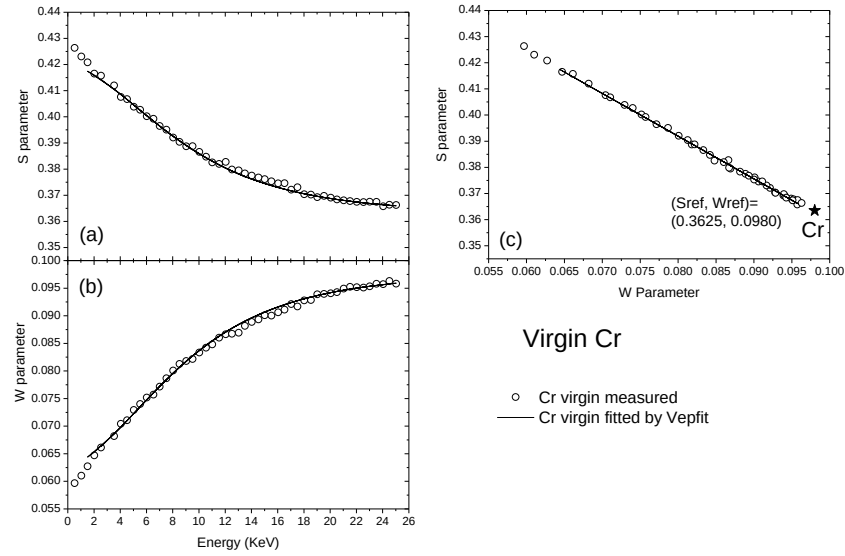


Figure III-4: Low (S) (a) and high (W) (b) momentum annihilation fraction as a function of positron energy and S as a function of W (c) for the virgin pure Cr samples. VEPFIT is used to fit the (S, W) curves with a model of one homogeneous layer.

The theoretical values of positron annihilation characteristics in the lattice of the FeCr model alloys without positron traps are calculated. The calculations are based on the assumption that the Fe and Cr atoms are well distributed in the matrix. In this case, the S , W values for FeCr should be the sum of the contribution of the annihilation with Fe and Cr electrons according to their proportions in FeCr alloy. For example, the theoretical value S_{lattice} for Fe-12Cr is the sum of 88% S_{lattice} for Fe and 12% S_{lattice} for Cr.

The results of the theoretical calculations are shown in Figure III-5. The $S_{\text{lattice}}(W_{\text{lattice}})$ points for the four FeCr alloys are close and align on the straight line connecting $S_{\text{lattice}}(W_{\text{lattice}})$ points for Fe and Cr. Compared to the measured ones, the calculated points have lower S values and higher W values. It indicates that there exist open volume defects in the measured samples.

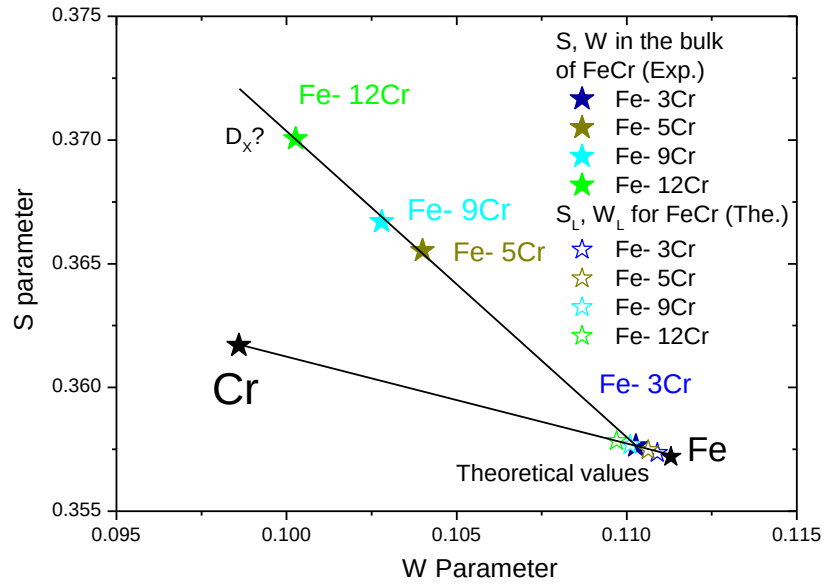


Figure III-5: The theoretical values of positron annihilation characteristics in FeCr model alloys compared to the S and W bulk values obtained by VEPFIT in virgin alloys.

- For Fe3Cr, S_{bulk} (W_{bulk}) point obtained by measurement is close to the calculated S_{Lattice} (W_{Lattice}) one. The difference is greater and greater with the increase of Cr concentration and their S_{bulk} (W_{bulk}) points align on one line named D_x . It means that the concentration of open volume defects existing in these samples increases with the increase of Cr concentration. The annealing treatments were not achieved in FeCr samples after mechanical polishing. Thus, it is very probable that the open volume defects exist in the sample bulk. The diffusion length (L^+) in FeCr samples (reported in Table III-2), decreases when the Cr content increases in the Fe-Cr alloys, which indicates that vacancy defects concentrations increase with the Cr concentration. Comparing these values (98- 120 nm) to the one obtained in pure Fe (160 nm), it suggests that the concentration of defects remains low enough for the study of defects induced by irradiation. It will have to take into account that this concentration depends on the sample.
- The chemical effect of impurities existing in the model alloys could also change the value of S and W if they decorate the vacancy defects or if they form precipitates for example. Silicon is a possible impurity that could contribute to this S, W evolution as a function of the Cr concentration in FeCr alloys^[119]. The Si content increases with the Cr one (0.002 at.% for Fe- 3Cr, 0.08 at.% for Fe- 5Cr, 0.18 at.% for Fe- 9Cr and 0.22 at.% for Fe- 12Cr) and the S and W values of Si lattice are 0.471(5) and 0.029(0) in agreement with an increase of S and a decrease of W as observed for the S, W values obtained in FeCr compared relative to pure Fe. But the Si content in Fe-9Cr and Fe-12Cr is close whereas the S, W are clearly higher for Fe- 12Cr also indicating that not only one effect dominates in the S, W evolution. Moreover the concentration of impurities like C, O and N is non-negligible in these alloys and change with the concentration of Cr. It is well known that vacancy defects can form complexes with these elements their binding energy is positive for all of them^[177].

- It is noted that the line representing the defect X (Dx) is superposed with the S(W) profiles of all FeCr model alloys. It means that the defects existing in bulk are also detected close to the surface and are the same in all FeCr model alloys. On the surface of samples, the defects could be dislocations introduced by mechanical polishing. The TEM^[134] results confirm the presence of the dislocations. The big binding energy between Cr and dislocations^[120] makes much higher density of dislocations in FeCr with much higher Cr content.

A model of two homogeneous layers has been used to fit the FeCr results. As shown in Table III-2, the thickness and positron diffusion length of the first layer are presented. They are all lower than the L^+ values in their respective second layer. This layer could correspond to remaining vacancy defects after mechanical polishing or to an effective passive layer of chromium oxide^[32]. This ~ 20- 120 nm thick layer could influence the S, W values measured after irradiation with low energy positrons, especially for positrons with energy lower than 5 keV. But for the high energy positrons, for example 25 keV, the average probed depth is ~ 1 μm in FeCr. Thus, their influence on the results after irradiation is negligible.

III.1.3. Conclusions

The quality of Fe and FeCr virgin samples has been examined by slow positron beam Doppler broadening (SPBDB) technique after their preparation.

The effective positron diffusion length in the Fe virgin sample ($L^+ = 160 \pm 2$ nm) reveals that the quantity of defects in the bulk of the Fe virgin samples is low. In addition, the results are reproducible and thus the quality of these Fe samples prepared by the same procedure is considered as good enough for the study of the defects induced by irradiation. The annihilation characteristics S and W obtained in the virgin sample are considered as the reference ones and can be defined as the annihilation characteristics of the Fe lattice: $S_{\text{ref}} = 0.357(2)$ and $W_{\text{ref}} = 0.111(3)$.

The positron annihilation characteristics differ from one FeCr alloy to another. The S_{bulk} (W_{bulk}) increases (respectively decreases) with the increase of the Cr concentration. Several reasons have been proposed to explain the results. The comparison of the measured S and W with the calculated values corresponding to annihilation in the lattice of the different alloys indicates that there exist open volume defects in the measured virgin samples. The trapping of positron at defects decorated or made of impurities such as Si, C, O and N cannot be discarded. These defects could be related to the dislocations which have also been observed in TEM. The vacancy defects concentration increases with the Cr content. But it remains low enough for the study of defects induced by irradiation.

III.2. Nature of Vacancy defects formed in Fe and FeCr by irradiation

The pure vacancy defects in Fe and FeCr samples have been studied by slow positron beam Doppler broadening (SPBDB) technique in this section. The vacancy defects have been introduced in Fe samples by 1.5 MeV helium irradiations. The 2 MeV helium irradiations have been performed to introduce the vacancy defects in FeCr (3 at.%- 12 at.%) samples. The fluence and Cr content effect on the formation of vacancy defects are studied.

III.2.1. Vacancy defects in bcc Fe induced by 1.5 MeV He irradiation

The vacancy defects have been introduced in Fe samples by 1.5 MeV helium irradiations at various fluences. The fluence effect is studied.

a) 1.5 MeV He irradiation conditions in Fe

The depth profiles of He concentrations and the corresponding damage are reminded in the Figure III-6, and the irradiation conditions are reported in Table III-3.

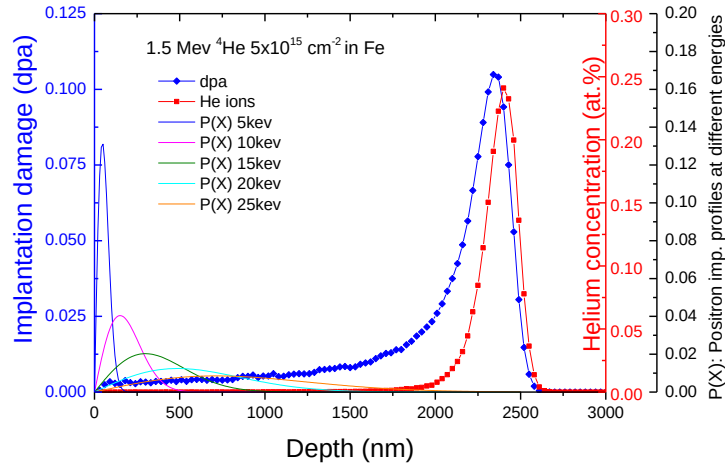


Figure III-6: Depth profile of defect production and atomic concentration calculated using SRIM for 1.5 MeV ^4He implanted in Fe at the fluence of $5 \times 10^{15} \text{ cm}^{-2}$ are compared to positron implantation profiles calculated for various energies $P(X)$.

The depth profiles of He concentrations and the corresponding damage are reminded in the Figure III-6, and the irradiation conditions are reported in Table III-3.

Matrix	Irradiation type	Fluence (at.cm^{-2})	Probed region	Damage dose at $\sim 720\text{nm}$ (dpa)	He atomic concentration at $\sim 720\text{nm}$ (appm)
Fe	1.5 MeV ^4He	10^{13}	0- 2 μm	1×10^{-5}	0.0004
		2×10^{13}	0- 2 μm	2×10^{-5}	0.0008
		10^{14}	0- 2 μm	1×10^{-4}	0.004
		2×10^{14}	0- 2 μm	2×10^{-4}	0.008
		5×10^{14}	0- 2 μm	5×10^{-4}	0.02
		10^{15}	0- 2 μm	1×10^{-3}	0.04
		10^{16}	0- 2 μm	1×10^{-2}	0.4
		10^{17}	0- 2 μm	1×10^{-1}	4

Table III-3: 1.5 MeV He irradiation conditions in Fe samples.

b) The primary knock- on atoms (PKA) energy

In order to explain the experimental results, the primary knock- on atoms (PKA) energy is calculated. The damage dose (dpa) induced in irradiated samples depends on the nature of implanted ions, their energy, and their fluence. However, even if the different irradiations generate the same damage dose (dpa), the size distribution of vacancy defects induced could be very different. The notion 'dpa' gives a global idea about the vacancy number in the entire irradiated region whereas the local density of vacancy depends on the primary knock-on atoms (PKA) energy. For a given dpa, the PKA with higher energy would generate the vacancy defects more condensed locally, indicating that it could lead to vacancy defects with larger size. For this reason, the calculations of the primary recoil spectrum, $P(E, T)$ as a function of the implanted ions energy (E) and the generated PKA energy (T), were carried out using SRIM software and the «full damage cascades» option. It represents the fractional number of PKA between the minimum displacement energy E_d (40 eV for Fe^[139, 146]), and energy T .

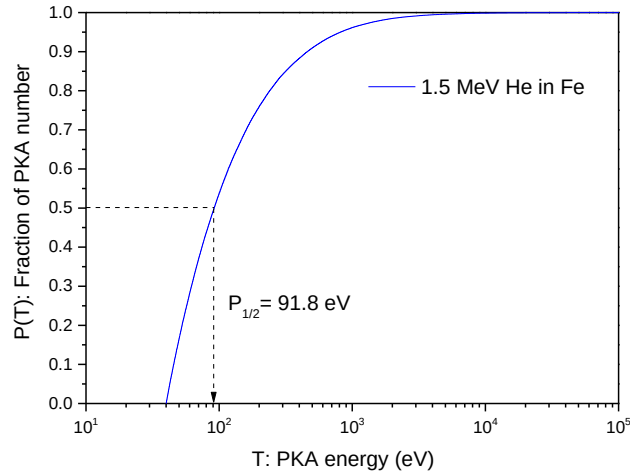


Figure III-7: The primary recoil spectrum $P(T)$ for 1.5 MeV He irradiation in Fe calculated by SRIM.

The primary recoil spectrum $P(T)$ is shown for the case of 1.5 MeV He irradiation in Fe in Figure III-7. The parameter $P_{1/2}$ represents the PKA energy at which $P(T)$ reaches the half of the total PKA population. For this case, $P_{1/2}$ is 91.8 eV. Norgett, Robinson, and Torrens (NRT) developed a secondary displacement model which gives the total number of displaced atoms N produced by a PKA with energy T as^[178]:

$$N = \frac{0.8T}{2E_d}$$

Thus the primary recoil spectrum could be expressed by the fraction of PKA as a function of displaced atoms number produced by PKA with energy T as shown in Figure III-8. It has been noted that 54% of PKA in this case could not induce any other atom displacement, 1% of PKA could generate a displacement cascade including more than 27 atoms and 45% of PKA generate a cascade including 1 - 27 atoms. It should be noted that this calculation does not consider the defects recombination. Thus, the fraction of PKA which could not induce cascade should be higher than 54% in the reality.

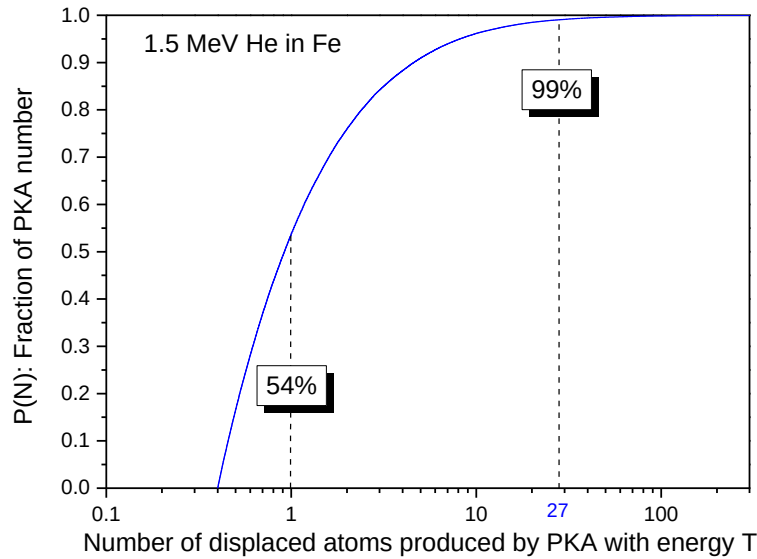


Figure III-8: The fraction of PKA as a function of number of displaced atoms produced by PKA with energy T for 1.5 MeV He irradiation in Fe calculated by SRIM.

Another parameter, $W(T)$, representing fraction of displacement damage as a function of PKA energy T has also been calculated by SRIM software using the «full damage cascades» option and is shown in Figure III-9. The parameter $W_{1/2}$ is defined as representing the PKA energy value below which half of the displacement damage is created. In the case of 1.5 MeV He irradiation in Fe, half of the displacement damage is created by the PKA with energy below 596 eV. $W(T)$ could also be expressed by the fraction of displacement damage $W(N)$ as a function of displaced atoms number produced by PKA with energy T as shown in Figure III-10. It has been noted that 16% of displacement damage leads to the formation of one vacancy at the maximum, 50% being in the form of fewer than 6 vacancies, 1% being in the form of more than 1210 vacancies. Also, the defects recombination is not considered. Thus, more than 50% of the displacement damage should be in the form of fewer than 6 vacancies.

Thus, compared to $P(T)$ parameter, $W(T)$ has a tighter link with the displacement damage named dpa.

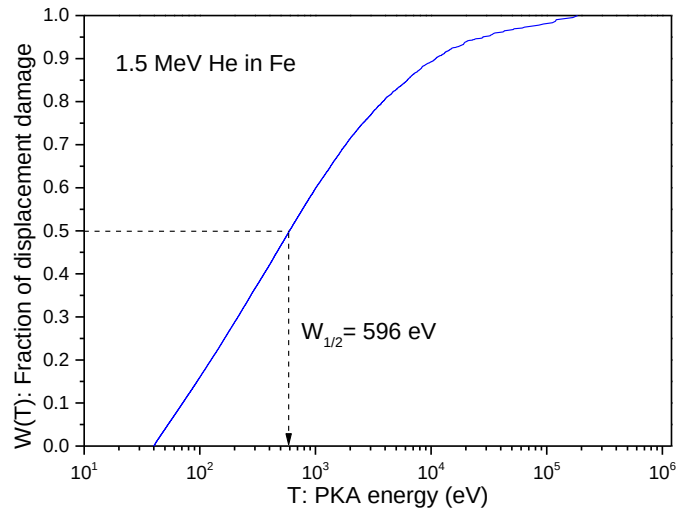


Figure III-9: Fraction of displacement damage as a function of PKA energy T for 1.5 MeV He irradiation in Fe calculated by SRIM.

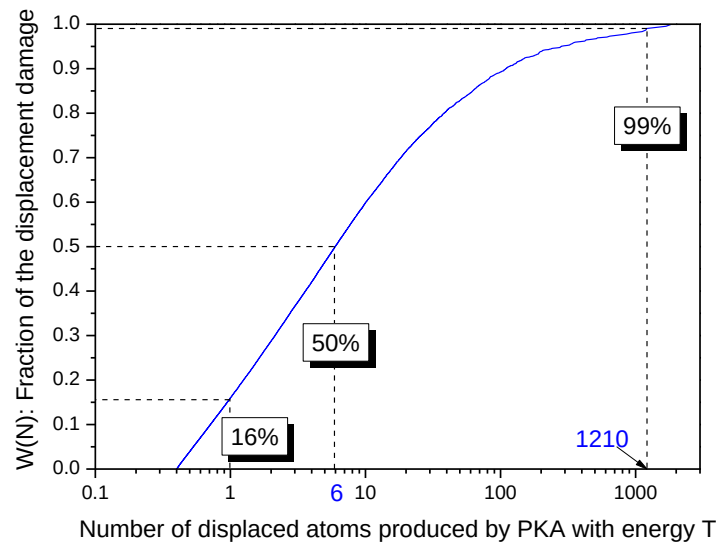


Figure III-10: Fraction of displacement damage as a function of number of displaced atoms produced by PKA with energy T for 1.5 MeV He irradiation in Fe calculated by SRIM.

c) PAS results

Figure III-11 shows the $S(E)$, $W(E)$ and $S(W)$ curves for pure Fe samples irradiated with 1.5 MeV ^4He at fluences from 1×10^{13} to $1 \times 10^{17} \text{ cm}^{-2}$ (corresponding to the dpa range from 10^{-5} to 10^{-1} dpa) and for the Fe virgin sample. The S and W positron annihilation characteristics in the ^4He irradiated Fe samples differ from the ones measured in the virgin Fe samples. Whatever the fluence, all the $S(E)$ values are higher in the irradiated samples than in the virgin ones when all the $W(E)$ values are, respectively, lower. This

indicates that ^4He ions have induced vacancy-related defects in their track region. The general look of $W(E)$ curves is reverse to that of $S(E)$. $S(E)$ curves depend on the fluence. For low fluences from 1×10^{13} to $5 \times 10^{14} \text{ cm}^{-2}$, the curves suggest the diffusion back of positrons to the surface and a large fraction of annihilation in the surface states. For higher fluences, diffusion back to the surface becomes negligible. For positrons with energy of approximately 22.5 keV, $S(E)$ increases as a function of E for low fluences and decreases for the highest ones. In Figure III-6, we can see that 25 keV positrons probe a region where the damage dose and the He concentration begin to increase because of the accumulation of cascades and stopping of the He ions. $S(E)$ increases with the damage dose. But when the fluence becomes equal or higher than $1 \times 10^{16} \text{ cm}^{-2}$, it decreases. At this fluence the He concentration becomes non negligible in the region probed by high energy positrons. He atoms can be trapped in vacancies and it could lead to a change of electron density and momentum distribution probed by positrons at the trap [179]. This effect of helium is negligible at low fluences when the He concentration is very low.

The curves for the fluence $1 \times 10^{16} \text{ cm}^{-2}$ have been fitted using Vepfit and the results are shown in Figure III-11. A model of three layers has been used. The first layer with a thickness of $\sim 34 \text{ nm}$ is considered as an oxide layer introduced during the irradiation. The second layer between $\sim 34 \text{ nm}$ and $\sim 1880 \text{ nm}$ corresponds to the track region of the irradiation and gives a positron diffusion length $L^+ \sim 100 \pm 66 \text{ nm}$. This L^+ is lower than the one obtained in Fe virgin sample, $L^+_{\text{Lattice}} = 160 \pm 2 \text{ nm}$, indicating that positron traps are created by irradiation. The S and W values in the second layer are respectively 0.4519 and 0.0601. The third layer beyond $\sim 1880 \text{ nm}$ corresponds to the region where the damage dose and the He concentration begin to increase.

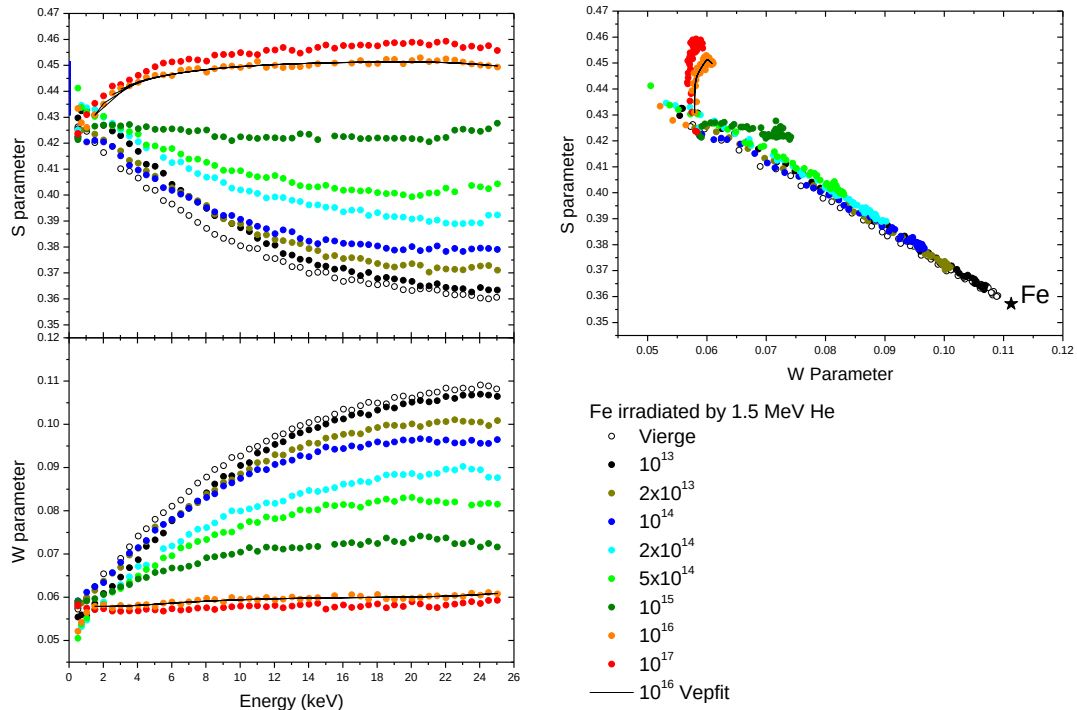


Figure III-11: $S(E)$, $W(E)$ and $S(W)$ for the Fe samples irradiated by 1.5 MeV He at various fluences from 1×10^{13} to $1 \times 10^{17} \text{ cm}^{-2}$.

In all samples, $S(E)$ changes very slightly in the energy range between 20 and 22 keV, the diffusion back of positron to surface and the annihilation fraction in cascade region are negligible. The average S , W values in this range are very close to those obtained by Vepfit. For example, the $(S_{\text{average}}, W_{\text{average}})$ is $(0.4520, 0.0600)$ compared to $(0.4519, 0.0601)$ obtained by Vepfit for the fluence $1 \times 10^{16} \text{ cm}^{-2}$. Thus, in the following we choose to consider the S and W values measured in the energy range between 20 and 22 keV as the annihilation characteristics in the track region of the ions. In this energy range S increases with the fluence. It indicates that damage increases when the irradiation fluence increases in the pure Fe samples.

The evolution of S_{average} as a function of W_{average} is plotted on Figure III-12. At low fluence from 1×10^{13} to $2 \times 10^{14} \text{ cm}^{-2}$ (from 1×10^{-5} to $2 \times 10^{-4} \text{ dpa}$), the S, W points follow the same straight line D_1 which goes through the $(S_{\text{ref}}, W_{\text{ref}})$ point. It indicates that the same nature of vacancy defects has been created for these low fluences. From the fluence of $5 \times 10^{14} \text{ cm}^{-2}$ ($5 \times 10^{-4} \text{ dpa}$), the S, W points begin to leave D_1 line. This indicates that the nature of vacancy defects has changed and larger vacancy-type defects are detected. When fluence increases, the shift from D_1 characteristic line increases indicating that vacancy clusters are detected and their size increases with the damage dose.

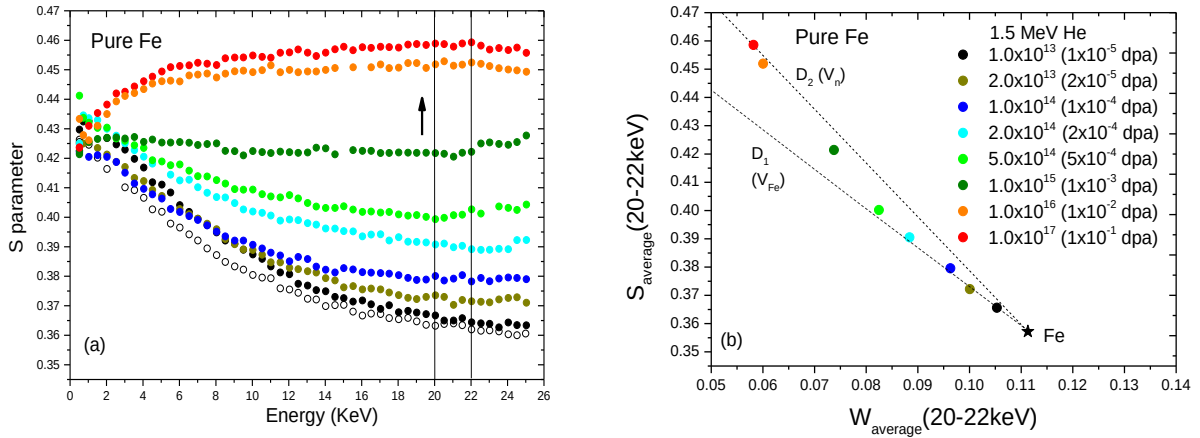


Figure III-12: Low (S) momentum fraction as a function of positron energy (a) and S as a function of W obtained by calculating the average value between positron energy 20 and 22 keV (b) in Fe samples before irradiation and after 1.5 MeV 4He irradiation at different fluences in the range from 1.0×10^{13} to $1.0 \times 10^{17} \text{ cm}^{-2}$.

d) Discussion

The $W(N)$ results which give the fraction of displacement damage as a function of displaced atoms number produced by PKA with energy T (see details in section 2.1 (b)) indicate that the recoiled atoms collisions in the case of 1.5 MeV He irradiation should lead to the formation of small cascades with essentially single vacancies as molecular dynamics modelling predicts^[180]. For irradiation conditions at low fluence from 1×10^{13} to $2 \times 10^{14} \text{ cm}^{-2}$ (from 1×10^{-5} to 2×10^{-4} dpa), the distance between these small cascades is great and thus the possibility of single vacancy clustering is low. For these reasons, we will propose that the D1 line in Figure III-12 is more likely characteristic of annihilation in single vacancy in Fe named $D_v(\text{Fe})$. For higher fluences, the formation of clusters could be explained by the migration of single vacancies generated by irradiation that could agglomerate leading to the formation of larger clusters when their concentration increases that means with the fluence. Indeed, migration temperature of V in Fe is below the room temperature (-53 to 5°C) as suggested by Takaki et al.^[107]. C Fu^[105, 106] has calculated the migration energy of small vacancy clusters and found it is lower than the one of the single vacancy indicating that small clusters can contribute to the formation of large ones. M. Eldrup et al. have also found that both the density and the average size of vacancy defects increase with increasing damage dose^[109]. T. Iwai et al.^[181] investigated accumulation of vacancy-type defects in iron produced by 1 MeV He irradiations at room temperature by positron beam both in situ during irradiations and after irradiations. Vacancy clusters have been observed from $\sim 1 \times 10^{-2}$ to 0.1 dpa and the results suggest that the S values are not likely to change under and after irradiation. Thus, the vacancy clusters induced in Fe by irradiation with ^4He 1.5 MeV (this study) could be considered to form during the irradiation by migration and agglomeration of single vacancy and small vacancy clusters. Between $1 \times 10^{16} \text{ cm}^{-2}$ and the highest fluence of $1 \times 10^{17} \text{ cm}^{-2}$, the S and W values don't change too much indicating that saturation occurs. This saturation could correspond to a maximum size of clusters that can be formed in these irradiation conditions. We will define the straight line going from Fe lattice S , W point to S , W point measured in sample implanted at the highest fluence as D2 characteristic of annihilation of positrons trapped in vacancy clusters named $D_{vn}(\text{Fe})$.

Being given the migration energy of the single vacancies it is therefore unlikely that they survive in the irradiated sample at room temperature. They should either disappear by diffusion into sinks or agglomerate with other vacancies into clusters or form pairs with some impurities which stabilizes them. It has to be noted that the carbon and oxygen concentrations in these iron samples are respectively about 52 appm and 169 appm (as given by the supplier Goodfellow but only 20 appm in our SIMS experiments). These atoms could be bound to single vacancies and stabilize them as it has been shown in the reference^[182] and more recently by C Barouh^[177] for the oxygen case. A. Vehanen et al. studied the electron irradiated iron-carbon systems by positron lifetime experiments and found that carbon-vacancy pairs are already detected at -53°C^[183]. Thus in our case, the D_1 line could be characteristic of the detection of single vacancies decorated with impurities such as carbon more probably than oxygen because the binding energy of the V-O pair is about 1.4 eV compared to about 0.5 eV for the V-C pairs^[177] so the probability to form V-C is higher at room temperature.

With the simple model of positron trapping at one deep trap as presented in section II.3.2(c) and S , W values obtained for fluences from 1×10^{13} to $2 \times 10^{14} \text{ cm}^{-2}$, the concentration of single vacancies

induced by these fluences can be obtained and is reported in Table III-4.

Experimental model			SRIM	C _v calculated using S/SRIM (%)
Fluence (ions/cm ²)	C _v calculated using W (V/at. of Fe)	C _v calculated using S (V/at. of Fe)	Damage (dpa)	
1x10 ¹³	(1.37±0.31)x10 ⁻⁶	(1.32±0.38)x10 ⁻⁶	1x10 ⁻⁵	13.2±3.8
2x10 ¹³	(3.1±0.40)x10 ⁻⁶	(2.77±0.73)x10 ⁻⁶	2x10 ⁻⁵	13.85±3.65
1x10 ¹⁴	(4.8±0.42)x10 ⁻⁶	(4.91±0.87)x10 ⁻⁶	1x10 ⁻⁴	4.91±0.87
2x10 ¹⁴	(10.30±1.52)x10 ⁻⁶	(10.40±1.69)x10 ⁻⁶	2x10 ⁻⁴	5.2±0.845

Table III-4: Measured concentration of single vacancy calculated by one deep trapping simple model of positron in Fe. The experimental values are compared to the SRIM calculation.

The single vacancy concentration could also be calculated by using the positron effective diffusion length L^+ as presented in section II.3.1(a, b):

$$L^+ = \sqrt{\frac{D_+}{\lambda_L}} \text{ and } L_{eff}^+ = \sqrt{\frac{D_+}{\lambda_L + \mu_d c_d}}$$

Where λ_L is the inverse of the positron lifetime in the lattice τ_L in Fe lattice, τ_L is 106-110 ps^[90, 168-170]. The positron diffusion length L^+ in Fe lattice without defects is 160±2 nm as shown in section III.1.1(b). Thus, the positron diffusion coefficient D_+ is calculated to be 2.327 cm².s⁻¹. For the Fe sample irradiated by 1.5 MeV He with the fluence 2x10¹⁴ cm², the effective positron diffusion length L_{eff}^+ is 132.8 nm obtained by Vepfit. For the single vacancy in Fe, the atomic specific trapping coefficient μ_v^{at} has been determined to be 1.1±0.2x10¹⁵ s⁻¹^[183]. With these parameters, the concentration of single vacancy in this sample is determined to be 3.727 appm. Compared to the value of 10.4 appm, obtained for this sample calculated using S, W, these values are in the same order of magnitude.

These calculations show a linear increase of single vacancy concentration as a function of the fluence (Figure III-13). These single vacancies concentrations are compared to the displacement damage (dpa) calculated by SRIM. The single vacancy concentrations obtained by experiments are much lower than those of SRIM calculations. The difference between the experimental values and the damage dose calculated by using SRIM may be due to different phenomena, including the annihilation of Frenkel pairs created during implantation which are recombined due to the mobility temperature of interstitials, far below the room temperature^[107]. However, this ratio in the range 0.049- 0.139 found in this study is lower than the values 0.3± 0.1 found by several molecular dynamics (MD) simulations for PKA energy higher than 2 keV^[136]. But it is close to the value for 2.8 MeV C⁺ irradiation in Fe (ratio= 0.17) studied by T.Iwai et al^[113]. In addition, the single vacancy concentrations are low compared to the carbon concentration 52 appm and or the oxygen one 169 appm (as given by the supplier Goodfellow but only 20 appm in our SIMS experiments). Thus, the carbon and oxygen atoms quantity is enough to be bound to single vacancies and stabilize them.

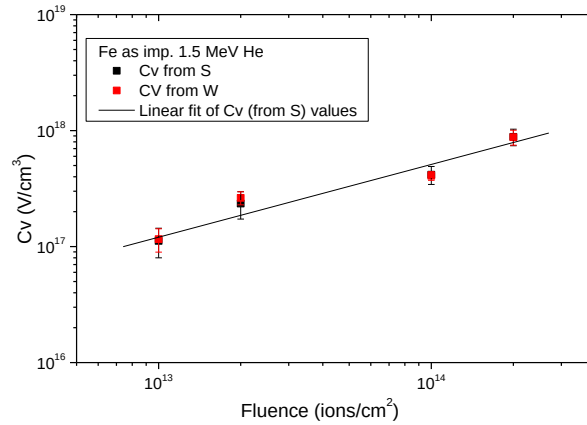


Figure III-13: Variation of the single vacancy concentration as a function of the fluence for Fe irradiated with 1.5 MeV He ions.

The nature of vacancy defects induced in Fe by irradiation with 1.5 MeV He depends on the fluence. At low fluence decorated C or O single vacancies are mainly detected. Their concentration increases with the fluence but not so quick as the damage dose calculated using SRIM. At high fluences (higher than $2 \times 10^{14} cm^{-2}$) vacancy clusters are detected and their size increases with the fluence up to a saturation reached for the fluence of $1 \times 10^{16} cm^{-2}$.

III.2.2. Vacancy defects in bcc FeCr induced by 2 MeV He irradiation

In this section we will see that vacancy defects have been introduced in FeCr samples by 2 MeV helium irradiations at various fluences. The fluence and Cr content effect on the formation of vacancy defects are studied.

a) 2 MeV He irradiation conditions in FeCr model alloys

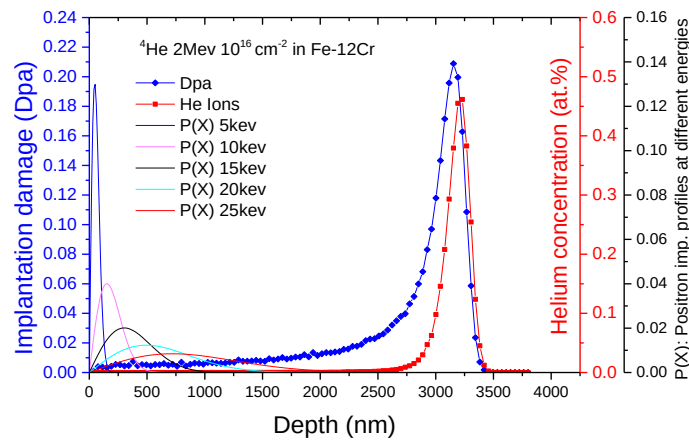


Figure III-14: Depth profile of defect production and atomic concentration calculated by SRIM for the Fe- 12Cr sample irradiated with 2 MeV He at the fluence of $10^{16} cm^{-2}$ are compared to positron implantation profiles calculated for various energies P(X).

The depth profiles of He concentrations and the corresponding damage are reminded for 2 MeV He in Fe-12 Cr in the Figure III-14 and the irradiation conditions in Table III-5. The irradiation conditions for 2 MeV He in Fe-3Cr, Fe-5Cr and Fe-9Cr are the same as for Fe-12Cr. The damage dose and He profiles are considered as equivalent for all alloys even if Cr concentration changes from 3- 12 at.%.

Matrix	Irradiation type	Fluence (at.cm ⁻²)	Probed region	Damage dose at ~720nm (dpa)	He atomic concentration at ~720nm (appm)
Fe-12Cr	2 MeV 4He	10 ¹⁴	0- 2 μm	6x10 ⁻⁵	0.00023
		2x10 ¹⁴	0- 2 μm	1.2x10 ⁻⁴	0.00046
		10 ¹⁵	0- 2 μm	6x10 ⁻⁴	0.0023
		10 ¹⁶	0- 2 μm	6x10 ⁻³	0.023
		1.3x10 ¹⁷	0- 2 μm	7.8x10 ⁻²	0.3

Table III-5: 2 MeV He irradiation conditions in Fe-12Cr samples.

b) Fluence effect in as-implanted Fe-Cr samples

Figure III-15 (a) presents positron annihilation characteristics S as a function of the positron energy and the $S_{\text{average}(20-22\text{keV})}$ ($W_{\text{average}(20-22\text{keV})}$) curves are also plotted for Fe-9Cr samples irradiated with 2MeV helium with fluences from 10¹⁴ to 1.3x10¹⁷ ions/cm² (6x10⁻⁵ to 7.8x10⁻² dpa). These data are compared to the results obtained for virgin sample. The fluence effect in as implanted Fe- 3Cr, Fe- 5Cr and Fe- 12Cr is the same as for the Fe- 9Cr alloy.

As in the case of 1.5 MeV He irradiated Fe, all the $S(E)$ values are higher in the irradiated samples than in the virgin one for all the fluences. All the $W(E)$ values are respectively lower and they are not illustrated here because their general behaviours are totally reverse to those of $S(E)$ curves. $S(E)$ curves depend on the fluence. For low fluences from 1x10¹⁴ to 1x10¹⁵ cm⁻², the curves suggest the diffusion back of positrons to the surface and a large fraction of annihilation at the surface states for low positron energy. For higher fluences, diffusion back to the surface becomes negligible. As in the case of 1.5 MeV He irradiated Fe, $S(E)$ changes very slightly in the energy range between 20 and 22 keV, the diffusion back of positrons to the surface and the annihilation fraction in cascade region are negligible. Thus, in the following we choose to consider the S and W values measured in the energy range between 20 and 22 keV as the annihilation characteristics in the track region of the ions. In this energy range S increases with the fluence (see arrow in Figure III-15(a)). It indicates that damage increases when the irradiation fluence increases in the FeCr samples.

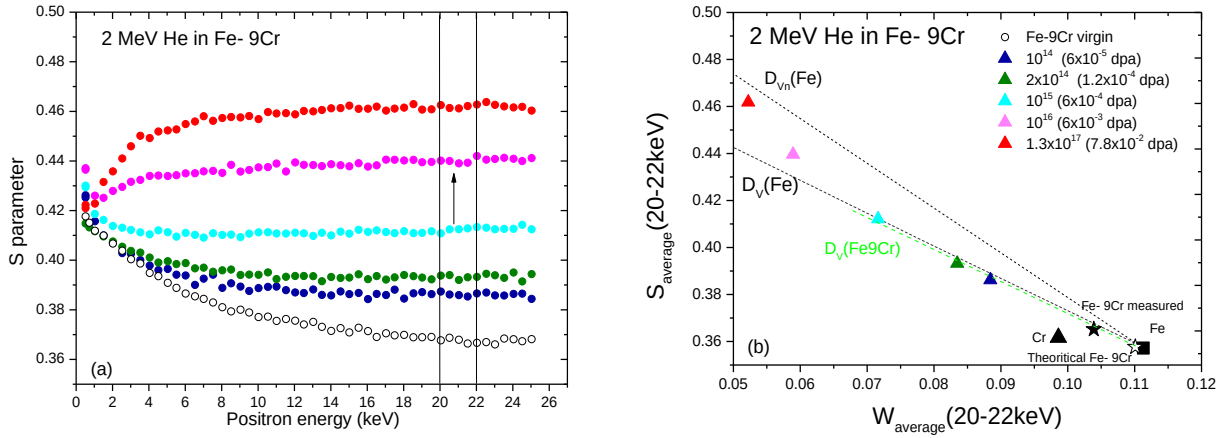


Figure III-15: S as function of positron energy (a) and W (b) for Fe-9Cr samples irradiated with 2MeV helium with different fluences.

Figure III-15(b) shows the average of the $S(E)$ values measured in the energy range from 20 to 22keV as a function of the average $W(E)$ values measured in the same energy range. The S , W points for measured virgin Fe-9Cr, Fe-9Cr theoretical lattice, pure Fe lattice and virgin Cr samples have also been plotted with the lines corresponding to the annihilation state in single vacancy in Fe ' $D_v(\text{Fe})$ ' and the one characteristic of annihilation in vacancy clusters ' $D_{vn}(\text{Fe})$ ' in Fe.

The nature of vacancy defects in Fe-9Cr depends on fluence as it has been already observed in pure Fe. At low fluences from 10^{14} to 10^{15} ions.cm⁻², the $S(W)$ points align on one straight line defined as $D_v(\text{Fe9Cr})$ which is parallel to the $D_v(\text{Fe})$ line. The PKA energy distribution $P(T)$ and $W(T)$ for 2 MeV He irradiation in FeCr are similar to those of 1.5 MeV He irradiation in Fe, indicating that the defects induced in these irradiation conditions should be mainly single vacancies for low fluences. It could indicate that this new straight line corresponds to the detection of the same defect as for the $D_v(\text{Fe})$ and the slight shift toward lower S and W would be due to the annihilation of positron in the vicinity of Cr atoms. As shown in the figure, this shift is similar to the difference between the S , W points for theoretical virgin Fe-9Cr and measured virgin pure Fe.

At high fluences from 10^{16} to 1.3×10^{17} ions.cm⁻², the $S(W)$ points go far away from single vacancy line and tend towards the $D_{vn}(\text{Fe})$ line corresponding to the annihilation of positrons trapped in vacancy clusters in Fe. It indicates that the size of the detected vacancy defects increases with the fluence. Single vacancy migration energies in Fe-Cr and pure Fe are very close ^[184] and its migration occurs near 205-210K ^[185]. Thus, the migration of single vacancies could lead to the formation of vacancy clusters in FeCr alloys.

The similar fluence effect is also found in as implanted Fe- 3Cr, Fe- 5Cr and Fe- 12Cr model alloys. For Fe3Cr and Fe- 5Cr alloys, the single vacancy is detected at fluences 10^{14} and 2×10^{14} ions.cm⁻². And vacancy clusters are detected in these two alloys from the fluence 10^{15} ions.cm⁻² whereas mainly single vacancies are observed in Fe- 9Cr alloy at this fluence. The case for Fe- 12Cr alloy is the same as for Fe- 9Cr alloy, the single vacancy is observed in the same fluence range from 10^{14} to 10^{15} ions.cm⁻².

c) The effect of Cr on microstructure evolution under irradiation

In Figure III-16, positron annihilation characteristics $S(E)$ and $W(E)$ as function of the positron energy are plotted for four FeCr model alloys irradiated with 2MeV helium at fluence of $1.3 \times 10^{17} \text{ cm}^{-2}$ (7.8×10^{-2} dpa) and for virgin samples.

As discussed in previous section, the S and W values measured in the energy range between 20 and 22 keV can also be considered as the annihilation characteristics in the track region of the ions. Figure III-16 (a) shows that all $S(E)$ values after irradiation are higher than the values obtained in their virgin state, indicating the presence of vacancy defects. As presented in the section III.1.2 dedicated to FeCr virgin samples, S of virgin samples increases with the increase of chromium concentration. But after 2 MeV helium irradiation at the same fluence, the S values decrease with the chromium concentration. This decrease of S after irradiation indicates that chromium effect could be involved in the damage evolution.

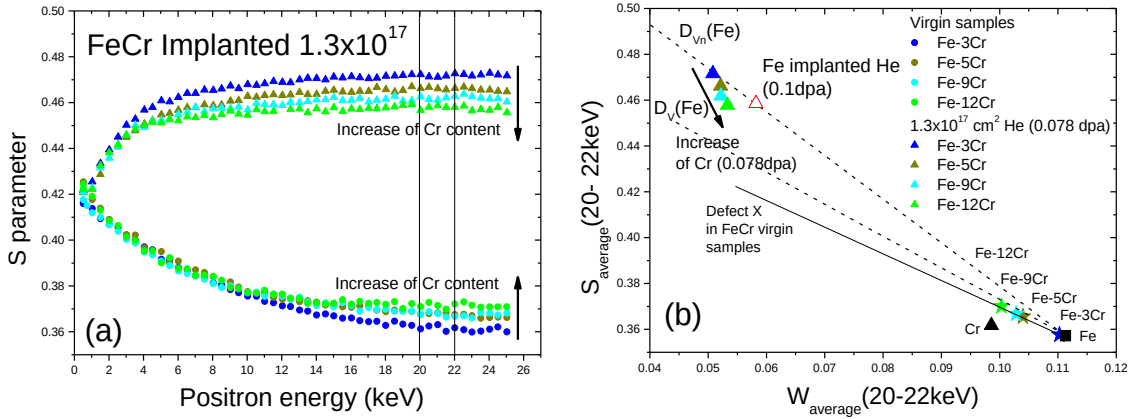


Figure III-16: S as function of positron energy (a) and W (b) for four FeCr model alloys irradiated with 2 MeV helium at fluence $1.3 \times 10^{17} \text{ cm}^{-2}$.

Figure III-16 (b) shows S as function of W as the average of the $S(E)$ and $W(E)$ values measured in the energy range from 20 to 22 keV for the four FeCr model alloys. The effect of the Cr content on the nature of the vacancy defects is observed. With the increase of Cr concentration, $S(W)$ points go away from the $D_{\text{vn}}(\text{Fe})$ line and move towards $D_{\text{v}}(\text{Fe})$ line indicating the size of vacancy clusters decreases with Cr concentration.

But it should be reminded that the measured annihilation characteristics of the virgin samples for four FeCr model alloys are not the same as shown in Figure III-16 (b). To subtract the effect of the quality of the virgin sample, $S_{\text{implanted}} - S_{\text{measured virgin}}$ and $W_{\text{measured virgin}} - W_{\text{implanted}}$ as function of dpa for four FeCr model alloys and also Fe samples are plotted in Figure III-17. $S_{\text{measured virgin}}$ represents the measured S value of virgin sample and $S_{\text{implanted}} - S_{\text{measured virgin}}$ represents the change of S after irradiation, and respectively the same for $W_{\text{measured virgin}} - W_{\text{implanted}}$. The figure illustrates that the change in S (or W) decreases monotonously when Cr concentration increases at each damage dose (from 6×10^{-5} to 7.8×10^{-2}

dpa). This means that the size or concentration of vacancies formed by irradiation decreases monotonously with Cr content at the same damage dose in the different conditions of fluences. The implanted Fe samples are also compared even if their damage level is slightly different from those of irradiated FeCr samples. The dotted line represents the Fe single vacancy S and W values which have been determined in the study of 316L alloy (Fe based alloy) irradiated with 1×10^{16} 1.5 MeV Helium ^[167]. The points above this line indicate the detection of vacancy clusters and the ones below this line represent the single vacancy with different concentrations or other defect like dislocation.

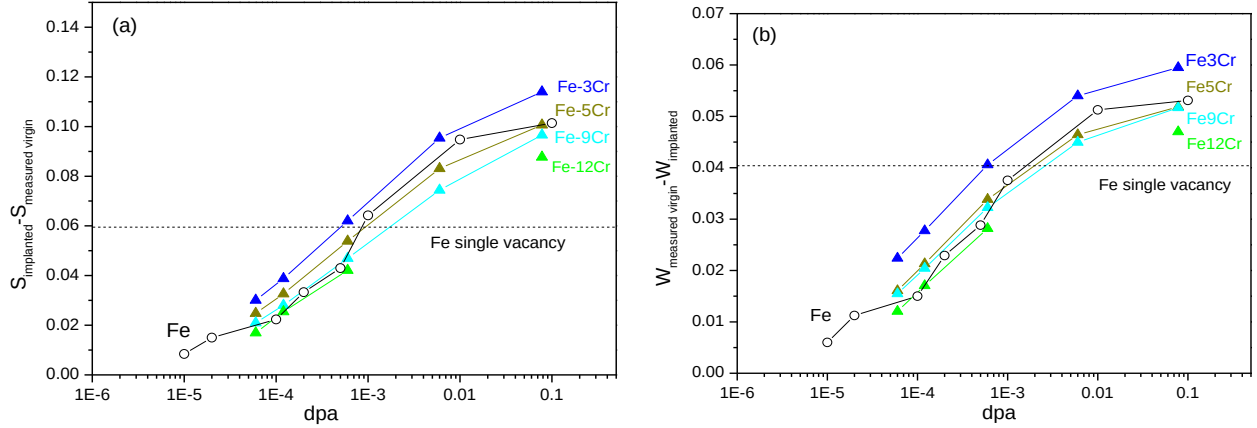


Figure III-17: $S_{\text{implemented}} - S_{\text{measured virgin}}$ (a) and $W_{\text{measured virgin}} - W_{\text{implemented}}$ (b) as function of dpa for four FeCr model alloys and Fe samples.

Another parameter $(S_{\text{implemented}} - S_{\text{theoretical virgin}}) / (W_{\text{theoretical virgin}} - W_{\text{implemented}})$ calculated as function of dpa for the four FeCr model alloys and Fe samples is reported in Figure III-18. In this calculation, the $S_{\text{theoretical virgin}}$ representing the theoretical S lattice value of FeCr alloy (as calculated in the section 1.2) is used. This parameter presents the absolute value of the $S(W)$ line slope. The slope increases in absolute value with the increase of vacancy defect size. It shows clearly that the vacancy size after irradiation decreases with the Cr concentration for the two highest fluences (1×10^{16} and $1.3 \times 10^{17} \text{ cm}^{-2}$). But this relationship is not clear for the three lowest fluences (1×10^{14} to $1 \times 10^{15} \text{ cm}^{-2}$) because the S and W values closer to the lattice point are more affected by the defects which exist in the virgin sample.

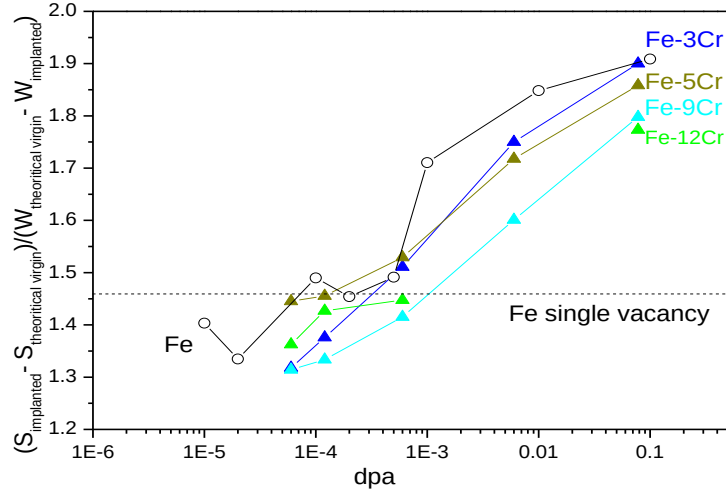


Figure III-18: Parameter $(S_{\text{implanted}} - S_{\text{theoretical virgin}})/(W_{\text{theoretical virgin}} - W_{\text{implanted}})$ as function of dpa for four FeCr model alloys and Fe samples.

The case of the highest fluence, corresponding to 0.078 dpa in FeCr and 0.1 dpa in Fe, is specially studied. The $S_{\text{implanted}} - S_{\text{measured virgin}}$ and the ratio $(S_{\text{implanted}} - S_{\text{theoretical virgin}})/(W_{\text{theoretical virgin}} - W_{\text{implanted}})$ are plotted as a function of Cr concentration for FeCr and Fe samples in Figure III-19. Figure III-19 (b) shows that $(S_{\text{implanted}} - S_{\text{theoretical virgin}})/(W_{\text{theoretical virgin}} - W_{\text{implanted}})$ decreases with Cr content, indicating that the vacancy size after irradiation at the same fluence decreases with the Cr concentration. The same trend is found for $(S_{\text{implanted}} - S_{\text{measured virgin}})$ of FeCr alloys in Figure III-19(a), but the data for pure Fe does not follow this trend. $(S_{\text{implanted}} - S_{\text{measured virgin}})$ for Fe is smaller than the value obtained for Fe3Cr whereas the vacancy clusters size in 0.1 dpa irradiated Fe is greater than the one observed in 0.078 dpa irradiated Fe3Cr. It is due to the formation of larger vacancy clusters which should consume a larger number of small vacancy clusters. Thus, the $(S_{\text{implanted}} - S_{\text{measured virgin}})$ difference between Fe and Fe3Cr reflects their vacancy clusters concentration difference. The vacancy cluster concentration is lower in Fe than in Fe-3Cr but the vacancy cluster size in Fe is larger.

With all these observations, it is concluded that the size of vacancy clusters after irradiation decreases with Cr concentration.

One of the explanations of this observation could be the formation of V-Cr complex. The mobility of vacancy could be reduced because of their binding with Cr atoms and which could limit the agglomeration of vacancies. In this case, the $S(W)$ points of the different irradiated FeCr models presented in Figure III-16 (b) should move towards the $S(W)$ point of Cr virgin sample because positrons are sensitive to chemical environment around vacancy. But it is not the case in this study, $S(W)$ points of irradiated samples are not aligned with the $S(W)$ point of Cr virgin sample. Thus, this hypothesis is not very plausible. In fact, the theoretical calculation predicts very weak V-Cr interactions, $E_{b-1NN}(\text{V-Cr}) = 0.057\text{eV}$ and $E_{b-2NN}(\text{V-Cr}) = 0.007\text{eV}$ ^[186]. Moreover the experimental results of Möslang et al ^[117] estimated the V-Cr binding energy to be less than 105 meV by using muon spectroscopy.

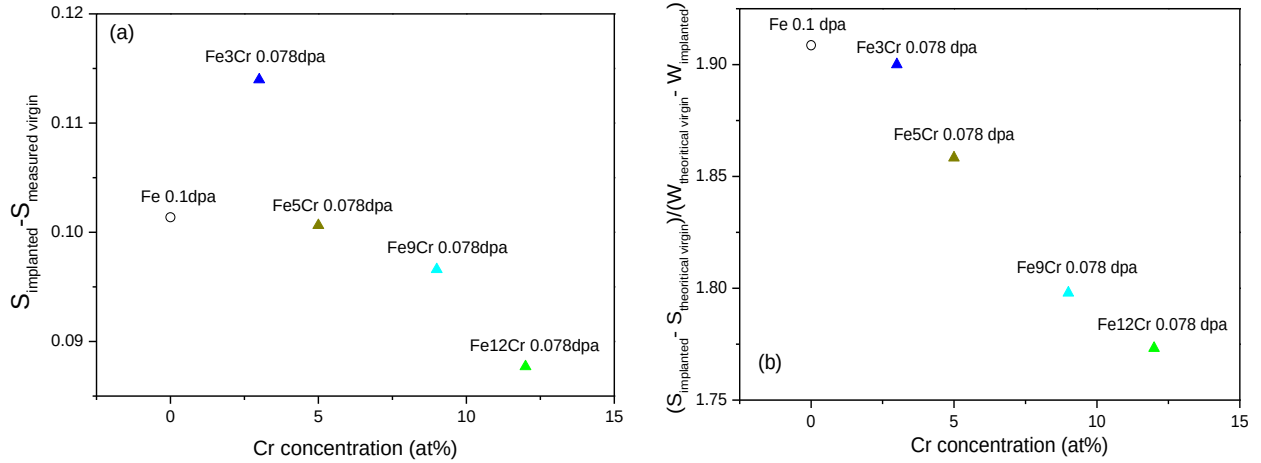


Figure III-19: $S_{\text{implemented}} - S_{\text{measured virgin}}$ (a) and $(S_{\text{implemented}} - S_{\text{theoretical virgin}}) / (W_{\text{theoretical virgin}} - W_{\text{implemented}})$ (b) as function of Cr concentration for FeCr and Fe samples irradiated with He at the highest fluence, 0.078 dpa for FeCr and 0.1 dpa for Fe.

Another explanation could be that Cr atoms interact strongly with self-interstitials (SIA). The binding energy of Cr with SIA is 0.3-0.4 eV per crowdion in the cluster^[186], acting as traps for migrating interstitial clusters produced in cascades. Thus, the mobility of these interstitial clusters reduces significantly and they become sinks for vacancies. The recombination of vacancies-interstitials is enhanced. The effects of chromium on reducing one-dimensional motion of interstitial-type dislocation loops are confirmed by TEM study in irradiated Fe-9Cr^[187].

In addition, the effect of Si content cannot be excluded because M.KUKSENKO^[134] whose thesis used the same FeCr samples as in this thesis has observed the formation of NiSiPCr-enriched clusters after neutron irradiation.

The results of our study show that the size of vacancy clusters formed by irradiation decreases monotonously with Cr content at 0.078 dpa for FeCr and 0.1 dpa for Fe. The same results have been observed by Marlies Lambrecht et al. who studied the 0.06 dpa neutron irradiated behavior of Fe-2.5wt.%Cr, Fe-5wt.%Cr, Fe-9wt.%Cr and Fe-12wt.%Cr model alloys by using both the positron lifetime and coincidence Doppler broadening techniques^[125]. The result shows clearly that the slope of $W(S)$ line changes with Cr content for 0.06 dpa irradiated FeCr, indicating the size of vacancy created by irradiation at the same damage dose decreases with Cr concentration.

Some researchers have found that the size or concentration of vacancies created by irradiation varies non-monotonously with Cr content. It firstly decreases when the Cr content increases and then it increases again from a threshold value of Cr concentration. This Cr threshold value is in the range from 5 to 9%. Two reasons have been proposed in these previous studies to explain non-monotonous evolution.

- The increase of vacancies size or concentration could be explained by the formation of α' phase. A strong repulsion exists between an SIA cluster and α' precipitates^[121, 185]. The SIA clusters created very close to α' precipitate will move rapidly away from these precipitates, so their mobility increases. Thus, the number of sites for recombination decreases locally and vacancies

size or concentration can increase when α' phase is present. The separation of α' phase always occurs in FeCr alloys with high Cr content (for example, 9% and 12%) [31].

- Another reason could be the different damage dose created by irradiation. Study shows that the diffusion of interstitial clusters depends on the concentration of Cr (due to the content of Cr in these clusters) and on their size [121]. For one size of interstitial clusters, their diffusion decreases first and increases when Cr content becomes higher than a threshold value, for example the threshold of the Cr concentration is 12% for 7 SIA clusters. When the size of the SIA clusters increases, this threshold value is shifted to lower Cr concentration. As discussed above, the diffusion increase of these SIA clusters could drive the formation of vacancy clusters. Thus, the irradiation created vacancies size or concentration has a non-monotonous variation with Cr content.

But it has to be noted that the monotonous decrease of the vacancies size and concentration with the Cr concentration is observed in this study. It could be due to the few number of α' phase in our samples as it has been presented in section II.1.2 of this thesis. Moreover compared to existing studies, the damage dose used for this project is small thus the interstitial cluster size should be small. So the vacancies size and concentration minimum should be reached at Cr content higher than 12% and is not observed in this study.

In conclusion, the effect of the Cr content on the nature of the vacancy defect is observed. With the increase of Cr concentration, the size of vacancy clusters decreases. Most plausible explanation is that Cr atoms interact strongly with interstitials and act as traps for migrating interstitial clusters produced in cascades. Thus, the mobility of these interstitial clusters reduces significantly and they become sinks for vacancies. The recombination of vacancies-interstitials is enhanced. The relation between vacancies size and Cr content is monotonous which could be explained by the few number of α' phase and relative small damage dose.

III.2.3. Conclusions

The vacancy defects induced by irradiation in Fe and FeCr samples have been studied by slow positron beam Doppler broadening (SPBDB) technique in this section.

The vacancy defects have been introduced in Fe samples by 1.5 MeV helium irradiations at various fluences from 10^{13} to 10^{17} cm^{-2} (1×10^{-5} to 1×10^{-1} dpa). The vacancy size and concentration increase with the fluence. For irradiation at low fluence from 1×10^{13} to $2 \times 10^{14} \text{ cm}^{-2}$ (from 1×10^{-5} to 2×10^{-4} dpa), the single vacancy is the main detected defect and the $D_V(\text{Fe})$ line characteristic of the annihilation of positrons as trapped in this type of defect is defined. For higher fluences (from 5×10^{-4} to 1×10^{-1} dpa), the formation of vacancy clusters is observed. The single vacancies detected in the study are probably bound to C or/and to O. The concentration of single vacancies induced for fluences from 1×10^{13} to $2 \times 10^{14} \text{ cm}^{-2}$, vary from 1 to 10 appm. The ratio, single vacancies concentrations/the displacement damage (dpa) calculated by SRIM, is in the range 0.049- 0.139.

The vacancy defects have been introduced in FeCr (3 at.%- 12 at.% Cr) samples by 2 MeV helium irradiations at various fluences from 1×10^{14} to $1.3 \times 10^{17} \text{ cm}^{-2}$ (6×10^{-5} to 7.8×10^{-2} dpa). The vacancy size and concentration increase with the fluence in all the four types of FeCr alloy. At low fluences from 10^{14} to

10^{15} ions.cm⁻² He in Fe9Cr sample, single vacancies are the main detected defects as in pure Fe. At high fluences from 10^{16} to 1.3×10^{17} ions.cm⁻² He, vacancy clusters are detected. The size or concentration of vacancies formed by irradiation decreases monotonously with Cr content at the same damage dose. The explanation could be the strong interaction of Cr atoms with self- interstitials (SIA) which could reduce the mobility of these interstitial clusters and consequently increasing the vacancy recombination on these sinks. The recombination of vacancies-interstitials is enhanced. The relation between vacancies size and Cr content is monotonous which could be explained by the few number of α' phase and relative small damage dose.

III.3. Evolution of vacancy defects under annealing

The nature of defects could evolve with the temperature. This evolution depends on several parameters like: their initial nature, their distribution in the matrix, their stability in the matrix and chemical environment. The four principal processes are the following: recombination of vacancy and interstitials, agglomeration of defects (vacancies or interstitials), transformation of defects without changing their stoichiometry, dissociation of defects (vacancy clusters or interstitials clusters). In this section, the behavior of vacancy defects induced by irradiation as function of annealing temperature has been studied in Fe and FeCr samples.

III.3.1. Post- irradiation annealing behavior of V defects in Fe samples

In order to study the post-irradiation annealing behavior of vacancy defects in Fe samples, the annealing experiments were realized at temperatures from 110°C up to 500°C under vacuum during 1 hour with a step of 50°C. The annealings were performed in electron bombardment furnace developed in laboratory CEMHTI (see Annex A1). After each annealing, the samples were measured using SPBDB to study the vacancy defects evolution. Two fluences were chosen: a low fluence of 2×10^{14} cm⁻², for which we have shown that the main defects are iron single vacancies, and a high fluence of 1×10^{16} cm⁻², where the formation of vacancy clusters is evident.

a) The behavior of single vacancy (low He fluence: 2×10^{14} cm⁻²)

As presented in the section III.2.1, the defects produced in the Fe sample irradiated with 1.5 MeV He at a low fluence of 2×10^{14} cm⁻² are mainly single vacancies. The evolutions of S(E), W(E) and S(W) curves at different temperature up to 500°C are presented in the Figure III-20. Only the S(W) points in the positron energy range from 20keV to 25keV are presented in order to have a clearer illustration in the Figure III-20 (c).

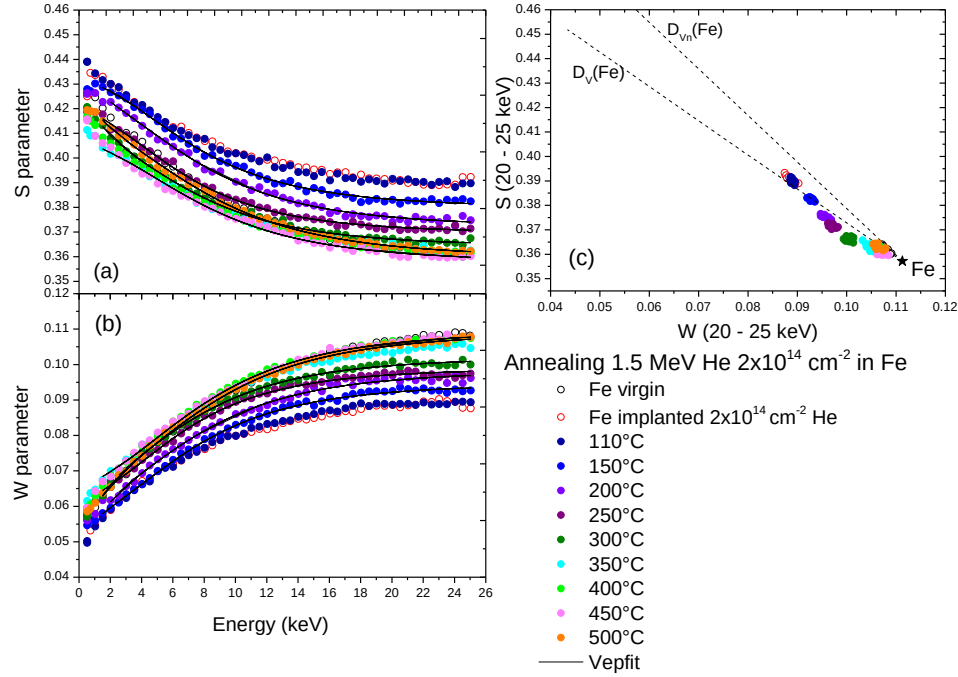


Figure III-20: $S(E)$, $W(E)$ and $S_{(20-25\text{keV})}(W_{(20-25\text{keV})})$ for the Fe samples irradiated with 1.5 MeV He at 10^{16} cm^{-2} and annealed at different temperature up to 500°C, compared to virgin and as implanted samples.

There is no difference observed after annealing at 110°C compared to the as irradiated sample. From 150°C to 500°C, a regular decrease in S and an increase in W are detected not only for the high positron energies (from 20 keV to 25 keV) which detect mainly the irradiated track region, but also for the low positron energies (from 0.5 keV to 2 keV) which detect mainly the close surface region of the sample. It means that the surface state is also changed with the annealing temperature. A slight increase in S and a decrease in W are observed at 500°C compared to the values obtained after annealing at 450°C. But the $S(E)$ and $W(E)$ curves at low energies return to the Fe virgin curve at 500°C, indicating that the virgin state of sample surface have been obtained. Thus, the increase in S and decrease in W for high positron energies at 500°C could be induced by the increase in S and decrease in W for the surface state because one part of high energy positrons also annihilate at the surface.

The Vepfit program is used to get the positron annihilation characteristics in the irradiated track region of the sample at different temperatures as shown in Figure III-21. The model of one layer or two layers has been used to fit the experimental data and the results are reported in Table III-6. Figure III-21 (a) illustrates the S values obtained by Vepfit as a function of the annealing temperature.

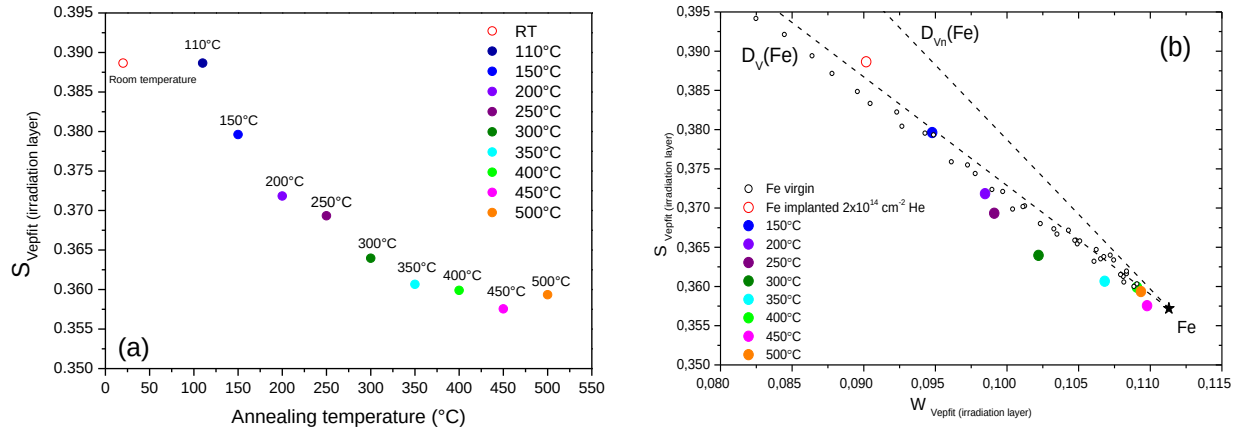


Figure III-21: S values for the irradiated layer obtained by Vepfit as a function of (a) the annealing temperature and (b) W values for irradiated Fe with 1.5 MeV He ions at $2 \times 10^{14} \text{ cm}^{-2}$ and annealed at different temperatures up to 500°C.

T (°C)	Layer 1				Layer 2		
	S	W	L^+ (nm)	Thickness (nm)	S_{bulk}	W_{bulk}	L^+ (nm)
As imp.	/	/	/	/	0.3887	0.0902	133
150	0.43	0.0616	7	13	0.3796	0.0948	134
200	0.4197	0.0706	5	12	0.3718	0.0985	145
250	/	/	/	/	0.3693	0.0991	130
300	0.4001	0.0737	11	32	0.3640	0.1022	135
350	/	/	/	/	0.3607	0.1068	144
400	/	/	/	/	0.3599	0.1091	140
450	/	/	/	/	0.3576	0.1098	155
500	0.4054	0.0725	10	26	0.3594	0.1094	162

Table III-6: Vepfit results for irradiated Fe with 1.5 MeV He ions at $2 \times 10^{14} \text{ cm}^{-2}$ and annealed at different temperatures up to 500°C.

S begins to decrease at 150°C and the S(W) point plotted in Figure III-21 (b) stays on the $D_v(\text{Fe})$ line representing the single vacancy in Fe and is closer to the Fe lattice point than the one before annealing. It means that only the concentration of Fe single vacancy is reduced. The concentration reduction could be caused by the migration of single vacancy and recombination with the interstitial. But the single vacancy migration temperature is below the room temperature (-53 to 5°C) as suggested by Takaki et al.

^[107]. 150°C is attributed to the migration temperature of vacancy clusters of size less than ten vacancies proposed by kinetic Monte Carlo simulation^[108] and experiment^[109]. In our case, the single vacancy is probably bound to carbon or oxygen impurities. Thus, the complex V-C or V-O could have a higher migration temperature compared to the pure single vacancy or they could dissociate at this temperature. A. Vehanen, has shown in an experimental study of electron irradiated Fe samples that the V-C pairs dissociates at 490K^[158]. This dissociation can occur during annealing at temperature between 110°C and 150°C when the V concentration is found to decrease. At 200°C, S continues to decrease and the S(W) point leaves the $D_V(\text{Fe})$ line, thus it seems that from this temperature positrons detect at least two types of defects: the Fe single vacancy and another trap with free volume lower than single vacancy. These new defects appearing at 200°C can be formed at this temperature or already exist in as-irradiated sample but were not detected due to the predominance of single vacancies. This new defect could be dislocation or vacancy-impurity complex. Among impurities one can consider He which is introduced by irradiations and C or O, the residual concentration of which is not negligible and could form complexes with vacancy as discussed in the previous section 2.1. First the concentration of He in the track region is too low (0.008 appm) for positron to detect V- He complex that could be formed. In addition, the NRA (nuclear reaction analysis) studies realized by Desgardin et al.^[150] show that helium profiles spread little after 800°C annealing in He irradiated Fe sample. Thus, the observation of V- He complex is not plausible. Concerning C or O, C. Barouh has recently shown that the binding energy of V with C atoms is lower than the one between V and O atoms^[177]. A. Vehanen has shown in an experimental study of electron irradiated Fe samples that the V-C pairs dissociates at 490K^[158]. This dissociation can occur during annealing at temperature between 110°C and 150°C when the V concentration is found to decrease. It allows the migration of new free single vacancies that can recombine or form new complexes such as oxygen complexes such as V-3O, V-4O or 2V-O4 which have binding energies between 0,5 and 1 eV^[177] and could present a small free volume. We will see in the next chapter IV section 2.4 that in oxygen implanted samples same type of defects seems to be observed after annealing and discussion will be detailed in this part of the manuscript.

Finally the presence of dislocations has been reported by Ward et al in 700 keV electron irradiated iron in the damage dose between 0.2 and 0.5 dpa^[188]. The dislocations are detected in deformed pure Fe by positron lifetime experiments^[183]. These results showed that after 325°C, positrons are only trapped at the remaining dislocations. Even if the damage dose induced in our experiment is ten times lower than the one used by Ward et al. the dislocation contribution to the S and W values obtained in this work cannot be discarded.

The effective positron diffusion length for 150°C is determined at the value of ~ 134 nm by Vepfit. Thus, the single vacancy concentration can be evaluated to be 3.55 appm, which is a lower value than the one obtained in the as-implanted sample (3.727 appm). For 250°C to 300°C, S continue to decrease and S(W) points are further and further from the $D_V(\text{Fe})$ line. It could be explained by the continued decrease of single vacancy concentration and the positron trapping in the new defects which becomes more dominant. From 350°C to 500°C, the S(W) points return gradually to the Fe lattice point. The effective positron diffusion length $L^+ = 160 \pm 2$ nm is obtained for 500°C which corresponds to the value in Fe virgin sample.

Annealing of low dpa irradiated samples containing mainly single vacancies leads to the detection of a new defect that can be dislocation or V impurity complexes.

b) The behavior of vacancy clusters (high He fluence: 10^{16} cm^{-2})

As presented in the section III.2.1, the defects produced in the Fe sample irradiated with 1.5 MeV He at a high fluence of $1 \times 10^{16} \text{ cm}^{-2}$ (corresponding to the damage dose of 0.01 dpa) are vacancy clusters. The evolutions of S(E), W(E) and S(W) curves at different temperature up to 500°C are presented in the Figure III-22.

There is no difference observed after annealing at 110°C and 150°C compared to the as implanted sample. At 200°C, S begins to decrease and W begins to increase. An important decrease of S is observed at 250°C and S(W) points are further from the $D_{Vn}(\text{Fe})$ line. S values continue to decrease at 300°C and 350°C. At 350°C, the S(W) points are located below the $D_V(\text{Fe})$ line. At higher temperature, S seems to be stabilized again while a new decrease is observed at annealing temperature of 450°C.

T (°C)	Layer 1				Layer 2		
	S	W	L^+ (nm)	Thickness (nm)	S_{bulk}	W_{bulk}	L^+ (nm)
As imp.	0.4468	0.0576	11	34	0.4519	0.0601	100
200	0.4401	0.059	18	58	0.4487	0.0618	112
250	0.4125	0.0706	21	139	0.4313	0.0682	120
300	0.4065	0.0745	39	306	0.4193	0.0729	130
350	0.3981	0.0760	23	169	0.3899	0.0845	135
450	0.3940	0.0761	11	30	0.3842	0.0871	140
500	0.3972	0.0747	11	43	0.3834	0.0881	146

Table III-7: Vepfit results for the Fe samples irradiated with 1.5 MeV He at 10^{16} cm^{-2} and annealed at different temperature up to 500°C.

The Vepfit program is used to get the positron annihilation characteristics in the irradiated track region of the sample at several temperatures (200°C, 250°C, 300°C, 350°C, 450°C, and 500°C). The ones for 110°C and 150°C are considered to be identical to the as implanted sample; the ones for 400°C identical to 350°C. A two layers model allows to fit the experimental data and the annihilation characteristics in the second layer represents the positron annihilation state in the irradiated track region. The results are reported in Table III-7.

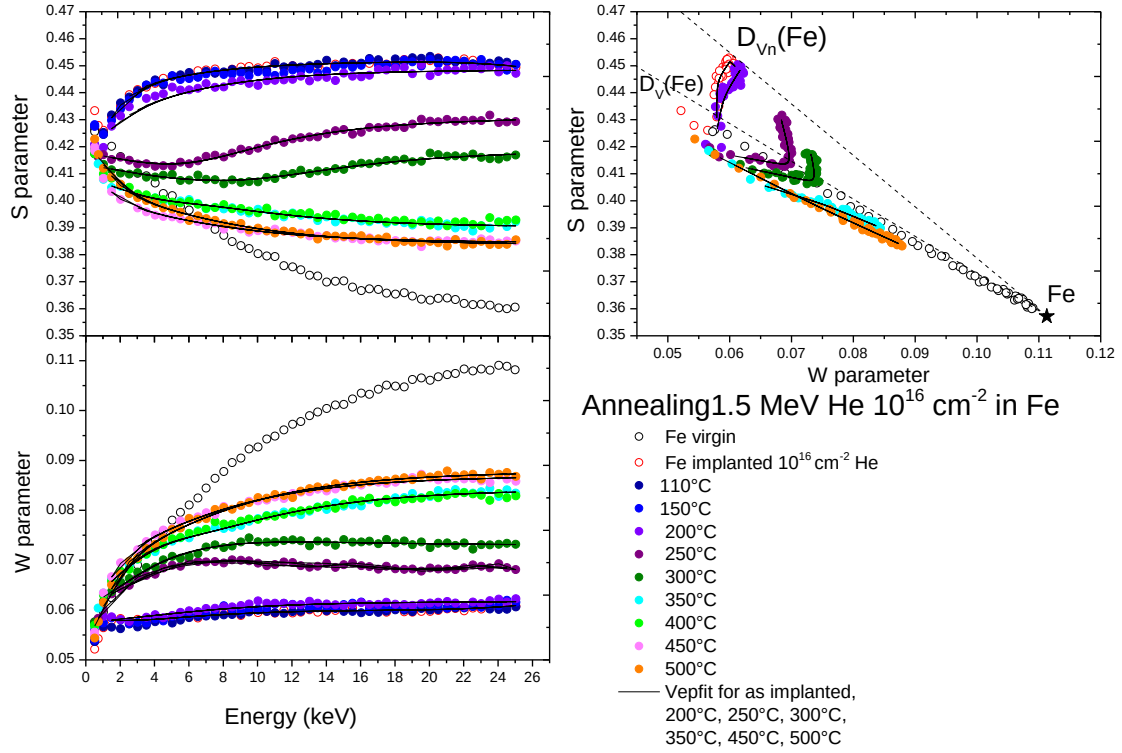


Figure III-22: S(E), W(E) and S(W) for the Fe samples irradiated with 1.5 MeV He at 10^{16} cm^{-2} and annealed at different temperature up to 500°C, compared to virgin and as implanted samples.

Figure III-23 (a) illustrates the S values obtained in the track region as a function of the annealing temperature. The S begins to decrease at 200°C and the corresponding S(W) point plotted in Figure III-23 (b) stays on the $D_{vn}(\text{Fe})$ line representing the annihilation characteristic of vacancy clusters in Fe and becomes closer and closer to the Fe lattice point. It means that only the concentration of Fe vacancy clusters is reduced. The concentration reduction could be caused by the dissociation/migration of vacancy or interstitials clusters and their recombination as it has been explained for the stage IV_B in Kinetic Monte Carlo and Rate Theory simulations realized by C. J. Ortiz et al.^[189]. An important decrease of S is observed at 250°C. The corresponding S(W) point is below the $D_{vn}(\text{Fe})$ line and moves towards $D_v(\text{Fe})$ line indicating that the size of vacancy clusters decreases. This observation could be explained by the fact that the vacancy clusters dissociate from temperature close to 250°C. This results are similar to that observed experimentally in the Takaki and *al.* study where these phenomena have been associated to the resistivity recovery stage observed between (247 and 277°C) in electron- irradiated iron^[190]. They are also in good agreement with the theoretical study performed by Fu and *al.* who found dissociation at 243°C^[191]. At 350°C, the S(W) point is below the $D_v(\text{Fe})$ line indicating that the concentration of vacancy clusters becomes low. But it has not yet returned onto the Fe lattice point indicating another positron trap like dislocation still exists in the sample. At 500°C, the S(W) point moves towards the Fe lattice point. The effective positron diffusion length obtained is $146 \pm 4 \text{ nm}$ after annealing at 500°C which is still lower than the value in Fe virgin sample $L^+ = 160 \pm 2 \text{ nm}$. It means that defects may still exist.

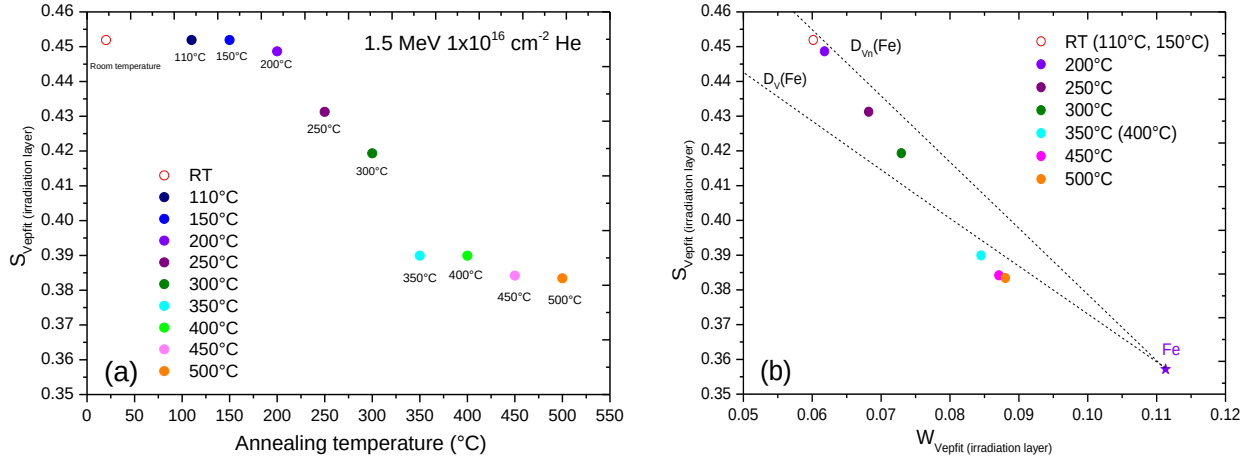


Figure III-23: S values for the irradiated layer obtained by Vepfit as a function of (a) the annealing temperature and (b) W values obtained by Vepfit for irradiated Fe with 1.5 MeV He ions at $1 \times 10^{16} \text{ cm}^{-2}$ and annealed at different temperatures up to 500°C.

The nature of the new defects can be discussed as it has been already done in the previous section which was dedicated to the annealing of the sample irradiated with He ions at low fluence. In the case developed in this chapter which describes the annealing of Fe irradiated sample at high fluence corresponding to the damage dose of 0.01 dpa, the presence of dislocations is very probable after irradiation if we refer to the results of Ward and al^[188]. Moreover the same authors have shown that these dislocations are still observed after annealing at temperature up to 465°C.

For the Fe samples irradiated with 1.5 MeV He at high fluences the recovery of the vacancy clusters is observed and begins at 200°C. New defects are detected after annealing at 350°C which could be dislocations that are still observed up to 500°C.

III.3.2. Post- irradiation annealing behavior of V defects in FeCr samples

In order to study the post-irradiation annealing behavior of V defects in FeCr samples, the annealing experiments under vacuum during 1 hour with a step of 50°C have been performed at temperatures from 110°C up to 450°C for Fe-12Cr samples and also 110°C up to 250°C for Fe- 3Cr, Fe- 5Cr and Fe- 9Cr samples for comparison. The annealings were performed in electron bombardment furnace developed in laboratory CEMHTI. After annealings, the samples were measured using SPBDB to study the vacancy defects evolution. Two fluences were chosen: a low fluence of $1 \times 10^{14} \text{ ions.cm}^{-2}$, for which mainly single vacancy defects are detected after irradiation, and a high fluence of $1.3 \times 10^{17} \text{ ions.cm}^{-2}$, where the formation of vacancy clusters is clear.

a) The behavior of single vacancy in FeCr (low He fluence: $1 \times 10^{14} \text{ cm}^{-2}$)

As presented in the section III.2.2, the defects produced in the FeCr sample irradiated with 2 MeV He at a low fluence $1 \times 10^{14} \text{ ions/cm}^2$ (corresponding to the damage dose of $6 \times 10^{-5} \text{ dpa}$) are mainly single vacancies.

The evolutions of $S(E)$, $W(E)$ and $S(W)$ curves of Fe-12Cr at different temperature 110°C, 150°C, 200°C, 250°C, 350°C, and 450°C are presented in the Figure III-24. It should be noted that the annealings at 300°C and 400°C are also realized although they are not measured by positrons. Only the $S(W)$ points in the positron energy range from 20keV to 25keV are presented in order to have a clear illustration.

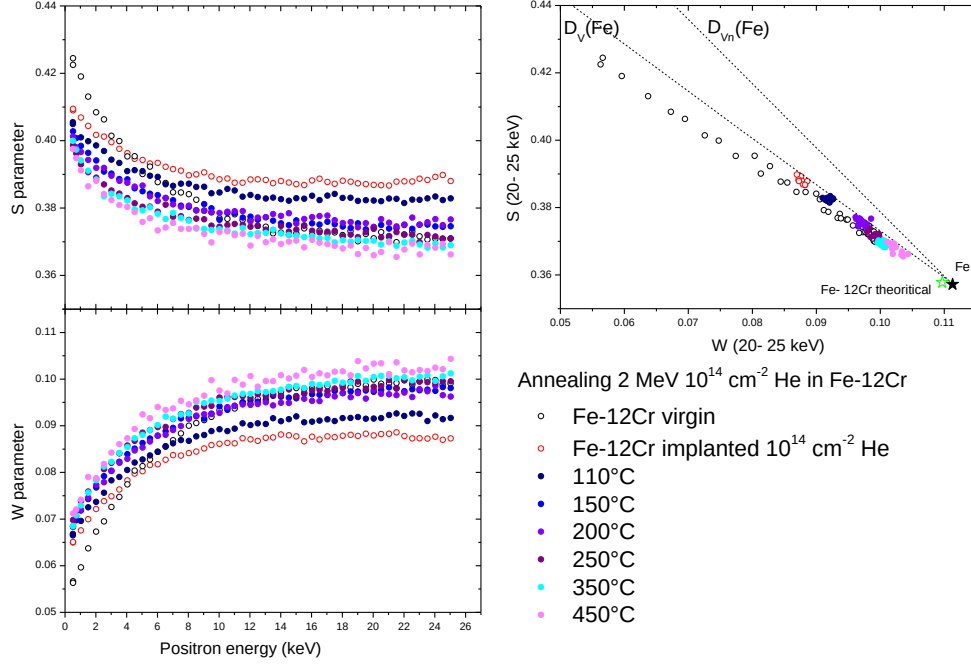


Figure III-24: $S(E)$, $W(E)$ and $S_{(20-25\text{keV})}(W_{(20-25\text{keV})})$ for the Fe12Cr sample irradiated with 2 MeV He at 10^{14} cm^{-2} and annealed at different temperature up to 450°C, compared to virgin and as implanted samples.

A decrease in S and an increase in W have already been observed after annealing at 110°C compared to the as implanted sample. From 150°C to 450°C, a regular decrease in S and an increase in W are detected for all the positron energies which detect mainly the irradiated track region, and the surface state is not changed compared to the as-implanted one. A slight increase in S and a decrease in W have been found for 200°C which is in the positron experiment error bars.

The $S_{\text{average}(20-22\text{keV})}$ and $W_{\text{average}(20-22\text{keV})}$ have been used to represent the irradiated track region of the sample at different temperature and are shown in Figure III-25. Figure III-25 (a) illustrates the $S_{\text{average}(20-22\text{keV})}$ values as a function of the annealing temperature. All the $S(W)$ points are aligned on $D_v(\text{Fe12Cr})$ line as shown in Figure III-25 (b).

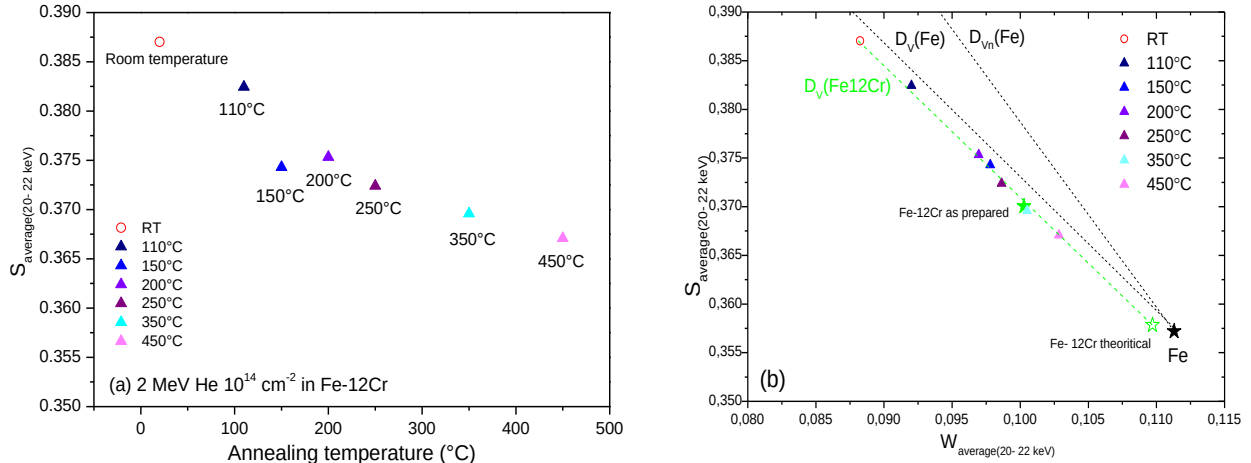


Figure III-25: $S_{\text{average}(20-22 \text{ keV})}$ values as a function of (a) the annealing temperature and (b) $W_{\text{average}(20-22 \text{ keV})}$ for irradiated Fe12Cr with 2 MeV He ions at $1 \times 10^{14} \text{ cm}^{-2}$ and annealed at different temperatures up to 450°C.

The S begins to decrease at 110°C and the corresponding $S(W)$ point remains on the $D_V(\text{Fe-12Cr})$ line and approaches the theoretical Fe-12Cr lattice point. Thus, it means that only the concentration of single vacancies is reduced already at 110°C. In Fe, the V concentration begins to decrease from 150°C which is explained by the effect of carbon bound to single vacancy slowing down the migration of single vacancy as explained in section III.3.1. The same effect of carbon should also exist in FeCr samples as there is a concentration of 1290 appm of carbon in Fe- 12Cr. Thus, the observed concentration decrease at 110°C is supposed to be caused by another annealing stage which could be the SIAs long-range migration. The resistivity recovery studies performed in FeCr by A.L. Nikolaev ^[124] showed that the SIAs long-range migration takes place at 220 K and occurs at temperature slightly above the vacancy migration one at 205- 210 K in FeCr model alloys. It is due to the SIAs trapping in traps which consist of Cr atoms. The temperature of this annealing stage could increase, for example 110°C (383 K) in this study. This increase could be due to the increases of the Cr atoms or other impurities number in the traps(for example NiSiPCr-enriched clusters observed by M.KUKSENKO in these samples ^[134]).

S value continues to decrease at 150°C and $S(W)$ point approaches the theoretical Fe-12Cr lattice point. This stage is induced by the migration of the single vacancies which were also probably bound to carbon impurities as in the case of single vacancy in Fe. From 150°C to 450°C, the S points decreases gradually and $S(W)$ points return gradually to the theoretical Fe- 12Cr lattice point. It is noted that the $S(W)$ point has reached the SW point obtained in the bulk of the as prepared Fe- 12Cr at 350°C and continues to approach the theoretical lattice SW point at 450°C. It means that the defects which exist in the sample before irradiation begin to recover at 350°C.

110°C up to 250°C annealings have been realized for Fe- 3Cr, Fe- 5Cr and Fe- 9Cr samples irradiated with 2 MeV He ions at 10^{14} cm^{-2} for comparison as presented in Annex A3. The annealing stages 110°C and 150°C are also observed in these samples.

b) The behavior of vacancy clusters in FeCr (high He fluence: $1.3 \times 10^{17} \text{ cm}^{-2}$)

As presented in the section III.2.2, the defects produced in the FeCr sample irradiated with 2 MeV He at a high fluence of $1.3 \times 10^{17} \text{ ions.cm}^{-2}$ (corresponding to the damage dose of $7.8 \times 10^{-2} \text{ dpa}$) are vacancy clusters. The evolutions of $S(E)$, $W(E)$ and $S(W)$ curves for the irradiated Fe12Cr samples annealed at different temperature up to 450°C are presented in the Figure III-26.

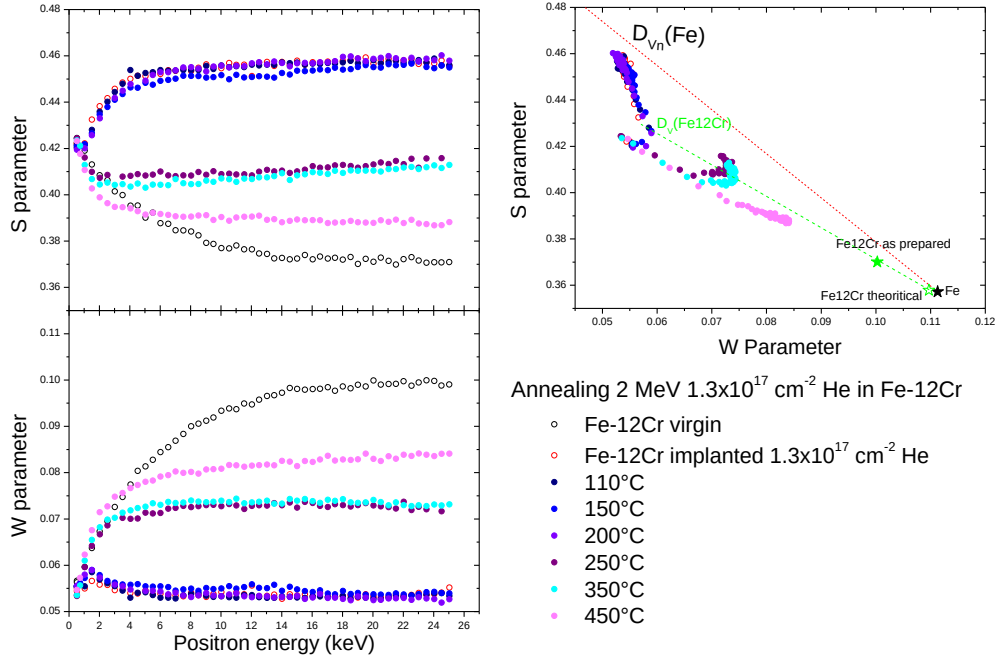


Figure III-26: $S(E)$, $W(E)$ and $S(W)$ for the Fe12Cr samples irradiated with 2 MeV He at $1.3 \times 10^{17} \text{ cm}^{-2}$ and annealed at different temperature up to 450°C , compared to virgin and as implanted samples.

There is no difference observed after annealing up to 200°C compared to the as implanted sample. The slight decrease in S and increase in W detected in the positron energy range from 1 to 16 keV at 150°C is supposed to be due to the positron experiment error. A drastic decrease of S is observed at 250°C and $S(W)$ points move towards the $D_v(\text{Fe12Cr})$ line. S points continue to decrease slightly at 350°C . At 450°C , the $S(W)$ points are located below $D_v(\text{Fe12Cr})$ line.

The Vepfit program is used to get the positron annihilation characteristics in the irradiated track region of the sample at several annealing temperatures (250°C , 350°C , 450°C). The positron annihilation characteristics at 110°C , 150°C and 200°C are considered to be identical to the as implanted sample because of their identical $S(E)$, $W(E)$ and $S(W)$ curves.

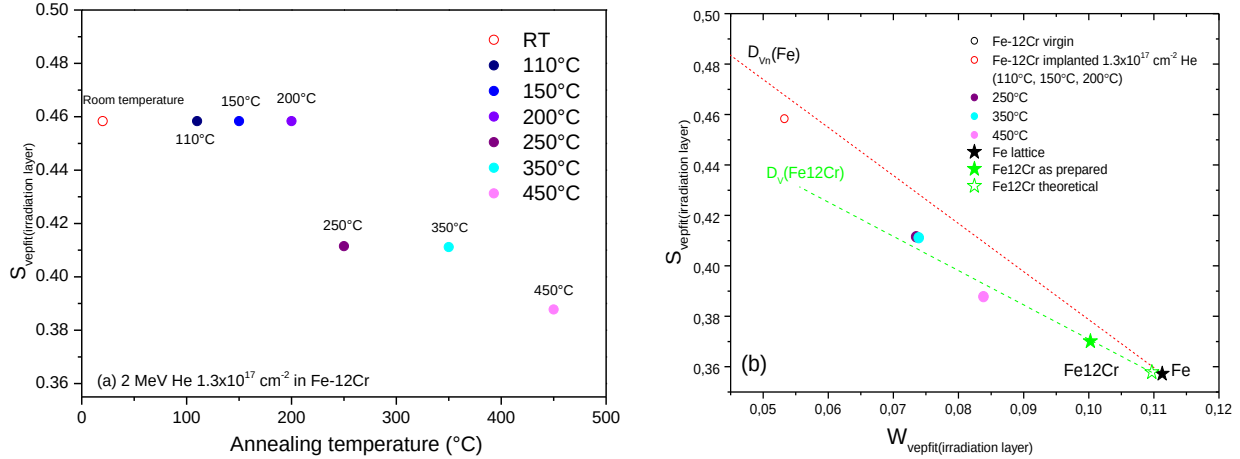


Figure III-27: S values for the irradiated layer obtained by Vepfit as a function of (a) the annealing temperature and (b) W values for irradiated Fe12Cr with 2 MeV He ions at $1.3 \times 10^{17} \text{ cm}^{-2}$ and annealed at different temperatures up to 450°C.

Figure III-27 (a) illustrates the S values as a function of the annealing temperature. The S begins to decrease at 250°C and the corresponding S(W) point illustrated in Figure III-27 (b) moves towards the $D_v(\text{Fe12Cr})$ line and approaches the FeCr lattice point. It means that both the vacancy clusters size and concentration decrease. This annealing stage is also observed for vacancy clusters in Fe as presented in section III.3.1. It is explained by the fact that the vacancy clusters dissociate from temperature close to 250°C which is similar to that observed experimentally by Takaki and *al.* (247 to 277°C) ^[190] and theoretically by Fu and *al.* (243°C) ^[191] in Fe. However compared to the experiments performed in Fe where the annealing stage begins at 200°C, this stage is observed at 250°C in Fe12Cr sample. This different behavior suggests that the temperature of vacancy or interstitials clusters dissociation/migration in FeCr is higher than that in pure Fe. A slight decrease in S is observed at 350°C compared to the value measured at 250°C but the S/W rate does not change. At 450°C, the S(W) point is below the $D_v(\text{Fe-12Cr})$ indicating that a large part of vacancy clusters are recovered. In the case of pure Fe, this recovery step is observed at lower temperature 350°C. This shift in temperature could also be caused by the higher migration temperature of vacancy clusters in Fe-12Cr. New defects are detected after annealing at 450°C it could be dislocations like in Fe. The dislocations loops of size 6 nm and number density $1.73 \times 10^{21} \text{ m}^{-3}$ have been detected in neutron- irradiated Fe-12.5 at% Cr at 573 K for conditions 0.6 and 1.5 dpa. And Object kinetic Monte Carlo and cluster dynamics simulations realized by A.Gokhman provide the quantitative agreement results with this experimental data ^[192].

Annealings at temperatures from 110°C up to 250°C have been performed for Fe- 3Cr samples irradiated with 2MeV He ions at $1.3 \times 10^{17} \text{ cm}^{-2}$ as presented in Annex A4. The S values begin to decrease already at 200°C and S/W rate does not change as in the case of vacancy clusters in Fe. It means that the vacancy clusters size does not change but their concentration decreases. The similar behavior of vacancy clusters in pure Fe and Fe3Cr samples indicates that 3at% Cr is not enough to change the annealing behavior of vacancy clusters in FeCr alloy.

III.3.3. Conclusions

In this section, the behavior of vacancy defects induced by irradiation with He ions has been studied as function of annealing temperature in Fe and FeCr samples.

In order to study the post-irradiation annealing behavior of V defects in Fe samples, the annealing experiments were performed at temperatures from 110°C up to 500°C under vacuum during 1 hour with a step of 50°C.

In the Fe samples irradiated at low fluence of $2 \times 10^{14} \text{ cm}^{-2}$, the concentration of Fe single vacancy begins to decrease at 150°C. The concentration reduction could be caused by the dissociation of V-C complex and the recombination of the free vacancies with the interstitials. From 200°C positrons detect at least two types of defects: Fe single vacancy and another one with free volume lower than single vacancy. This new defect could be dislocation. After annealing at 500°C, a large part of the defects have been eliminated.

In the Fe samples irradiated at high fluence of $1 \times 10^{16} \text{ cm}^{-2}$, the concentration of Fe vacancy clusters begins to reduce at 200°C. It could be due to the migration of vacancy clusters and their recombination with interstitials. The size of vacancy clusters decreases at 250°C. This observation could be explained by the fact that the vacancy and interstitials clusters dissociate from temperature close to 250°C. At 350°C, a major fraction of vacancy clusters are recovered. After annealing at 500°C defects are still detected that could be dislocations or vacancy-impurity complexes.

Same study has been carried out in FeCr. In the Fe-12Cr samples irradiated at low fluence of $1 \times 10^{14} \text{ cm}^{-2}$, the concentration of single vacancy in Fe-12Cr is reduced already at 110°C which is at lower temperature than in pure Fe. This elimination could be due to the SIAs long-range migration. The V concentration continues to decrease at 150°C. This stage can be explained by the V-C pairs dissociation as in the case of Fe. In the Fe-12Cr samples irradiated at high fluence of $1 \times 10^{16} \text{ cm}^{-2}$, the vacancy clusters size and concentration begin to decrease at 250°C. It could be due to the vacancy clusters dissociation. On the contrary, the annealing stage observed at 200°C in Fe doesn't occur in Fe12Cr sample. It suggests that the temperature of vacancy clusters migration in Fe12Cr is higher than that in pure Fe. A large part of the vacancy clusters are recovered at 450°C which is 100°C higher than in the case of Fe. This shift in vacancy recovery could also be explained by the higher migration temperature of vacancy clusters in Fe12Cr. On the contrary, a similar behavior of vacancy clusters has been observed in pure Fe and Fe3Cr samples. It indicates that 3at% Cr is not enough to change the annealing behavior of vacancy clusters in FeCr alloy.

III.4. Conclusions

In section III.1, the quality of Fe and FeCr virgin samples has been examined by slow positron beam Doppler broadening (SPBDB) technique after their preparation.

The effective positron diffusion length in the Fe virgin sample ($L^+ = 160 \pm 2 \text{ nm}$) reveals that the quantity of open-volume defects in the bulk of the Fe virgin samples is low. In addition, the results are reproducible and thus the quality of these Fe samples prepared by the same procedure is considered as very good. The annihilation characteristics S and W obtained in the virgin sample are considered as the

reference ones and can be defined as the annihilation characteristics of the Fe lattice: $S_L = 0.357(2)$ and $W_L = 0.111(3)$.

The positron annihilation characteristics differ from one FeCr alloy to another. The S_{bulk} (W_{bulk}) increases (decreases) with the increase of the Cr concentration. There exist open volume defects and their concentration increases with the Cr content. But it remains low enough for the study of defects induced by irradiation. The trapping of positron at defects decorated or made of impurities such as Si, C or O cannot be discarded.

In section III.2, the vacancy defects induced by irradiation in Fe and FeCr samples have been studied by slow positron beam Doppler broadening (SPBDB) technique.

The vacancy defects have been introduced in Fe samples by 1.5 MeV helium irradiations at various fluences from 10^{13} to 10^{17} cm^{-2} (1×10^{-5} to 1×10^{-1} dpa). The vacancy size and concentration increase with the fluence. For irradiation at low fluence from 1×10^{13} to $2 \times 10^{14} \text{ cm}^{-2}$ (from 1×10^{-5} to 2×10^{-4} dpa), the single vacancy is the main detected defect and the $D_V(\text{Fe})$ line characteristic of the annihilation of positrons as trapped in this type of defect is defined. For higher fluences (from 5×10^{-4} to 1×10^{-1} dpa), the formation of vacancy clusters is observed. The single vacancies detected in the study are probably bound to C or/and to O. The concentration of single vacancies induced for fluences from 1×10^{13} to $2 \times 10^{14} \text{ cm}^{-2}$, vary from 1 to 10 appm. The ratio, single vacancies concentrations/the displacement damage (dpa) calculated by SRIM, is in the range 0.049- 0.139.

The vacancy defects have been introduced in FeCr (3 at.-%- 12 at.-% Cr) samples by 2 MeV helium irradiations at various fluences from 1×10^{14} to $1.3 \times 10^{17} \text{ cm}^{-2}$ (6×10^{-5} to 7.8×10^{-2} dpa). The vacancy size and concentration increase with the fluence in all the four types of FeCr alloy. At low fluences from 10^{14} to $10^{15} \text{ ions.cm}^{-2}$ He in Fe9Cr sample, single vacancies are the main detected defects as in pure Fe. At high fluences from 10^{16} to $1.3 \times 10^{17} \text{ ions.cm}^{-2}$ He, vacancy clusters are detected. The size or concentration of vacancies formed by irradiation decreases monotonously with Cr content at the same damage dose. The explanation could be the strong interaction of Cr atoms with self- interstitials (SIA) which could reduce the mobility of these interstitial clusters and consequently increasing the vacancy recombination on these sinks. The recombination of vacancies-interstitials is enhanced. The relation between vacancies size and Cr content is monotonous which could be explained by the few number of α' phase and relative small damage dose.

In section III.3, the behavior of vacancy defects induced by irradiation with He ions has been studied as function of annealing temperature in Fe and FeCr samples.

In order to study the post-irradiation annealing behavior of V defects in Fe samples, the annealing experiments were performed at temperatures from 110°C up to 500°C under vacuum during 1 hour with a step of 50°C .

In the Fe samples irradiated at low fluence of $2 \times 10^{14} \text{ cm}^{-2}$, the concentration of Fe single vacancy begins to decrease at 150°C . The concentration reduction could be caused by the dissociation of V-C complex and the recombination of the free vacancies with the interstitials. From 200°C positrons detect at least two types of defects: Fe single vacancy and another one with free volume lower than single

vacancy. This new defect could be dislocation. After annealing at 500°C, a large part of the defects have been eliminated.

In the Fe samples irradiated at high fluence of $1 \times 10^{16} \text{ cm}^{-2}$, the concentration of Fe vacancy clusters begins to reduce at 200°C. It could be due to the migration of vacancy clusters and their recombination with interstitials. The size of vacancy clusters decreases at 250°C. This observation could be explained by the fact that the vacancy and interstitials clusters dissociate from temperature close to 250°C. At 350°C, a major fraction of vacancy clusters are recovered. After annealing at 500°C defects are still detected that could be dislocations or vacancy-impurity complexes.

Same study has been carried out in FeCr. In the Fe-12Cr samples irradiated at low fluence of $1 \times 10^{14} \text{ cm}^{-2}$, the concentration of single vacancy in Fe-12Cr is reduced already at 110°C which is at lower temperature than in pure Fe. This elimination could be due to the SIAs long-range migration. The V concentration continues to decrease at 150°C. This stage can be explained by the V-C pairs dissociation as in the case of Fe. In the Fe-12Cr samples irradiated at high fluence of $1 \times 10^{16} \text{ cm}^{-2}$, the vacancy clusters size and concentration begin to decrease at 250°C. It could be due to the vacancy clusters dissociation. On the contrary, the annealing stage observed at 200°C in Fe doesn't occur in Fe12Cr sample. It suggests that the temperature of vacancy clusters migration in Fe12Cr is higher than that in pure Fe. A large part of the vacancy clusters are recovered at 450°C which is 100°C higher than in the case of Fe. This shift in vacancy recovery could also be explained by the higher migration temperature of vacancy clusters in Fe12Cr. On the contrary, a similar behavior of vacancy clusters have been observed in pure Fe and Fe3Cr samples. It indicates that 3at% Cr is not enough to change the annealing behavior of vacancy clusters in FeCr alloy.

Chapter IV.

The interaction between vacancy and yttrium, titanium and oxygen in bcc Fe

IV. The interaction between vacancy and yttrium, titanium and oxygen in bcc Fe

The interaction between vacancy and yttrium, titanium and oxygen in bcc Fe is studied in this chapter.

In section IV.1, the creation of vacancy defects by implantation with heavy ions Y, Ti and O is discussed. The conditions of the Y, Ti, O implantations are firstly reminded and the corresponding primary knock-on atoms (PKA) energy is compared. The positron experiments results are then presented and the Y, Ti, O- vacancy interactions are revealed with the help of Y, O depth profiles obtained by SIMS. In addition, vacancy clusters depth profile and the ion channeling effect in polycrystalline Fe will be discussed.

In section IV.2, the evolution of vacancy defects distribution after annealing in Y and O implanted samples is discussed. The annealing experiments were performed at temperatures from 100°C up to 750°C under vacuum during 1 hour with a step of 50°C for 1.2 MeV Y $3 \times 10^{15} \text{ cm}^{-2}$ implanted samples. For O implanted samples, the effect of their storage at room temperature has been firstly studied. Then the evolution of vacancy defects after annealing at temperatures from 100°C up to 550°C is studied. The positron experiments results are presented and the Y, O effects on annealing behavior of vacancy defects are revealed with the help of Y, O depth profiles obtained by SIMS after annealing.

Finally, in section IV.3, one mechanism at the atomic scale is suggested for the ODS nanoparticles nucleation with the results obtained in this thesis.

IV.1. Creation of vacancy defects with heavy ions Y, Ti and O

In this section, the creation of vacancy defects induced in Fe by irradiation with heavy ions Y, Ti and O is discussed. The conditions of 1.2 MeV Y, 700 keV Ti, 285 keV and 650 keV O implantations are firstly reminded and the corresponding primary knock-on atoms (PKA) energy is compared. The positron experiments results are then presented and the Y, Ti, O- vacancy interactions are discussed in regard with the theoretical results and the help of Y, O depth profiles measured by SIMS. In addition, vacancy clusters depth profile and the ion channeling effect in polycrystalline Fe will be discussed.

IV.1.1. Y, Ti and O implantations in bcc Fe

a) Y, Ti and O implantations conditions in bcc Fe simulated by SRIM

The conditions of 1.2 MeV Y, 700 keV Ti and 285 keV O implantations are reminded in Table IV.1 and the damage and element depth profiles calculated by using SRIM are plotted in the Figure IV-1. The choices of these implantation conditions have been explained in Chapter II section 2.1.

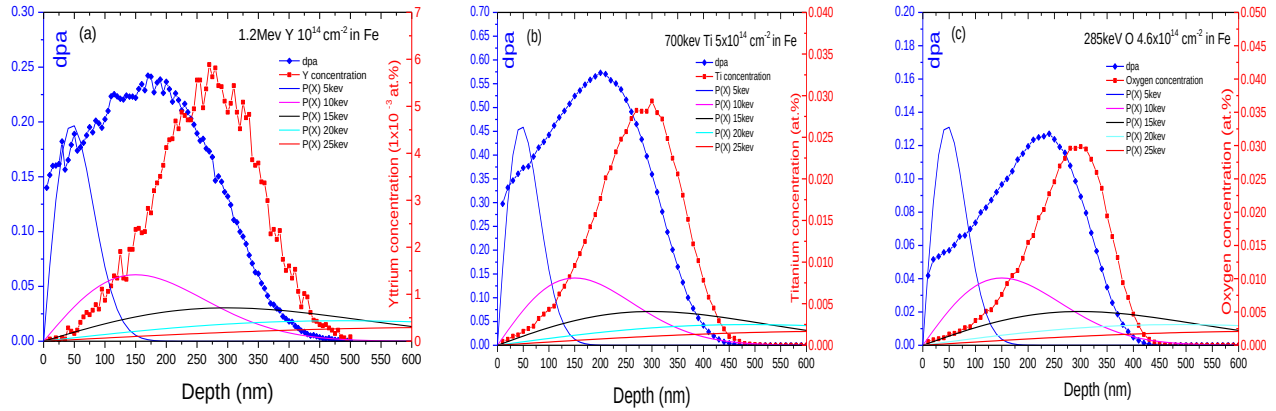


Figure IV-1: Depth profiles of defect production and atomic concentration for (a) 1.2 MeV Y in Fe (b) 700 keV Ti in Fe (c) 285 keV O implantations in Fe compared to positron implantation profiles calculated for various energies P(X).

Ions	Implantation T (°C)	Implantation Energy	Ions range Rp (nm)	Fluence (cm^{-2})	Max. damage dose (dpa)	Concentration (appm)	Concentration/dpa at Rp
Y	RT and low temperature (LN ₂)	1.2 MeV	262 nm	10^{14}	0.24	60	250
				2×10^{15}	4.85	1170	241
				3×10^{15}	7.27	1760	242
Ti	RT	700 keV	262 nm	5×10^{14}	0.57	300	526
				2×10^{15}	2.28	1170	513
				3×10^{15}	3.42	1760	515
O	RT	285 keV	262 nm	4.6×10^{14}	0.13	300	2308
				1.8×10^{15}	0.5	1170	2340
				2.7×10^{15}	0.75	1760	2347

Table IV.1: The results of SRIM calculations for 1.2 MeV Y, 700keV Ti and 285keV O implantations in Fe samples.

The depth profiles of damage and concentration for 650 keV O implantations are compared to the 285 keV O implantations ones in Figure IV-2 (a) and the O concentration/dpa ratio comparison is shown in Figure IV-2 (b). The O concentration/dpa ratio is slightly higher (+7% at Rp) in 285 keV O implantation than in the in 650 keV O case. Thus, the O effect should be more pronounced in 285 keV O implantation. This ion concentration/dpa ratio increases when the mass of the incident ions decreases from Y, Ti to O as reported in Table IV.1. The O implantations conditions are reminded in Table IV.2. The choices of these implantation conditions have been explained in Chapter II section 2.1.

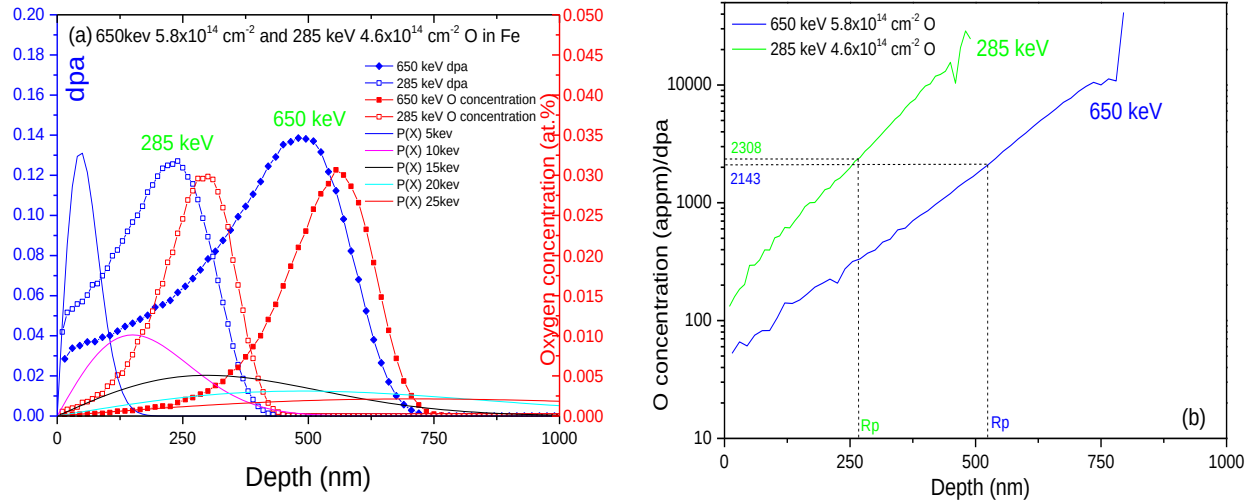


Figure IV-2: (a) Depth profile of defect production and atomic concentration for 285 keV O in Fe and 650 keV O in Fe compared to positron implantation profiles calculated for various energies P(X) (b) the O concentration/dpa ratio comparison.

Ions	Implantation T (°C)	Implantation Energy	Ions range Rp (nm)	Fluence (cm ⁻²)	Max. damage dose (dpa)	Concentration (appm)	Concentration/dpa at Rp
O	RT	285 keV	262nm	4.6x10 ¹⁴	0.13	300	2308
				1.8x10 ¹⁵	0.5	1170	2340
				2.7x10 ¹⁵	0.75	1760	2347
O	RT	650 keV	510 nm	5.8 x10 ¹⁴	0.14	300	2143
				2.2x10 ¹⁵	0.52	1160	2231

Table IV.2: The results of SRIM calculations for 650 keV O and 285keV O implantations in Fe samples.

b) The primary knock- on atoms (PKA) energy

In order to explain the experimental results, the primary knock-on atoms (PKA) energy are calculated for 1.2 MeV Y, 700 keV Ti, 285 keV O and 650 keV O implantations. Four parameters, P(T), P(N), W(T) and W(N), are calculated as for the 1.5 MeV He irradiated Fe samples presented in section Chapter III section 2.1. P(T) represents the fraction of PKA number as function of PKA energy T. P(N) stands for the fraction of PKA number as function of displaced atoms number produced by PKA with energy T. W(T) represents the fraction of displacement damage as function of PKA energy T. W(N) stands for the fraction of displacement damage as function of displaced atoms number produced by PKA with energy T. All these calculations were carried out using SRIM software in the «full damage cascades» option.

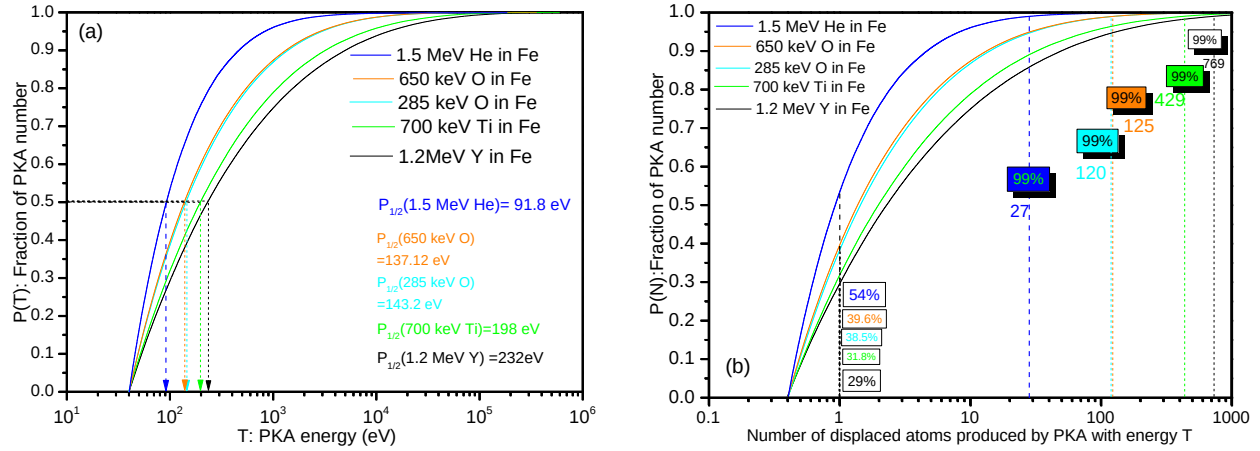


Figure IV-3: The fraction of PKA number as function of (a) PKA energy and (b) displaced atoms number produced by PKA with energy T for 1.2 MeV Y, 700 keV Ti, 285 keV O, 650 keV O and 1.5 MeV He implanted Fe samples.

The curves $P(T)$, $P(N)$ are presented in Figure IV-3 and $W(T)$, $W(N)$ curves are illustrated in Figure IV-4. The PKA energy $P_{1/2}$ is the energy of the PKA for which half of PKA have energy lower than this value. For 1.2 MeV Y implantations, this value is 232 eV. 29% of PKA in 1.2 MeV Y implantations could not induce any other atom displacement, 1% of PKA could generate a displacement cascade including more than 769 atoms and 70% of PKA generate a cascade including 1- 769 atoms. The PKA energy value $W_{1/2}$ is the energy of the PKA for which half of the displacement damage is created by PKA with energy lower than this value. This value is $\sim 50 \text{ keV}$ for 1.2 MeV Y implantations. Only 0.7% of displacement damage is in the form of the one vacancy at the maximum, 49% being in the form of 499- 7560 vacancies, 1% being in the form of more than 7560 vacancies. It should be noted that these calculations do not consider the defects recombination. Thus, the displacement damage in the form of the one vacancy is less than 0.7%.

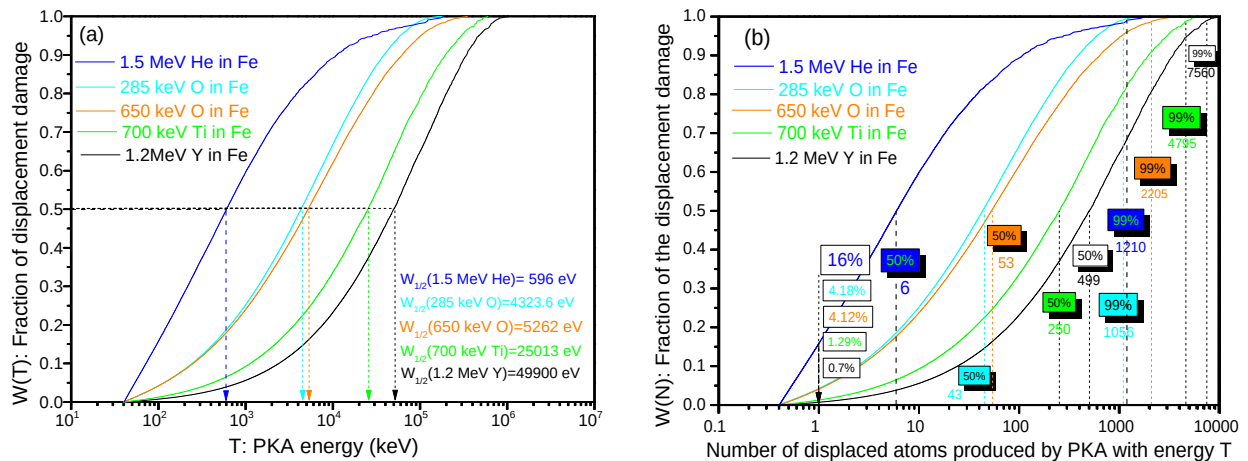


Figure IV-4: The fraction of displacement damage as function of (a) PKA energy and (b) displaced atoms number produced by PKA with energy T for 1.2 MeV Y, 700 keV Ti, 285 keV O, 650 keV O and 1.5 MeV He implanted Fe samples.

These parameters are also determined for 1.5 MeV He, 700 keV Ti, 285 keV O and 650 keV O implantations in pure Fe and are summarized in Table IV.3. The fraction of displacement damage in the form of one displacement is much smaller in 1.2 MeV Y, 700 keV Ti, 285 keV O and 650 keV O implanted Fe samples (respectively 0.7%, 1.29%, 4.18%, 4.12%) than the one in 1.5 MeV He irradiated Fe samples (16%). The PKA energy $P_{1/2}$ and $W_{1/2}$ in these cases are also much higher. All indicate that the major introduced vacancy defects in these Y, Ti, O implanted samples should be vacancy clusters.

Ions	Implantation Energy	$P_{1/2}$ (eV)	P(N) (<1 displaced atom)	Displaced atoms (P(N): 99%- 100%)	$W_{1/2}$ (keV)	W(N) (<1 displaced atom)	Displaced atoms (W(N): 50%- 99%)
Y	1.2 MeV	232	29%	>769	50	0.7%	499- 7560
Ti	700 keV	198	31.8%	>429	25	1.29%	250- 4795
O	285 keV	143	38.5%	>120	4.3	4.18%	43- 1056
O	650 keV	137	39.6%	>125	5.3	4.12%	53- 2205
He	1.5 MeV	92	54%	>27	0.6	16%	6- 1210

Table IV.3: P(T), P(N), W(T) and W(N) parameters for 1.5 MeV He, 1.2 MeV Y, 700 keV Ti, 285 keV O and 650 keV O implantations in pure Fe.

IV.1.2. PAS results in as implanted samples

a) 1.2 MeV Y implantation

The 1.2 MeV Y implantation at the lowest fluence of $1.0 \times 10^{14} \text{ cm}^{-2}$ is firstly studied. As shown in Figure IV-5 (a), $S(E)$ increases fast from 0.5 to 4 keV and reaches a plateau value from 4 to 15 keV. From 15 keV, $S(E)$ begins to decrease. Figure IV-5 (b) shows that, from 0.5 to 4 keV, the corresponding S, W points go towards the $D_{vn}(\text{Fe})$ line which indicates vacancy clusters are formed in this region. S, W points remain superposed from 4 to 15 keV which means the size and the concentration of vacancy clusters do not change or that positrons are no more able to detect this change due to size or trapping saturation. In the positron energy range from 15 keV, S, W points evolve along the $D_{vn}(\text{Fe})$ line towards the (S_L, W_L) Fe lattice point. It indicates that the size of defects does not change but their concentration decreases in the probed depth range.

Compared to the result of 1.5 MeV ^4He irradiated at the highest fluence $1.0 \times 10^{17} \text{ cm}^{-2}$ implanted Fe sample, the $S(E)$ values of 1.2 MeV yttrium implanted Fe are much higher and S, W points are further from the (S_L, W_L) point and slightly above the $D_{vn}(\text{Fe})$ line. It indicates that the vacancy cluster concentration is much higher in Y implanted sample. It could be explained by the higher damage dose accumulated with Y irradiation which reaches 0.24 dpa for the Y lowest fluence implantation compared to 0.1 dpa for sample irradiated with ^4He at the highest fluence. Moreover the vacancy cluster size is slightly larger for implantation with Y. It could be due to the difference in PKA (Primary Knock-on Atom) energies for both projectile ions. Heavier ions produce more PKAs with high energy than lighter ions. PKAs which can induce collision cascades in which the displacement local density depends on their energy. Half of the displacement damage is created by PKA with energy lower than 0.6 keV for 1.5 MeV He irradiation case whereas this PKA energy is 50 keV for 1.2 MeV Y as showed in Table IV.3. Molecular dynamics simulations show PKA with higher energy produce larger vacancy clusters^[193]. For example C.J.

Ortiz have calculated the cascade induced by 30 keV Fe recoils in Fe using Molecular Dynamics^[189]. They showed that vacancy and interstitials clusters are formed and their size distribution at the end of the cascades is large from 2 to 15 and 12 respectively.

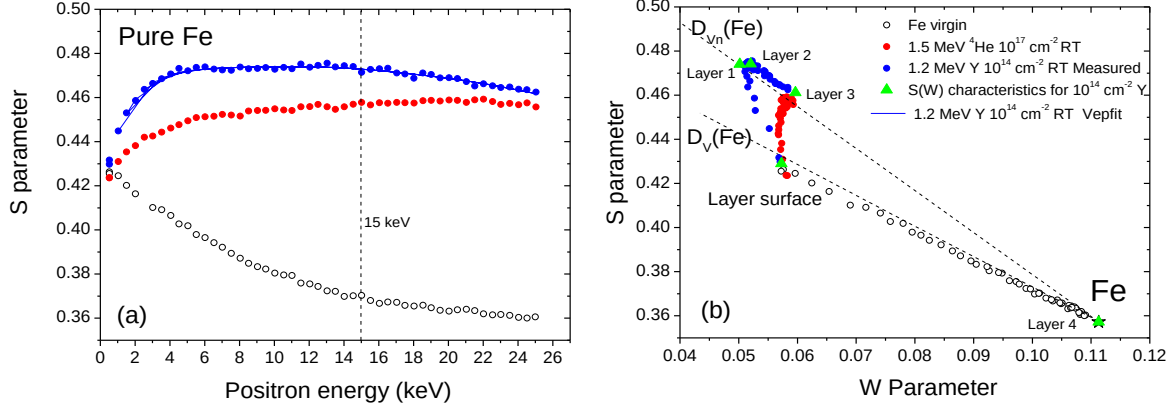


Figure IV-5: (a) Low (S) momentum fraction as a function of positron energy (b) and S as a function of W in Fe samples for 1.2 MeV Y implantation at fluence $1.0 \times 10^{14} \text{ cm}^{-2}$ compared to 1.5 MeV He irradiation at fluence $1.0 \times 10^{17} \text{ cm}^{-2}$.

Another observation has attracted our attention. The S(E) curve of 1.2 MeV Y implantation begins to decrease from 15 keV instead of 10 keV energy from which a fraction of positron should annihilate in the defect-free Fe lattice as suggested by the depth damage profile calculated by SRIM (Figure IV-1 (a)). It indicates that positrons detect vacancy clusters deeper than expected by SRIM. A structure of four layers allows to fit the S(E) and W(E) experimental curves with Vepfit. The S and W values of each of these layers are plotted in Figure IV-5 (b) and indicate that vacancy clusters are detected in the first three layers. The first layer spreads from surface to ~ 58 nm, the second spreads up to ~ 666 nm and the third stops at the depth of ~ 1662 nm. For these three layers the effective positron diffusion length L^+ changes from 10 to 15 nm. In the fourth layer the S, W and L^+ correspond to the one of Fe lattice. So vacancy clusters are detected up to ~ 1662 nm. The Vepfit results are reported in Table IV.4.

The 1.2 MeV Y implantations at higher fluences have been compared. Figure IV-6 shows S(E), W(E) and S(W) curves for pure Fe samples implanted with 1.2 MeV Y at fluences from 1×10^{14} to $3 \times 10^{15} \text{ cm}^{-2}$ (damage at the maximum varies from 0.24 to 7.27 dpa) and for Fe virgin sample. For all fluences, the S(E) curves in the Y implanted Fe samples differ from the one measured in the virgin Fe sample. Whatever the fluence, all the S(E) values are higher in the implanted samples than in the virgin one. This indicates that Y ions have induced vacancy-related defects. The decrease of S parameter with the increase of Y fluence has to be noticed. Generally, higher fluence creates greater damage in material and S should increase or remain stable if positron trapping saturation was reached. Thus, this unexpected decrease of S indicates that yttrium effect is involved in this damage evolution. The shape of S(E) imply that a complicated damage structure exists.

Y fluence (cm ⁻²)	Layer 1				Layer 2			
	S	W	L ⁺ (nm)	Thickness (nm)	S	W	L ⁺ (nm)	Thickness (nm)
1x10 ¹⁴	0.4740	0.0502	10	58	0.4742	0.0520	12	666
2x10 ¹⁵	0.4553	0.0572	16	98	0.4316	0.0657	15	465
3x10 ¹⁵	0.4493	0.0604	28	120	0.4209	0.0693	15	445
Y fluence (cm ⁻²)	Layer 3							
	S	W	L ⁺ (nm)	Thickness (nm)				
1x10 ¹⁴	0.4611	0.0597	15	1662				
2x10 ¹⁵	0.4668	0.0545	10	1514				
3x10 ¹⁵	0.4652	0.0543	10	1547				

Table IV.4: Vepfit results for Fe implanted with 1.2 MeV Y ions at 1x10¹⁴ cm⁻², 2x10¹⁵ cm⁻² and 3x10¹⁵ cm⁻².

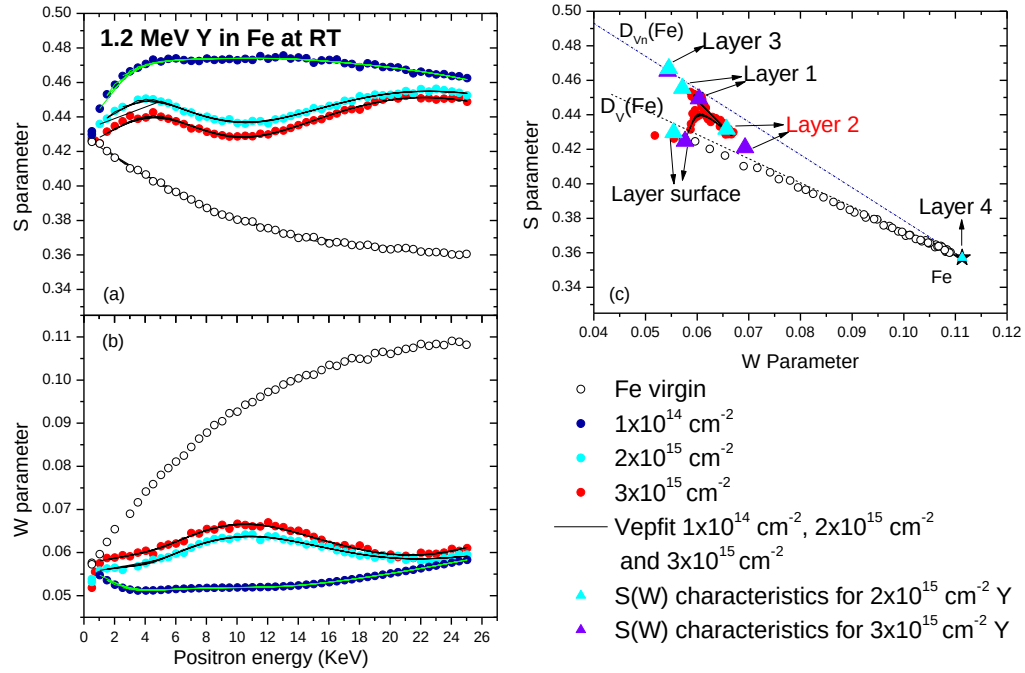


Figure IV-6: S(E), W(E) and S(W) for the Fe samples irradiated with 1.2 MeV yttrium at various fluences from 1x10¹⁴ to 3x10¹⁵ cm⁻² at room temperature and Vepfit results.

A structure of four layers is found to be the simplest model to fit S(E) and W(E) data for all three fluences using Vepfit program. The depth structure is shown in Figure IV-7 (a) for fluences 2x10¹⁵ and 3x10¹⁵ cm⁻² and the (S, W) points corresponding to these layers are plotted in Figure IV-7 (b). The characteristics of annihilation in single vacancy (D_v(Fe) line) and vacancy clusters (D_{vn}(Fe) line) in bcc Fe have been determined by 1.5 MeV ⁴He irradiation^[176] as presented in Chapter III section 2.1. As shown in Figure IV-7 (b), the (S, W) points of layer 1 are close to D_{vn}(Fe) line indicating vacancy clusters are

detected in this region. The (S, W) point of layer 1 determined for the highest fluence $3 \times 10^{15} \text{ cm}^{-2}$ is closer to Fe lattice point than the one found for the $2 \times 10^{15} \text{ cm}^{-2}$ implanted sample, indicating the vacancy cluster concentration is lower for the highest fluence. The points in layer 2 drift towards $D_v(\text{Fe})$ line for both highest fluences indicating the size and concentration of vacancy clusters detected in layer 2 decrease compared to those of layer 1. For the fluence of $3 \times 10^{15} \text{ cm}^{-2}$, the point is closer to $D_v(\text{Fe})$ line than for $2 \times 10^{15} \text{ cm}^{-2}$ indicating the decrease is more significant for higher fluence. The points found for the layer 3 return to $D_{vn}(\text{Fe})$ line indicating the size and concentration of detected vacancy clusters are larger in this region than in all the others. Finally, positrons detect a fourth layer where the S and W values are equal to the annihilation characteristics in defect free Fe called S_{Lattice} and W_{Lattice} . As shown in **Figure IV-7** (a), the layer boundaries are approximately the same for both highest fluences. The first layer spreads from surface to $109 \pm 11 \text{ nm}$, the second spreads up to $455 \pm 10 \text{ nm}$ and the third stops at the depth of $1530 \pm 16 \text{ nm}$. For these three layers, the positron effective diffusion length L^+ changes from 10 to 30 nm as reported in Table IV.4. In the fourth layer, the S, W and L^+ values correspond to the one of Fe lattice. So vacancy clusters are detected up to $\sim 1530 \text{ nm}$. This depth is much deeper than the damage profile calculated by SRIM as observed in the lowest fluence implanted sample. It has to be noted that the S values (W values) of the second layer are lower (higher) than those of the first and third layer.

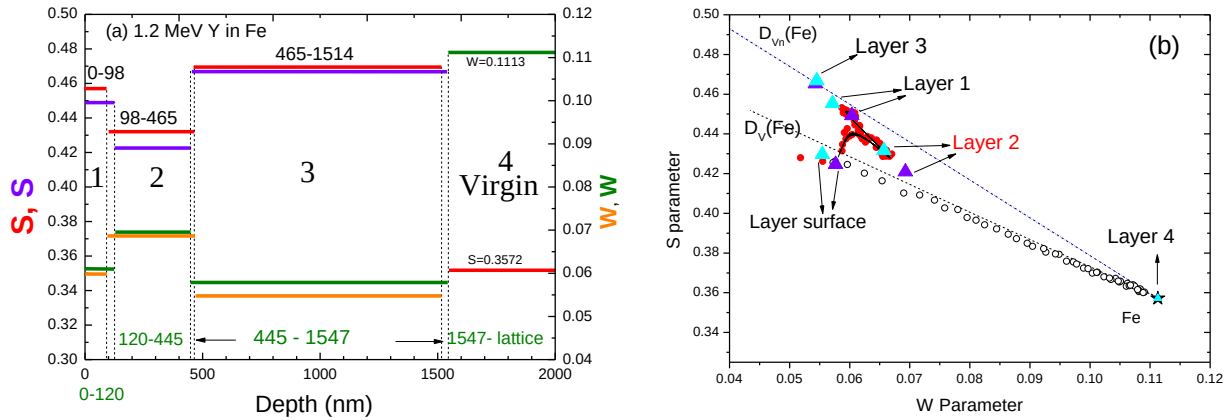


Figure IV-7: (a) A structure of four layers obtained by Vepfit (b) S(W) plot of the layers for the Fe samples irradiated by 1.2 MeV yttrium at fluences 2×10^{15} (red for S; orange for W) and 3×10^{15} (purple for S; green for W) cm^{-2} .

A low temperature implantation has also been performed for 1.2 MeV Y to study the irradiation temperature effect. The sample holder is cooled using liquid nitrogen flow. Figure IV-8 shows S(E), W(E) and S(W) curves for the Fe samples irradiated by 1.2 MeV yttrium at the fluences of 1×10^{14} , $2 \times 10^{15} \text{ cm}^{-2}$ at room temperature (RT) and low temperature (LN_2). The results of the fit are also plotted. As for the case of irradiation at RT, the S and W values obtained show that Y ions have also induced vacancy-related defects. The shapes of curves for the RT and LN_2 irradiated samples at the same fluence are similar which means a close damage structure exists. Nevertheless some differences can be observed between the data obtained for the different irradiation temperatures.

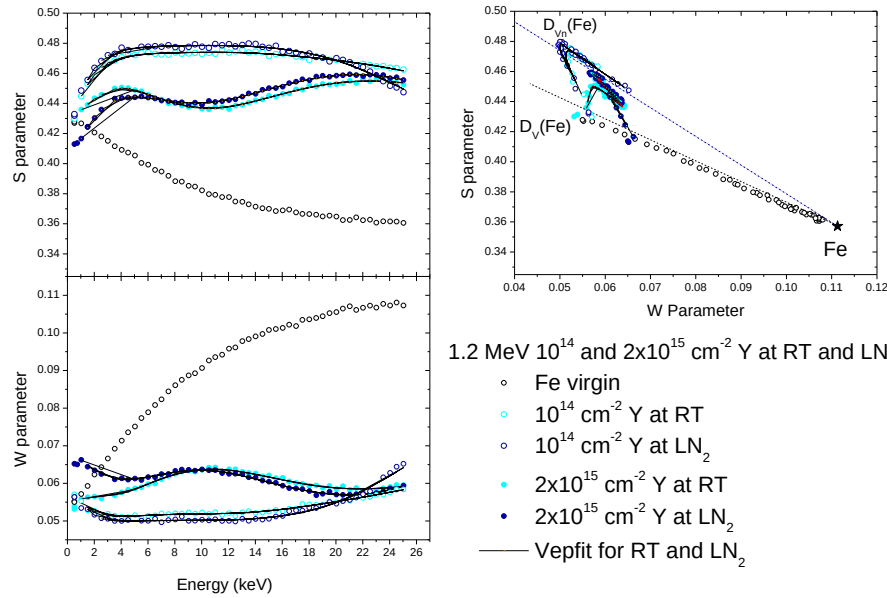


Figure IV-8: $S(E)$, $W(E)$ and $S(W)$ for the Fe samples irradiated by 1.2 MeV yttrium at fluence $2 \times 10^{15} \text{ cm}^{-2}$ at room temperature and low temperature (LN_2) and Vepfit results.

A structure of four layers is also obtained by Vepfit for the low temperature implanted Fe sample as for the room temperature implanted one as illustrated for the fluence of $2 \times 10^{15} \text{ cm}^{-2}$ in Figure IV-9 (a). The corresponding $S(W)$ annihilation characteristics of the layers are shown in Figure IV-9 (b). The layer thickness is similar. But S value of layer 2 and 3 (W value) for the low temperature implanted sample is higher (lower) than that for the RT implanted one. For the low temperature implanted sample, the $S(W)$ point of layer 2 is closer to the $V_n(\text{Fe})$ line which means that the created vacancy clusters are larger. Their $S(W)$ point of layer 3 is on the $V_n(\text{Fe})$ line but farer from the Fe lattice point than that of RT implanted sample indicating that the created vacancy cluster concentration is higher in this layer for the low temperature irradiated sample. Thus, the low temperature irradiation increases the concentration or size of vacancy clusters.

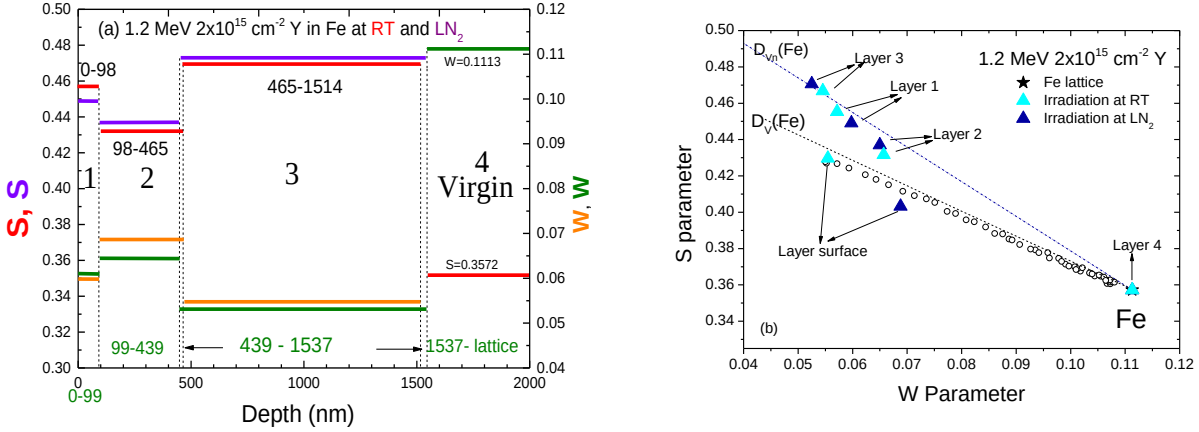


Figure IV-9: (a) A structure of four layers obtained by Vepfit for the Fe samples irradiated by 1.2 MeV yttrium at fluences 2×10^{15} at room temperature (red for S; orange for W) and low temperature (purple for S; green for W) cm^{-2} . (b) S(W) annihilation characteristics of layers.

The same results have been observed for the low fluence of $1 \times 10^{14} \text{ cm}^{-2}$ as shown in Figure IV-10. S value of layer 1, layer 2 and 3 (W value) for the low temperature implanted sample is higher (lower) than that for the RT implanted one. For the low temperature implanted sample, S(W) points of the three layers are on the $V_n(\text{Fe})$ line but farer from the Fe lattice point than that of RT implanted sample indicating that the created vacancy cluster concentrations are higher for low temperature irradiation. It is worth to note that the thickness of layer 3 is approximately one half narrower for LN₂ implanted sample than that for RT implanted sample which indicates that the vacancy clusters distribution is thinner in LN₂ implanted sample.

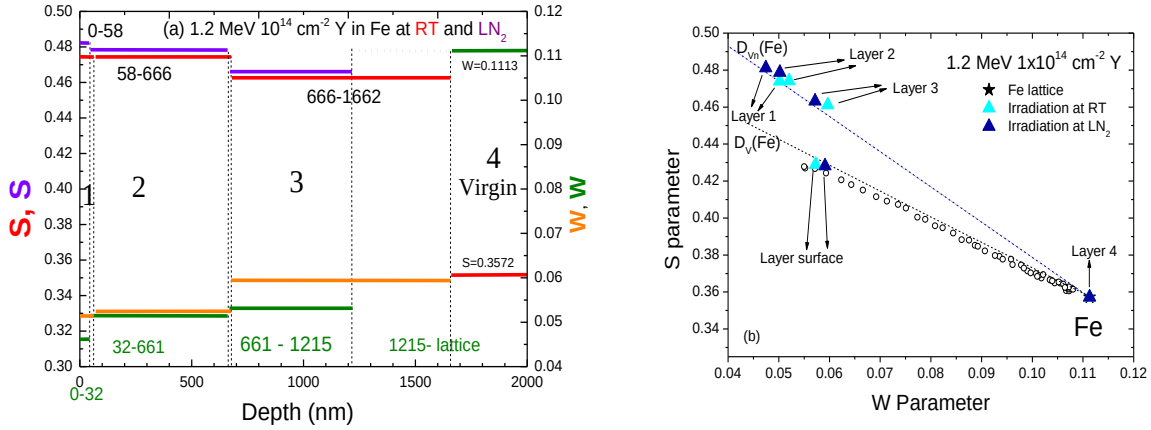


Figure IV-10: (a) A structure of four layers obtained by Vepfit for the Fe samples irradiated by 1.2 MeV yttrium at fluences 1×10^{14} at room temperature (red for S; orange for W) and low temperature (purple for S; green for W) cm^{-2} . (b) S(W) annihilation characteristics of layers.

Y fluence (cm ⁻²)	Layer 1				Layer 2			
	S	W	L ⁺ (nm)	Thickness (nm)	S	W	L ⁺ (nm)	Thickness (nm)
1x10 ¹⁴ RT	0.4740	0.0502	10	58	0.4742	0.0520	12	666
1x10 ¹⁴ LN ₂	0.4812	0.0474	10	32	0.4787	0.0502	12	661
2x10 ¹⁵ RT	0.4553	0.0572	16	98	0.4316	0.0657	15	465
2x10 ¹⁵ LN ₂	0.4490	0.0598	12	99	0.4370	0.0650	15	439
Y fluence (cm ⁻²)	Layer 3							
	S	W	L ⁺ (nm)	Thickness (nm)				
1x10 ¹⁴ RT	0.4611	0.0597	15	1662				
1x10 ¹⁴ LN ₂	0.4632	0.0572	15	1215				
2x10 ¹⁵ RT	0.4668	0.0545	10	1514				
2x10 ¹⁵ LN ₂	0.4706	0.0525	10	1537				

Table IV.5: Vepfit results for implanted Fe with 1.2 MeV Y ions at 1x10¹⁴ cm⁻², 2x10¹⁵ cm⁻² at room temperature (RT) and low temperature (LN₂).

b) 700 keV Ti implantation

Figure IV-11 shows S(E), W(E) and S(W) curves for pure Fe samples implanted with 700 keV Ti at fluences from 5x10¹⁴ to 3x10¹⁵ cm⁻² (maximum damage varies from 0.57 to 3.42 dpa) and for Fe virgin sample. As in the samples implanted with 1.2 MeV Y, the S parameter in the Ti implanted ones differs from the one measured in the virgin Fe sample. Whatever the fluence, all the S(E) values are higher in the implanted samples than in the virgin one. This indicates that Ti ions have induced vacancy-related defects. S parameter decreases and W parameter increases when the Ti fluence increases which indicates that Ti effect is involved in the damage evolution. But it should be noted that this decrease is less pronounced than the one observed in Y implanted samples although the Ti concentration/dpa ratio is higher than the Y concentration/dpa one. This means that the Ti effect on the S decrease is less pronounced than that of Y.

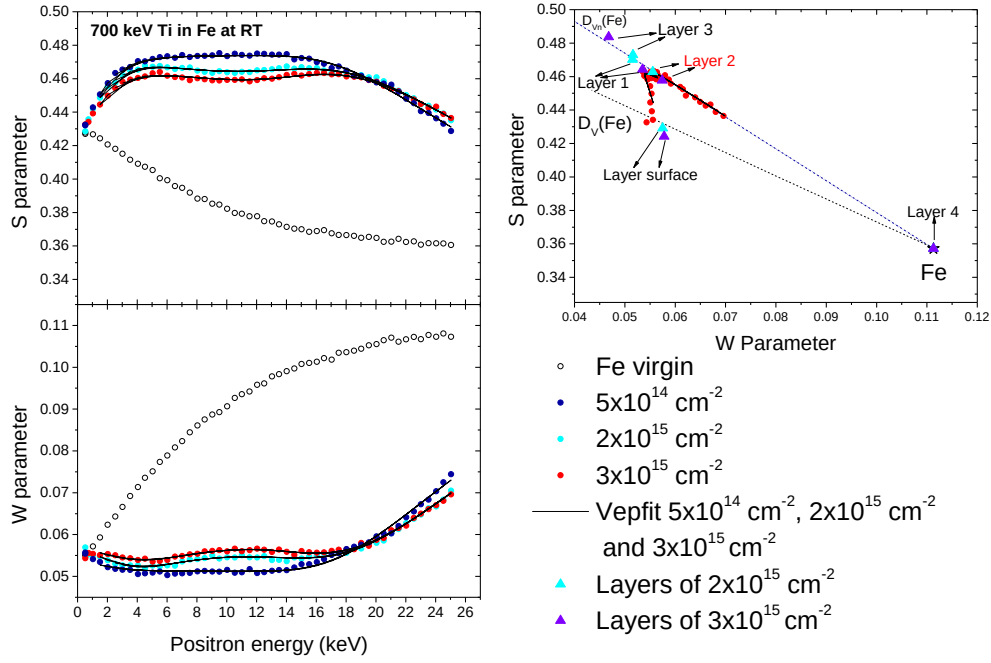


Figure IV-11: $S(E)$, $W(E)$ and $S(W)$ for the Fe samples irradiated by 700 keV titanium at various fluences from 5×10^{14} to $3 \times 10^{15} \text{ cm}^{-2}$ at room temperature and Vepfit results.

A structure of four layers is also found to be the simplest model to fit $S(E)$ and $W(E)$ data for fluences of 2×10^{15} and $3 \times 10^{15} \text{ cm}^{-2}$. On the contrary, a structure of two layers is sufficient to fit the data for the lowest fluence at $1 \times 10^{14} \text{ cm}^{-2}$. The Vepfit results are reported in Table IV.6. The depth structure for fluences at 2×10^{15} and $3 \times 10^{15} \text{ cm}^{-2}$ is shown in Figure IV-12(a) and the (S, W) points obtained for these layers are plotted in Figure IV-12(b).

Ti fluence (cm^{-2})	Layer 1				Layer 2			
	S	W	L^+ (nm)	Thickness (nm)	S	W	L^+ (nm)	Thickness (nm)
5×10^{14}	0.4740	0.0512	11	877	virgin	virgin	virgin	virgin
2×10^{15}	0.4702	0.0515	12	102	0.4628	0.0556	15	479
3×10^{15}	0.4642	0.0535	11	119	0.4577	0.0574	15	584
Ti fluence (cm^{-2})	Layer 3							
	S	W	L^+ (nm)	Thickness (nm)				
5×10^{14}	/	/	/	/				
2×10^{15}	0.4729	0.0516	10	985				
3×10^{15}	0.4837	0.0468	10	960				

Table IV.6: Vepfit results for implanted Fe with 700 keV Ti ions at $5 \times 10^{14} \text{ cm}^{-2}$, $2 \times 10^{15} \text{ cm}^{-2}$ and $3 \times 10^{15} \text{ cm}^{-2}$.

As shown in Figure IV-12 (b), the (S, W) points of layer 1 are close to $D_{Vn}(Fe)$ line indicating vacancy clusters are formed in this region. The point of layer 1 determined for the highest fluence $3 \times 10^{15} \text{ cm}^{-2}$ is closer to the Fe lattice point than the one found for $2 \times 10^{15} \text{ cm}^{-2}$ implanted sample and the S(W) point is slightly below the $D_{Vn}(Fe)$ line. It indicates the vacancy cluster size is smaller. The points of layer 2 drift towards the Fe lattice point for both fluences indicating the concentration of vacancy clusters detected in layer 2 decreases compared to those of layer 1. The points of layer 3 go away from the Fe lattice point along the $D_{Vn}(Fe)$ line indicating the concentration of detected vacancy clusters is larger in this region. It has to be noted that the point of layer 3 determined for the highest fluence $3 \times 10^{15} \text{ cm}^{-2}$ is farer from the Fe lattice point than the one found for $2 \times 10^{15} \text{ cm}^{-2}$ implanted sample. Finally, positrons detect the layer 4 where the S and W values are equal to the annihilation characteristics in defect free Fe called S_{Lattice} and W_{Lattice} . As shown in Figure IV-12 (a), the layer boundaries are approximately the same for both highest fluences. The first layer spreads from surface to $110 \pm 8 \text{ nm}$, the second spreads up to $531 \pm 52 \text{ nm}$ and the third stops at the depth of $972 \pm 12 \text{ nm}$. For these three layers the positron effective diffusion length L^+ changes from 10 to 15 nm. In the fourth layer the S, W and L^+ correspond to the annihilation characteristics of Fe lattice. So vacancy clusters are detected up to $\sim 970 \text{ nm}$. This depth is also deeper than the damage profile calculated by SRIM. It has to be noted that the S values (W values) of the second layer are lower (higher) than those of the first and third layer. Compared to the Y implanted samples, the layer 1 and layer 2 are in the same depth range but the layer 3 spreads further in the Y implanted samples. It indicates that 1.2 MeV Y implantations induce vacancy defects further in depth than the 700 keV Ti implantations.

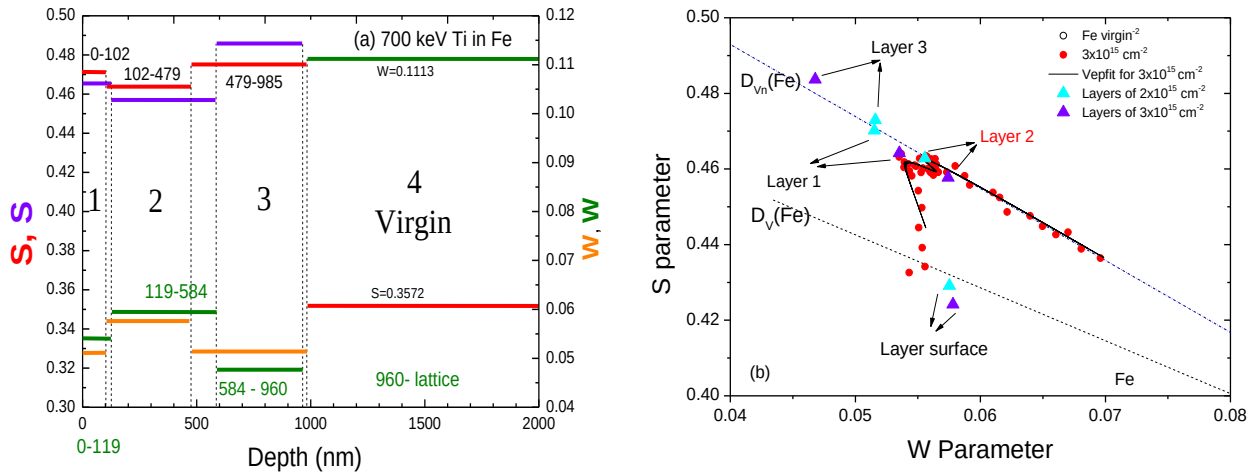


Figure IV-12: (a) A structure of four layers obtained by Vepfit for the Fe samples irradiated by 700 keV Ti at fluences 2×10^{15} (red for S; orange for W) and 3×10^{15} (purple for S; green for W) cm^{-2} and (b) S(W) curve with annihilation characteristics of layers.

c) 285 keV and 650 keV O implantations

Figure IV-13 shows S(E) curves for the Fe samples implanted with (a) 650 keV O at the fluence of $5.8 \times 10^{14} \text{ cm}^{-2}$ and (b) 285 keV O at the fluence of $4.6 \times 10^{14} \text{ cm}^{-2}$ with different storage time at room temperature. In these low O fluences implanted Fe samples, no evolution with the storage time at room temperature is observed.

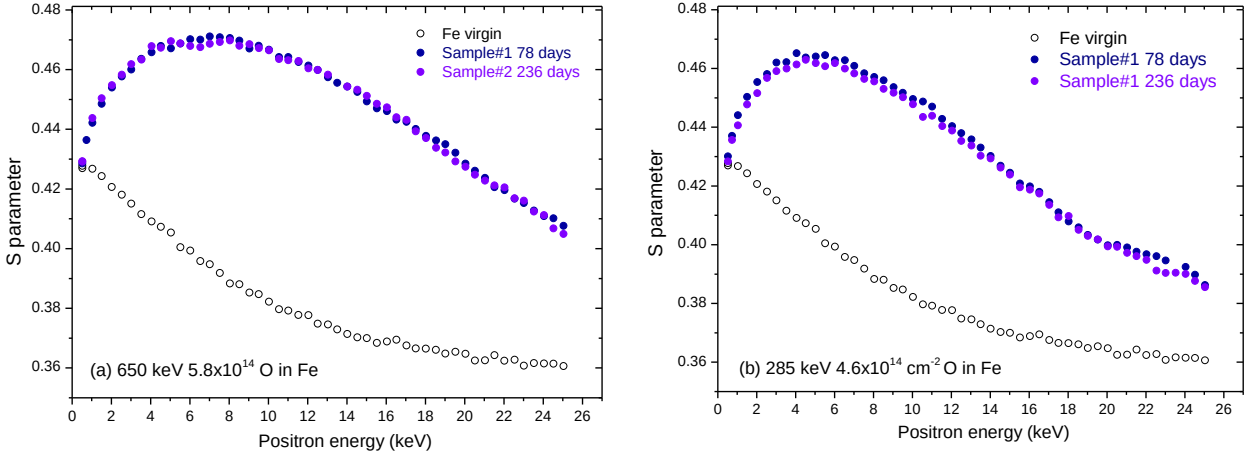


Figure IV-13: $S(E)$ curves for (a) 650 keV $5.8 \times 10^{14} \text{ cm}^{-2}$ O in Fe (b) 285 keV $4.6 \times 10^{14} \text{ cm}^{-2}$ O in Fe samples with different storage time at room temperature.

Figure IV-14 shows $S(E)$ curves evolution for the Fe samples implanted with (a) 650 keV O at the fluence of $2.2 \times 10^{15} \text{ cm}^{-2}$, (b) 285 keV O at $1.8 \times 10^{15} \text{ cm}^{-2}$ and (c) 285 keV O at $2.7 \times 10^{15} \text{ cm}^{-2}$ with different storage time at room temperature. It is observed in each case that these $S(E)$ curves of the samples irradiated with the same O implantation conditions evolve with the storage time at room temperature. After ~ 235 days storage following the irradiation, the $S(E)$ curves become stable and the S values are higher in all the three cases compared to the ones obtained at the early storage time. The $S(E)$ evolutions at room temperature after the irradiation have not been observed in He, Y and Ti irradiated Fe samples.

After ~ 235 days storage at room temperature following irradiation, the samples irradiated with O at high fluences become stable. Thus, $S(E)$, $W(E)$ and $S(W)$ curves are compared in Figure IV-15 for pure Fe samples implanted with 285 keV O at fluences from 4.6×10^{14} to $2.7 \times 10^{15} \text{ cm}^{-2}$ (maximum damage varies from 0.13 to 0.75 dpa) stored during the same time ~ 235 days and for Fe virgin sample. As in the samples implanted with 1.2 MeV Y and 700 keV Ti, O ions have induced vacancy-related defects. S parameter is lower when the O fluence increases which indicates that O effect is involved in the damage evolution.

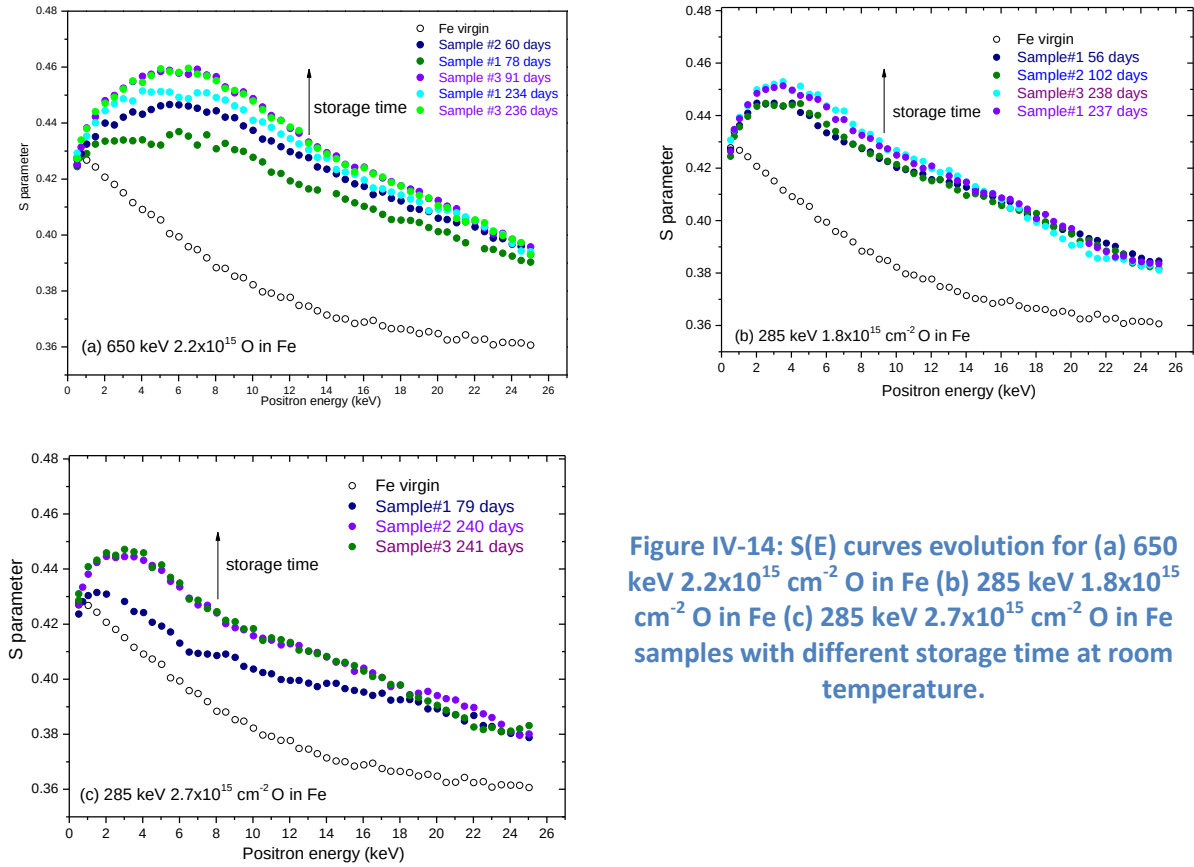


Figure IV-14: S(E) curves evolution for (a) 650 keV $2.2 \times 10^{15} \text{ cm}^{-2}$ O in Fe (b) 285 keV $1.8 \times 10^{15} \text{ cm}^{-2}$ O in Fe (c) 285 keV $2.7 \times 10^{15} \text{ cm}^{-2}$ O in Fe samples with different storage time at room temperature.

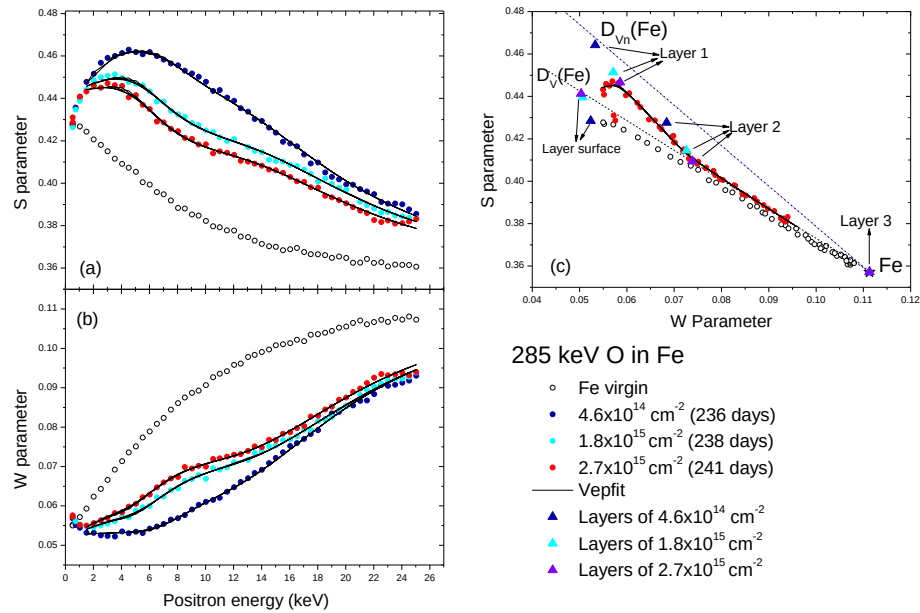


Figure IV-15: S(E), W(E) and S(W) for the Fe samples irradiated by 285 keV oxygen at various fluences from 4.6×10^{14} to $2.7 \times 10^{15} \text{ cm}^{-2}$ after ~ 240 days storage at room temperature and Vepfit results.

A structure of three layers is found to be the simplest model to fit S(E) and W(E) data for all three fluences. The Vepfit results for the layer 1 and 2 are reported in Table IV.7 and the layer 3 corresponding to the Fe lattice is not presented in the table. The depth structure is shown in Figure IV-16 for the fluences of 1.8×10^{15} and $2.7 \times 10^{15} \text{ cm}^{-2}$ and the (S, W) points of these layers are plotted in Figure IV-15 (c).

285 keV O fluence (cm^{-2})	Layer 1				Layer 2			
	S	W	L^+ (nm)	Thickness (nm)	S	W	L^+ (nm)	Thickness (nm)
4.6×10^{14}	0.4642	0.0533	10	177	0.4276	0.0684	10	506
1.8×10^{15}	0.4514	0.0571	10	116	0.4145	0.0726	10	565
2.7×10^{15}	0.4466	0.0586	10	97	0.4094	0.0738	10	541

Table IV.7: Vepfit results for implanted Fe with 285 keV O ions at $4.6 \times 10^{14} \text{ cm}^{-2}$, $1.8 \times 10^{15} \text{ cm}^{-2}$ and $2.7 \times 10^{15} \text{ cm}^{-2}$.

The (S, W) points determined in layer 1 are close to $D_{\text{vn}}(\text{Fe})$ line indicating vacancy clusters are formed in this region. The point of layer 1 determined for the highest fluence $2.7 \times 10^{15} \text{ cm}^{-2}$ is closer to Fe lattice point than the one found for $1.8 \times 10^{15} \text{ cm}^{-2}$ implanted sample and moreover it moves towards the $D_{\text{v}}(\text{Fe})$ line. It indicates that the vacancy cluster concentration is lower and size is smaller for the highest fluence. The points corresponding to layer 2 move further towards $D_{\text{v}}(\text{Fe})$ line for all fluences indicating the size and concentration of vacancy clusters detected in this layer decrease compared to those of layer 1. For the fluence of $2.7 \times 10^{15} \text{ cm}^{-2}$, the point is situated on the $D_{\text{v}}(\text{Fe})$ line indicating that positrons detect vacancy defects with free volume close to single vacancy. Finally, positrons detect the layer 3 where the S and W values are equal to the annihilation characteristics in defect free Fe called S_{Lattice} and W_{Lattice} . As shown in Figure IV-16, the first layer spreads from surface to $106 \pm 9 \text{ nm}$ and the second spreads up to $553 \pm 12 \text{ nm}$. For these two layers L^+ is $\sim 10 \text{ nm}$. In the third layer the S, W and L^+ values correspond to the one of Fe lattice. So vacancy defects are detected up to the depth of $\sim 553 \text{ nm}$. This depth nearly corresponds to the damage profile calculated by SRIM. It has to be noted that the S values (W values) of the second layer are lower (higher) than those of the first layer. Compared to the Y and Ti implanted samples, the layer 1 and 2 are in the same depth range but there is not a vacancy cluster layer between layer 2 and virgin bulk. It indicates that 285 keV O implantations create the vacancy defects shallower in depth than 1.2 MeV Y and 700 keV Ti implantations.

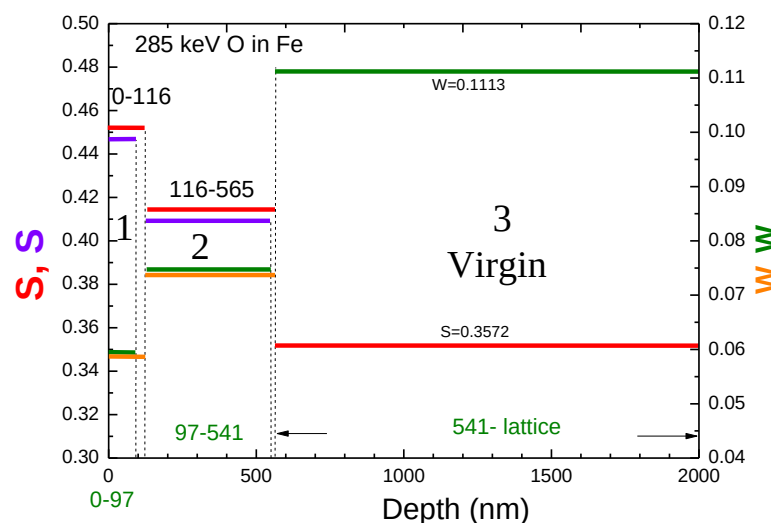


Figure IV-16: A structure of three layers obtained by Vepfit for the Fe samples irradiated by 285 keV oxygen at fluences 1.8×10^{15} (red for S; orange for W) and 2.7×10^{15} (purple for S; green for W) cm^{-2} after ~ 240 days storage at room temperature.

The effect of O implantation energy is also studied. In Figure IV-17, the S(E), W(E) and S(W) curves are plotted for pure Fe samples implanted with 285 keV O at fluences 4.6×10^{14} , $1.8 \times 10^{15} \text{ cm}^{-2}$ (maximum damage corresponds to 0.13 and 0.5 dpa) and 650 keV O at fluences 5.8×10^{14} , $2.2 \times 10^{15} \text{ cm}^{-2}$ (Max. damage 0.14 and 0.52 dpa) after ~ 240 days storage at room temperature. As the fluence effect observed in 285 keV O implanted samples, the decrease of S parameter with the O fluence is also observed in 650 keV O implanted samples. A damage structure of three layers is also obtained by using Vepfit and the results are reported in Table IV.8. Vacancy clusters are observed in layer 1 and the size or concentration of vacancy clusters decrease in layer 2. This decrease is more pronounced for higher fluence at $2.2 \times 10^{15} \text{ cm}^{-2}$ than the one of 5.8×10^{14} .

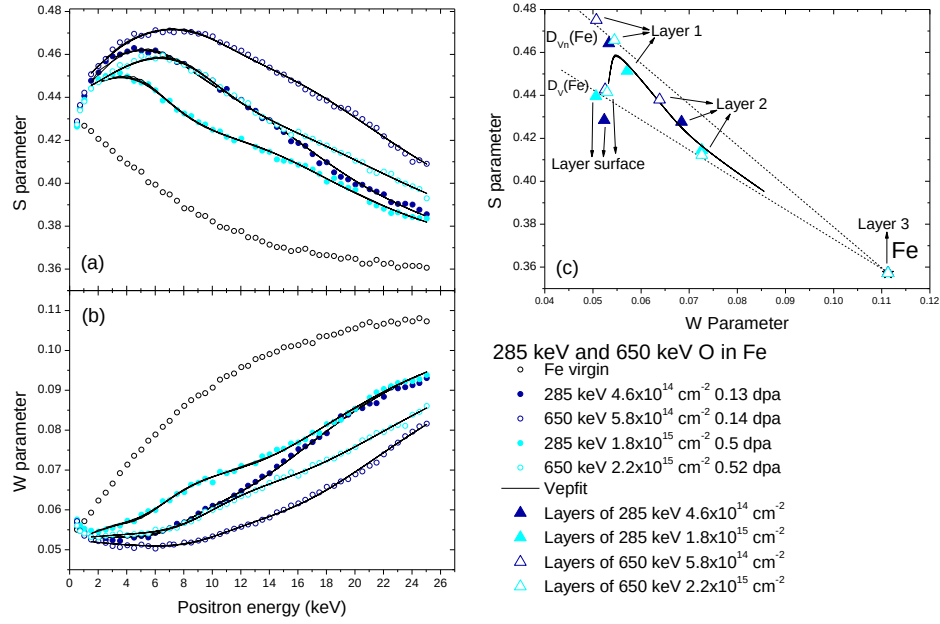


Figure IV-17: S(E), W(E) and S(W) for the Fe samples irradiated with 285 keV O at fluences 4.6×10^{14} , $1.8 \times 10^{15} \text{ cm}^{-2}$ and with 650 keV O at fluences 5.8×10^{14} , $2.2 \times 10^{15} \text{ cm}^{-2}$ after ~ 240 days storage at room temperature and Vepfit results.

285 keV O fluence (cm^{-2})	Layer 1				Layer 2			
	S	W	L ⁺ (nm)	Thickness (nm)	S	W	L ⁺ (nm)	Thickness (nm)
4.6×10^{14}	0.4642	0.0533	10	177	0.4276	0.0684	10	506
1.8×10^{15}	0.4514	0.0571	10	116	0.4145	0.0726	10	565
650 keV O fluence (cm^{-2})	Layer 1				Layer 2			
	S	W	L ⁺ (nm)	Thickness (nm)	S	W	L ⁺ (nm)	Thickness (nm)
5.8×10^{14}	0.4751	0.0507	26	296	0.4380	0.0639	15	819
2.2×10^{15}	0.4657	0.0545	43	265	0.4122	0.0726	15	866

Table IV.8: Vepfit results for implanted Fe with 285 keV O ions at $4.6 \times 10^{14} \text{ cm}^{-2}$, $1.8 \times 10^{15} \text{ cm}^{-2}$ and with 650 keV O ions at $5.8 \times 10^{14} \text{ cm}^{-2}$, $2.2 \times 10^{15} \text{ cm}^{-2}$ after ~ 240 days storage at room temperature.

The damage structure comparison between 285 keV and 650 keV O implantations is shown in Figure IV-18. It should be noted that the depth range of layer 1 for 650 keV O is deeper than the one for 285 keV O. In addition, the vacancy clusters are detected up to $842 \pm 23 \text{ nm}$ for 650 keV O that is deeper than in 285 keV O ($\sim 553 \text{ nm}$). This depth nearly corresponds to the damage profile calculated by SRIM. The S values (W values) of 650 keV O implanted samples are higher (lower) than those obtained in the 285 keV O implanted samples which could be explained by their higher $W_{1/2}$ energy (5.3 keV) compared to the one in 285 keV O (4.3 keV). The higher $W_{1/2}$ energy introduces more vacancy clusters with larger size.

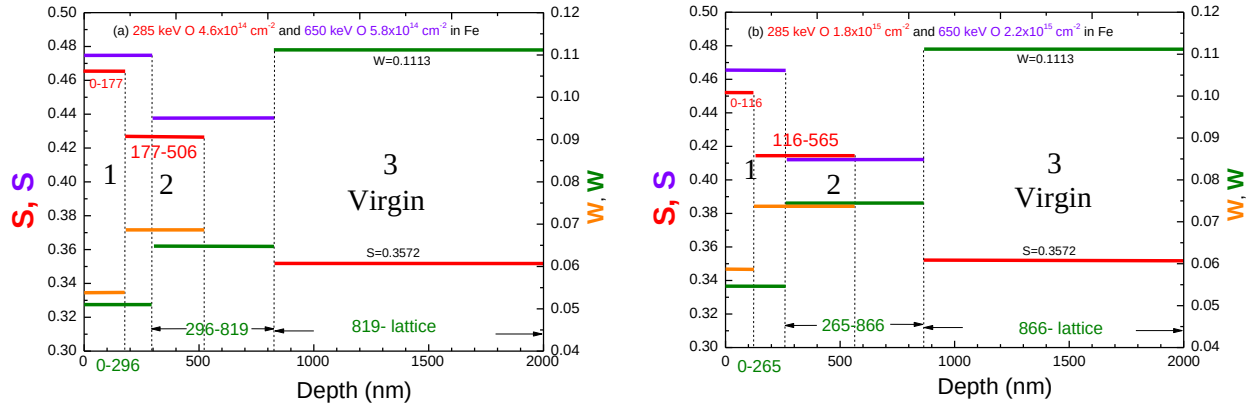


Figure IV-18: (a) The damage structure of three layers obtained by Vepfit for the Fe samples irradiated by 285 keV O at fluences $4.6 \times 10^{14} \text{ cm}^{-2}$ (red for S; orange for W) and 650 keV at $5.8 \times 10^{14} \text{ cm}^{-2}$ (purple for S; green for W) and (b) for the Fe samples irradiated by 285 keV O at fluences $1.8 \times 10^{15} \text{ cm}^{-2}$ (red for S; orange for W) and 650 keV at $2.2 \times 10^{15} \text{ cm}^{-2}$ (purple for S; green for W).

The implantations with heavy ions Y, Ti and O have induced vacancy clusters in Fe. Their size and concentration distribution depends on the nature and energy of the ions. For the heaviest ions Y and Ti damage is detected deeper than expected from the SRIM calculations with the most pronounced effect for the heaviest ions Y. In all cases the defects depth distribution shows a lower size of vacancy defects in the region of expected stopping of the incident ions. This effect of the ions on the damage formation is more pronounced for respectively O, Y and Ti.

IV.1.3. SIMS results in Y and O as implanted samples

a) Y implantation profile

The Y concentration profile in the sample implanted at the fluence of $3 \times 10^{15} \text{ cm}^{-2}$ is measured by SIMS as shown in Figure IV-19. The SIMS experiments conditions for obtaining the Y concentration profile are described in Chapter II section 4.3. It is compared to the Y profile calculated by SRIM and Marlowe code. Calculation with Marlowe code has modeled the sample as having an isotropic distribution of orientations. The peak of Y profile obtained by SIMS measurement has a maximum of 1663 appm at the depth of 201 nm. Compared to the SRIM calculation, it is closer to the surface as for the Marlowe calculations. It is interesting to notice that Y depth profile is broader in depth for SIMS measurements and Marlowe calculations than for SRIM calculations. This difference could be due to channeling of the heavy ions which is not expected in SRIM because the material is considered as amorphous.

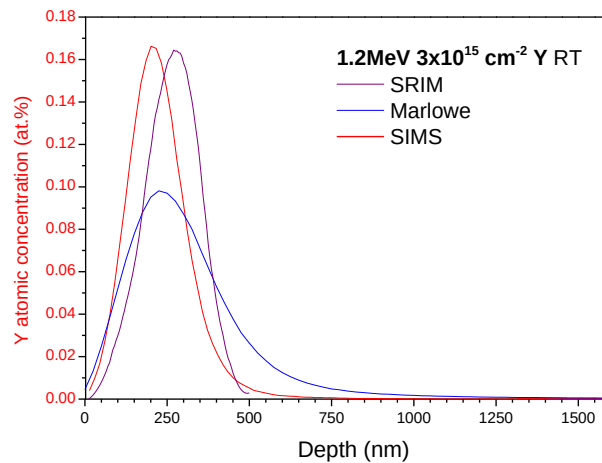


Figure IV-19: Y concentration profiles in 1.2 MeV Y implanted Fe at fluence $3 \times 10^{15} \text{ cm}^{-2}$ measured by SIMS and calculated by SRIM and Marlowe.

b) O implantation profile

The O concentration profiles in the Fe sample implanted with 285 keV O at the fluence of $2.7 \times 10^{15} \text{ cm}^{-2}$ and with 650 keV O at the fluence of $2.2 \times 10^{15} \text{ cm}^{-2}$ are measured by SIMS after ~ 235 days storage as shown in Figure IV-20 and Figure IV-21. The SIMS experiments conditions for obtaining the O concentration profile is described in Chapter II section 4.3. The peak of O profile obtained by SIMS measurement has a maximum of 2005 appm at the depth of 239 nm for the 285 keV O case. The peak of O profile obtained by SIMS measurement and Marlowe calculation is closer to the surface and also O profile stops deeper than the O profile calculated by SRIM. The same conclusion is obtained for the 650 keV O case but the Marlowe calculation is not performed for this implantation condition.

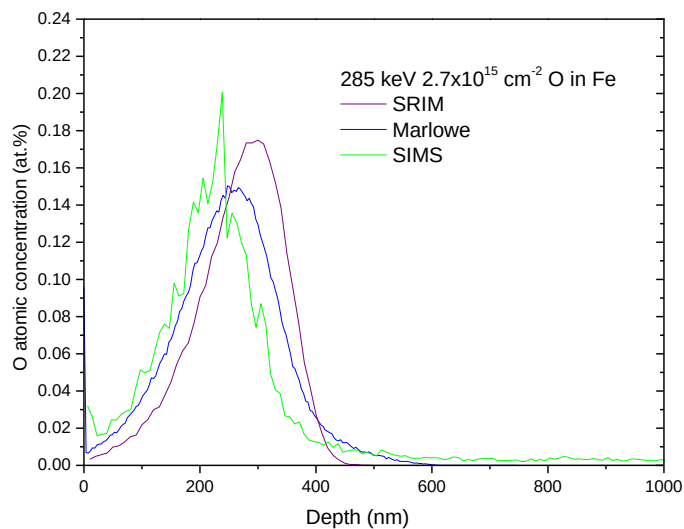


Figure IV-20: O concentration profiles in 285 keV O implanted Fe at fluence $2.7 \times 10^{15} \text{ cm}^{-2}$ measured by SIMS after ~ 235 days storage and calculated by SRIM and Marlowe.

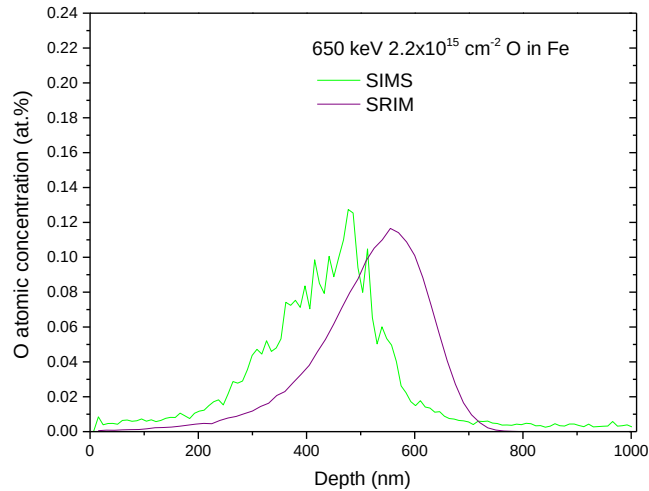


Figure IV-21: O concentration profiles in 650 keV O implanted Fe at fluence $2.2 \times 10^{15} \text{ cm}^{-2}$ measured by SIMS after ~ 235 days storage and calculated by SRIM.

IV.1.4. The irradiation temperature effect in Y implanted sample

As presented in section 1.2 of this chapter, the created vacancy cluster concentrations and size are higher in the LN_2 implanted Y sample than the RT implanted one. The vacancy cluster distribution is also thinner in the LN_2 implanted one.

One hypothesis has been proposed to explain the observed results. In the case of the implantation at room temperature, the single vacancies in Fe could migrate because the migration temperature of V in Fe is below the room temperature (-53 to 5°C)^[107]. In addition, the irradiation could induce the local heating of the sample. Thus, the vacancy clusters in Fe could also migrate if this temperature is higher than Vn migration temperature. For example, 150°C is attributed to the migration temperature of vacancy clusters of size less than ten vacancies proposed by kinetic Monte Carlo simulation^[108] and experiment^[109]. Thus, this type of vacancy clusters could migrate if the local temperature exceeds 150°C . In the case of the irradiation at low temperature (Liquid nitrogen), the single vacancies and vacancy clusters could not migrate and recombination is smaller. After irradiation the vacancy concentration is thus larger when irradiation is performed at LN_2 compared to the one at room temperature where recombination is large during irradiation. After irradiation the samples are stored at room temperature. The introduced single vacancies and small vacancy clusters become mobile during the storage and can form large vacancy clusters or recombine with interstitials. Because the concentration of vacancy defects is larger in LN_2 irradiated sample the agglomeration probability is higher compared to the room temperature irradiations. The limited migration of vacancy clusters in the LN_2 irradiated sample could also explain their thinner depth distribution (or thinner layer 3).

IV.1.5. Vacancy clusters depth profile and ion channeling in polycrystalline Fe

Figure IV-22 shows the $S(E)$ and $S(W)$ comparison for the Fe samples irradiated by 1.2 MeV Y at fluence $1 \times 10^{14} \text{ cm}^{-2}$, 700 keV Ti at fluence $5 \times 10^{14} \text{ cm}^{-2}$ and 285 keV O at fluence $4.6 \times 10^{14} \text{ cm}^{-2}$. It has to be noted that the $S(E)$ curves are different for the three ions implanted samples: the $S(E)$ curve of Y implanted sample begins to decrease at higher positron energy than that of Ti and O. Their damage structures obtained by Vepfit are compared in Figure IV-23 and the Vepfit results are compared in Table IV.9. A damage structure of 4 layers are found for 1.2 MeV Y at the fluence of $1 \times 10^{14} \text{ cm}^{-2}$, 2 layers for 700 keV Ti at fluence $5 \times 10^{14} \text{ cm}^{-2}$, 3 layers for 285 keV O at fluence $4.6 \times 10^{14} \text{ cm}^{-2}$. The forth layer for the Y case, the second layer for the Ti case and the third layer for the O case correspond to the Fe lattice non damaged region.

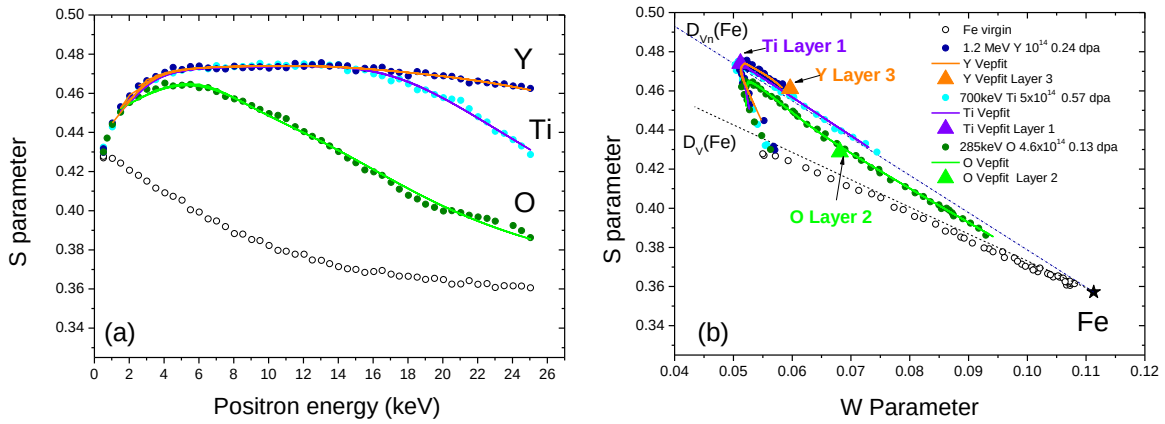


Figure IV-22: $S(E)$ and $S(W)$ comparison for the Fe samples irradiated by 1.2 MeV Y at fluence $1 \times 10^{14} \text{ cm}^{-2}$, 700 keV Ti at fluence $5 \times 10^{14} \text{ cm}^{-2}$ and 285 keV O at fluence $4.6 \times 10^{14} \text{ cm}^{-2}$.

As shown in Figure IV-22 (b), the vacancy clusters are detected in the third layer of Y implanted sample, the first layer of Ti one and the second layer of O one. It is noted that these vacancy clusters spreads up to $\sim 1662 \text{ nm}$ in Y implanted sample, $\sim 877 \text{ nm}$ in Ti implanted sample and $\sim 506 \text{ nm}$ in O implanted sample as shown in Figure IV-23. But SRIM calculations suggest that Y, Ti, O ions should all stop at $\sim 500 \text{ nm}$ with their respective incident energy. It indicates that positrons detect vacancy clusters deeper than expected by SRIM.

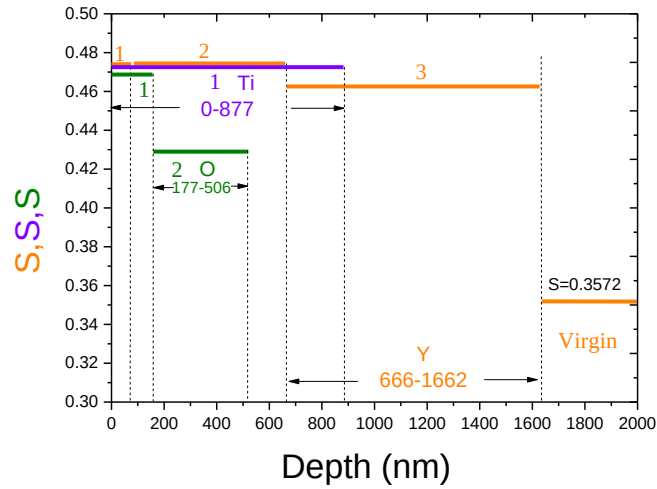


Figure IV-23: The comparison of damage structure for the Fe samples irradiated by 1.2 MeV Y at fluence $1 \times 10^{14} \text{ cm}^{-2}$ (orange), 700 keV Ti at fluence $5 \times 10^{14} \text{ cm}^{-2}$ (violet) and 285 keV O at fluence $4.6 \times 10^{14} \text{ cm}^{-2}$ (green).

Ions energy and fluence	Layer 1				Layer 2			
	S	W	L ⁺ (nm)	Thickness (nm)	S	W	L ⁺ (nm)	Thickness (nm)
1.2 MeV 1×10^{14} Y	0.4740	0.0502	10	58	0.4742	0.0520	12	666
700 keV 5×10^{14} Ti	0.4740	0.0512	11	877	virgin	virgin	Virgin	virgin
285 keV 4.6×10^{14} O	0.4642	0.0533	10	177	0.4276	0.0684	10	506
Ions energy and fluence	Layer 3							
	S	W	L ⁺ (nm)	Thickness (nm)				
1.2 MeV 1×10^{14} Y	0.4611	0.0597	15	1662				
700 keV 5×10^{14} Ti	/	/	/	/				
285 keV 4.6×10^{14} O	virgin	virgin	virgin	virgin				

Table IV.9: Vepfit results comparison for the Fe samples irradiated by 1.2 MeV Y at fluence $1 \times 10^{14} \text{ cm}^{-2}$, 700 keV Ti at fluence $5 \times 10^{14} \text{ cm}^{-2}$ and 285 keV O at fluence $4.6 \times 10^{14} \text{ cm}^{-2}$.

Channeling of ions in crystalline solids which is not taken into account in SRIM code could explain this observation. Kinomura et al. have observed this channeling phenomenon for 150 keV Ar implantation in polycrystalline Fe with grain sizes of the order of $10 \mu\text{m}$ [194]. The implanted Fe samples in this study are polycrystalline with mean grain sizes of 20 - $100 \mu\text{m}$ dramatically larger than the projection range of the Y, Ti and O ions (260 nm). Calculations with Marlowe code in which the sample has been modeled as having an isotropic distribution of orientations show that channeling of the Y ions is not negligible in these implantation conditions. It shows that one part of the 1.2 MeV Y ions could be also implanted in the third layer of the Fe sample. This channeling effect of Y atoms in Fe depends on the grain orientation which has been shown in Chapter 2, Section 4.3. The average Y profile obtained by SIMS in Figure IV-24 also shows that one part of the 1.2 MeV Y ions is implanted in the third layer of the Fe sample.

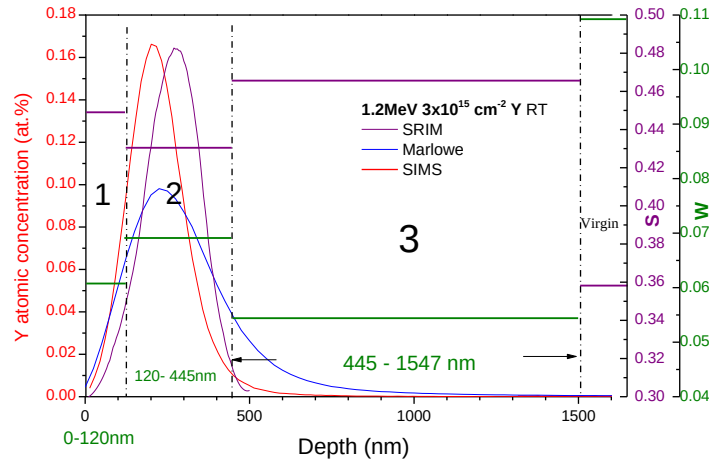


Figure IV-24: Y concentration profiles in 1.2 MeV Y implanted Fe at fluence $3 \times 10^{15} \text{ cm}^{-2}$ measured by SIMS and calculated by SRIM and Marlowe which are superimposed with VEPFIT results.

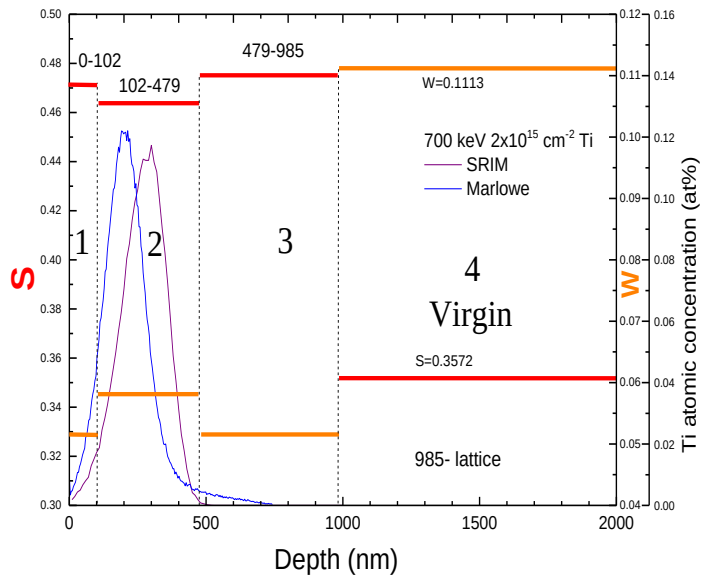


Figure IV-25: Ti concentration profiles in 700 keV Ti implanted Fe at fluence $2 \times 10^{15} \text{ cm}^{-2}$ calculated by SRIM and Marlowe which are superimposed with VEPFIT results.

This effect is also observed in the pure iron implanted with 700 keV Ti at fluence $2 \times 10^{15} \text{ cm}^{-2}$ as shown in Figure IV-25. Vacancy clusters spreads up to $\sim 985 \text{ nm}$. In this case, calculations with Marlowe code also show that one part of the 700 keV Ti ions is implanted in the third layer of the Fe sample. Compared to the case of 1.2 MeV Y implantation which has the same projection range calculated by SRIM, this region is less deep in the 700 keV Ti implantation. It means that the channeling of Ti ions is less pronounced than for Y ions.

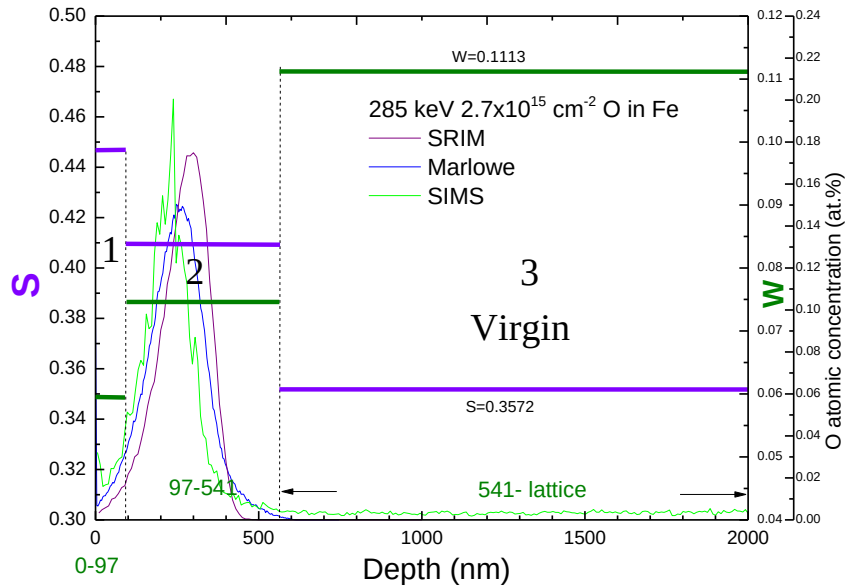


Figure IV-26: O concentration profiles in 285 keV O implanted Fe at fluence $2.7 \times 10^{15} \text{ cm}^{-2}$ measured by SIMS and calculated by SRIM and Marlowe which are superimposed with VEPFIT results.

In the case of 285 keV O implantations in Fe, the channeling effect is even less pronounced than that of 700 keV Ti implantations as shown in Figure IV-26. Vacancy clusters spreads up to ~ 541 nm which is just slightly deeper than depth of 500 nm calculated by SRIM. Marlowe calculation and SIMS measurement of 285 keV O implantation profile in Fe also correspond well to the damage structure.

In conclusion, the ions channeling effect decreases with the ion masses as illustrated for the Y, Ti, O cases.

But it has to be noticed that the implanted Y and Ti are detected not as deep as the vacancy clusters. Thus, another mechanism induces vacancy clusters at unexpected depth. It could be due to the migration of vacancy defects (single vacancies and small clusters). Their migration during the irradiation has been confirmed by the deeper vacancy clusters depth profile found in room temperature implanted sample compared to the implantation performed at low temperature (LN_2) as presented in section 1.4 of this chapter.

IV.1.6. Y, Ti, O ions- Vacancy interactions

a) Y effect on vacancy defects formation

As presented in the previous section, the $S(E)$ values decrease with the implanted Y fluences which indicates that Y ions are involved in the damage formation. A damage structure of four layers is found for the Y implanted samples. The vacancy clusters are found in the three first layers and the fourth layer corresponds to the Fe lattice that means it is not damaged. The size or concentration of vacancy clusters is smaller in layer 2 than the one in layer 1 and 3.

The Y concentration profile in the sample implanted at the fluence of $3 \times 10^{15} \text{ cm}^{-2}$ measured by SIMS is superimposed on the defect profile obtained by VEPFIT as shown in Figure IV-27. The layer 2 where the vacancy size and concentration decrease falls in the zone where the Y concentration is the highest. We can conclude that yttrium is involved in damage evolution. Two hypotheses are proposed to explain the experimental results. The first is that the $V_m - Y_n$ complexes are formed. The migration temperature of V in bcc Fe is below the room temperature (-53 to 5°C) as suggested by Takaki et al. [107]. But the mobility of vacancy could be reduced due to their binding to Y as it is expected from the calculation ($E_{b-1NN}(V - Y_{\text{sub}}) = 1.45 \text{ eV}$ [195]). This binding could limit the agglomeration of vacancies. The diffusivity of Y in Fe has been estimated to be about six orders lower than that of tracer Fe atoms at 273 K experimentally as shown in Figure IV-29 [63, 64]. Thus, the high binding energy between Y and vacancy and also the low diffusivity of Y could reduce the vacancy migration in the presence of Y ions. The mean size of free volume of the vacancy complexes in this region is low because the position of the SW point for layer 2 in the sample implanted at the highest fluence slightly above the straight line corresponding to annihilation in single vacancies. They could be 4- 5 vacancies as the ones observed in ODS alloys by positrons [196]. The $V_m - Y_n$ complex configurations have been calculated by Caroline Barouh, PhD student in CEA Saclay [197]. First Y is located in the vacancy in a substitutional position in the complexe V-Y and in one of them for $V_2 - Y$ one. As shown in Figure IV-28, the Y atoms prefer to stay in the center of vacancy clusters V_m when $m = 3 - 6$ vacancies. It has to be noted that these configurations could give a positron signal underestimating the vacancy clusters size if compared to a 3D- configuration of a pure cluster with the same number of vacancies. For example, positron trapped in the Y- V_4 complex would give a signal of vacancy size equivalent to 2 vacancies instead of 4 vacancies.

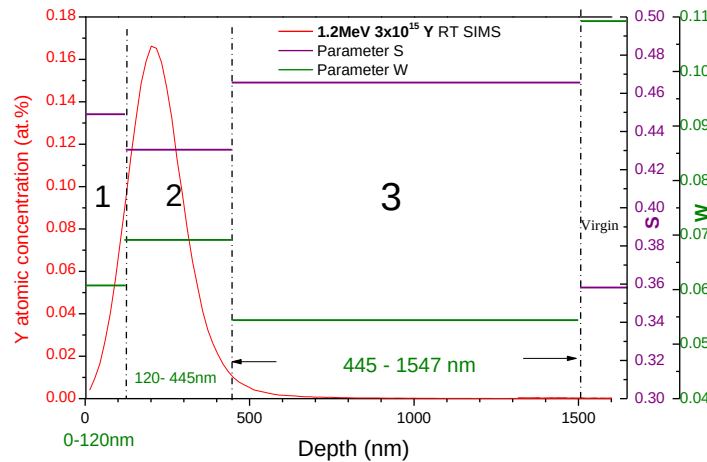


Figure IV-27: Y concentration profiles in 1.2 MeV Y implanted Fe at fluence $3 \times 10^{15} \text{ cm}^{-2}$ measured by SIMS superimposed with VEPFIT results of damage structure (purple for S; green for W).

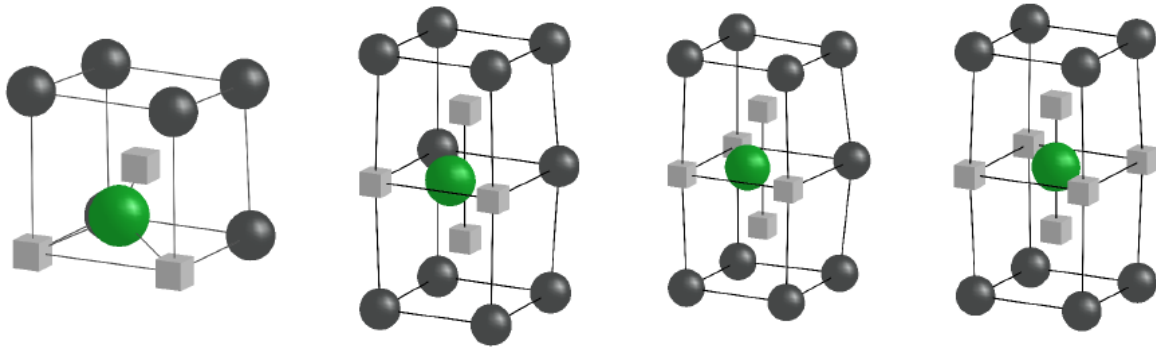


Figure IV-28: The V_m-Y_n complex configurations ($n=1$, $m=3-6$) calculated by Caroline Barouh^[197] (PhD student in CEA Saclay).

The second hypothesis that could explain the PAS results is the formation of Y_m-X_n precipitates (where $X=Y$, $O...$). The positron affinity for Y (-5.31 eV^[86]) is greater in absolute value than the Fe one (-3.84 eV^[86]) making the trapping of positrons at Y precipitates possible. The maximum Y concentrations measured by SIMS for the fluences of 2×10^{15} and 3×10^{15} cm⁻² are 1100 and 1660 at. ppm respectively which are higher than its solubility in iron (290 atomic ppm (at. ppm) in iron at 800°C^[128]). Although the excess vacancy increases the solubility, precipitates could exist. As presented in Chapter II section 3.1, the Y precipitates containing three or more Y atoms could be detected by the positrons. The positron studies of Alinger et al.^[87] and Ortega et al.^[198] shown that precipitate Y_2O_3 could be detected by positron. The concentration of O in the as-received Fe samples is 169 appm as given by the supplier but 20 appm as measured by SIMS, the precipitate Y_2O_3 could thus be possibly detected in the present study. The most plausible explanation for the experimental results is that a combination of both hypotheses, it is to say, the formation of the complexes V_m-Y_n and precipitates Y_m-X_n leads to a decrease in the size and concentration of vacancy clusters.

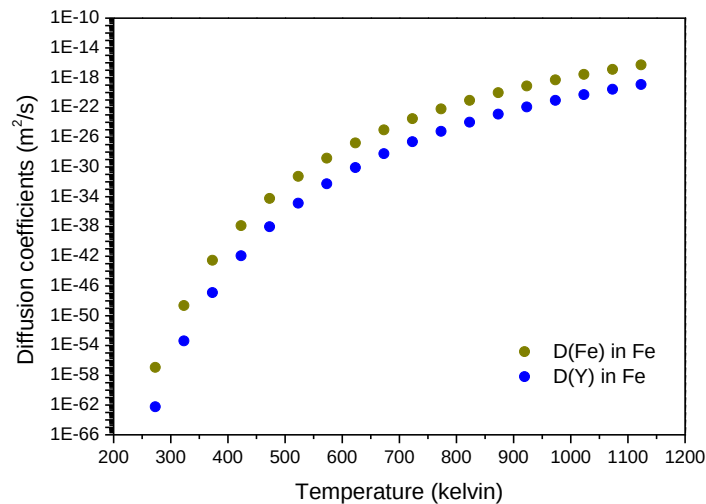


Figure IV-29: The iron and yttrium diffusion coefficient in iron by fitting a classical nucleation-growth-coarsening model to small-angle neutron scattering data^[63, 64].

b) Ti, O effect on vacancy defects formation compared to Y effect

The SIMS measurement of Ti concentration profiles has not been performed in this thesis. But the Ti profile in 700 keV Ti implanted Fe sample at fluence $2 \times 10^{15} \text{ cm}^{-2}$ calculated by SRIM and Marlowe shows that the layer 2 where the vacancy size and concentration decrease, falls in the zone where the Ti concentration is the highest as illustrated in Figure IV-30. As in the Y implanted samples, we could conclude that Ti is involved in damage evolution. One hypothesis is proposed to explain the experimental results: the $V_m\text{-Ti}_n$ complexes are formed. A positive binding energy also exists between vacancy and Ti although the value is relatively low ($E_{b-1NN}(V\text{-Ti}_{\text{sub}}) = 0.26 \text{ eV}$ [65, 126]) compared to the one between V- Y ($E_{b-1NN}(V\text{-Y}_{\text{sub}}) = 1.45 \text{ eV}$ [195]). Thus, the mobility of vacancy could be reduced by binding with Ti but this mobility decrease should be less efficient than the one obtained for Y. This could explain why the S decrease observed when the Ti fluence increase is less pronounced than for Y implanted samples. The maximum Ti concentrations calculated by SRIM for the fluences of 2×10^{15} and $3 \times 10^{15} \text{ cm}^{-2}$ are 1170 and 1760 at. ppm respectively. Contrary to the Y implanted samples, the Ti precipitations in these implanted samples should not influence the positron signal because the negative formation energy of Ti in Fe ($E_f(\text{Ti}_{\text{sub}}) = -0.80 \text{ eV}$ [126, 127], -0.92 eV [83]) implies that the solubility of Ti in Fe should be high.

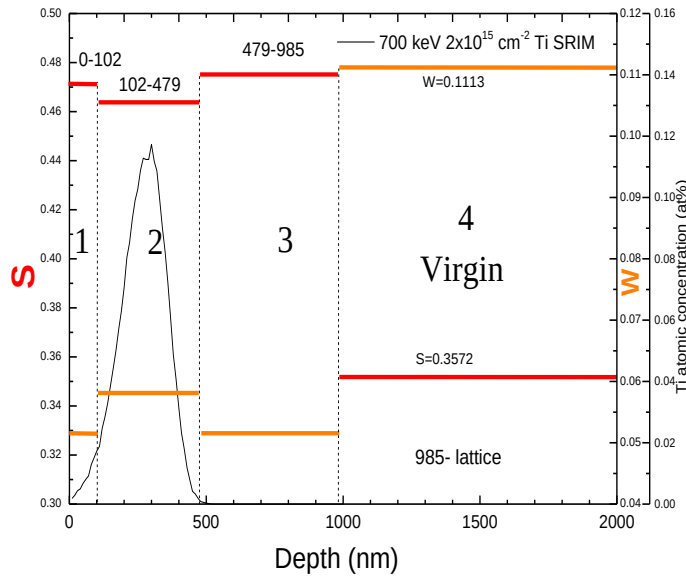


Figure IV-30: Ti concentration profiles in 700 keV Ti implanted Fe at fluence $2 \times 10^{15} \text{ cm}^{-2}$ calculated by SRIM superimposed with VEPFIT results of damage structure (red for S; orange for W).

After ~ 235 days storage at room temperature following irradiation, the samples implanted with O at high fluences become stable. The decrease of S parameter with the O fluence is also observed as presented in Figure IV-15. The O profile in 285 keV O implanted Fe sample at the fluence of $2.7 \times 10^{15} \text{ cm}^{-2}$ measured by SIMS shows that the layer 2 where the vacancy size and concentration decrease falls in the zone where the O concentration is the highest as illustrated in Figure IV-31. O is involved in damage evolution. Two hypotheses are proposed to explain the experimental results.

The first is that the V_m - O_n complexes are formed. A high binding energy is also obtained by calculation for V- O_{int} complex even in 2NN position ($E_{b-1NN}(O_{int}-V) = 1.65$ eV^[126] 1.45 eV^[81]; $E_{b-2NN}(O_{int}-V) = 0.75$ eV^[126] 0.60 eV^[81]). This binding could limit the agglomeration of vacancies. The positron results suggest that the mean size of free volume in V_m - O_n complex should be low, close to the one of the single vacancy. It could be for example O- single vacancy, because the position of the SW point for layer 2 in the sample implanted at the highest fluence is slightly above $D_V(Fe)$ line. Some V_m - O_n complex configurations have been calculated by Caroline Barouh et al.^[177] as shown in Figure IV-32. For example, the V_4 - O_2 complex has a planar structure which would also give a signal of vacancy size equivalent to 2 vacancies instead of 4 vacancies. The second hypothesis that could explain the PAS results is the detection of iron oxide phase which always exists in Fe matrix. The most plausible explanation for the experimental results is that a combination of these two hypotheses.

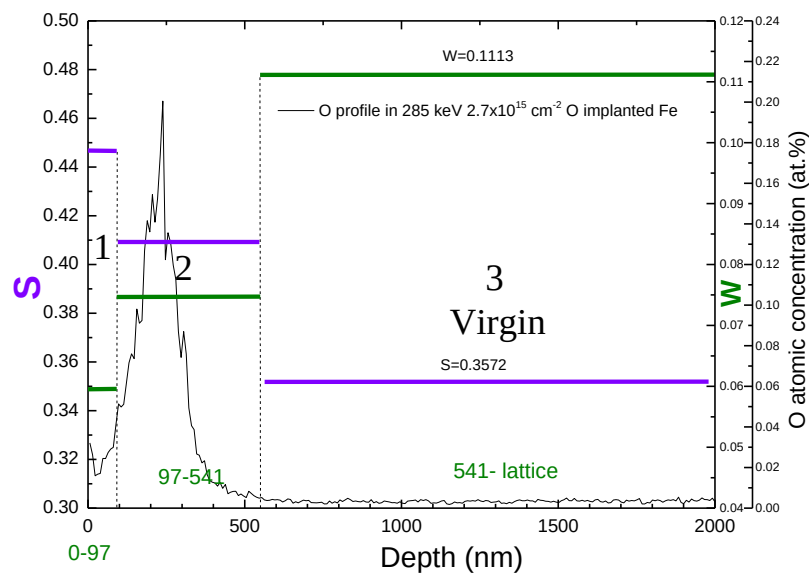


Figure IV-31: O concentration profiles in 285 keV $2.7 \times 10^{15} \text{ cm}^{-2}$ O implanted Fe measured by SIMS after ~ 235 days storage superimposed with VEPFIT results of damage structure.

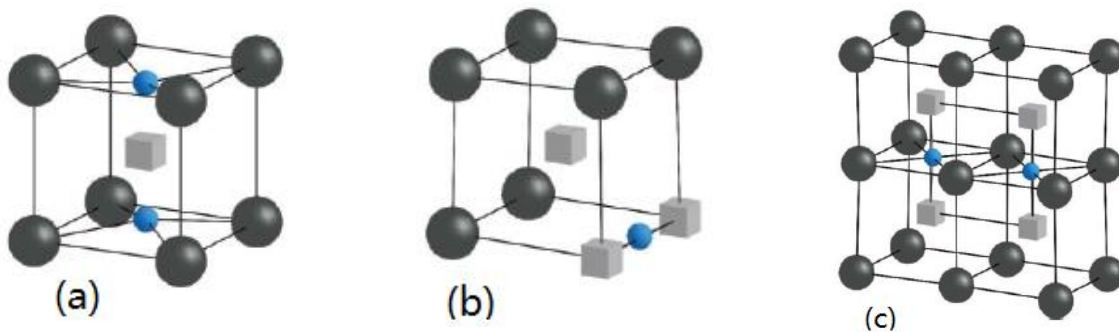


Figure IV-32: Schematic representation of the lowest energy clusters configurations found for: (a) VO_2 (b) V_3O (c) V_4O_2 . O atoms are represented by blue spheres, Fe atoms by black spheres, and V by grey cubes^[177].

As shown in Figure IV-33, the O concentration profile in 650 keV $2.2 \times 10^{15} \text{ cm}^{-2}$ O implanted Fe measured by SIMS is also superimposed with Vepfit results of damage structure. Most O atoms are also located in the layer 2 where the decrease of vacancy concentration and size is detected. This observation also confirms the hypothesis that the $V_m\text{-O}_n$ complex is formed and the detection of iron oxide phase.

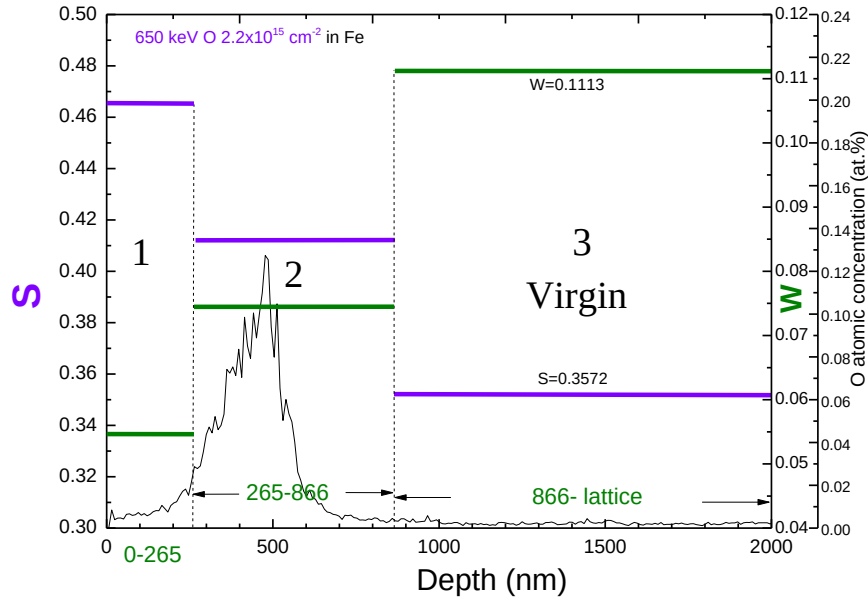


Figure IV-33: O concentration profile in 650 keV $2.2 \times 10^{15} \text{ cm}^{-2}$ O implanted Fe measured by SIMS after ~ 235 days storage superimposed with VEPFIT results of damage structure.

It has been shown that the vacancy defects distribution is affected by the presence of the Y, Ti and O. The size of the vacancy defects decreases in the region where the elements concentration is the highest. Interactions of these elements with vacancies are expected by DFT calculations with the highest binding energy for Oxygen and Yttrium for which the larger effect on the vacancy size distribution is observed. This binding can lead to the formation of $V_m\text{-X}_n$ ($X=Y, O, Ti$) complexes that could reduce the V migration and agglomeration during implantations.

IV.1.7. Conclusions

In this section, the creation of vacancy defects with heavy ions Y, Ti and O has been studied.

Vacancy clusters are detected in all implanted Fe samples whatever the nature of the ion, their energy, fluence and irradiation temperature. The vacancy concentration or size is the highest for the low fluences and the depth distribution shows channelling of the ions and vacancy migration during implantation. For high fluences there is a layer where the vacancy defects are smaller which corresponds to the implantation peak as measured by SIMS. It indicates the Y, Ti and O elements influence the defects formation. It could be due to the interaction that are possible between vacancy and the element which can lead to their binding and a reduced migration and consequently agglomeration of vacancies. This

effect is less pronounced for Ti for which the binding energy with vacancy is the lowest in this layer where some V_n-X_m ($X=Y, Ti, O$) can be detected.

IV.2. Evolution of vacancy defects distribution after annealing in Y and O implanted samples

In this section, the evolution of vacancy defects distribution after annealing in Y and (including during the RT storage) O implanted samples is discussed. The annealing experiments were performed at temperatures from 100°C up to 750°C under vacuum during 1 hour with a step of 50°C for the Fe sample implanted with 1.2 MeV Y at the fluence of $3 \times 10^{15} \text{ cm}^{-2}$. The effect of storage at room temperature has been firstly studied for O implanted sample. The annealing experiments were also performed at temperatures from 100°C up to 550°C under vacuum during 1 hour with a step of 50°C for the sample implanted with 650 keV O at the fluence of $2.2 \times 10^{15} \text{ cm}^{-2}$ stored at RT during ~ 235 days. The positron experiments results are then presented and the Yttrium and Oxygen effects on annealing behavior of vacancy defects are discussed with the help of Y, O depth profiles obtained by SIMS after annealing.

IV.2.1. PAS results in post- irradiation annealed samples

a) Effect of annealing in Y implanted samples

In order to study the post-irradiation annealing behavior of V defects in Y implanted Fe samples and their interaction with the solute Y, the annealing experiments were performed at temperatures from 100°C up to 750°C under vacuum during 1 hour with a step of 50°C. The 100°C up to 550°C annealing experiments are performed in situ in SPBDB machine developed by CEMHTI Orleans laboratory and the sample is measured with positrons after each annealing. The 600°C up to 750°C annealing experiments are performed in electron bombardment furnace and the sample is measured with positrons just after 750°C annealing. The Fe sample implanted with 1.2 MeV Y at the fluence of $3 \times 10^{15} \text{ cm}^{-2}$ is chosen because the Y concentration is the highest. In this case, the effect of yttrium on vacancy clusters annealing behavior should be revealed more easily.

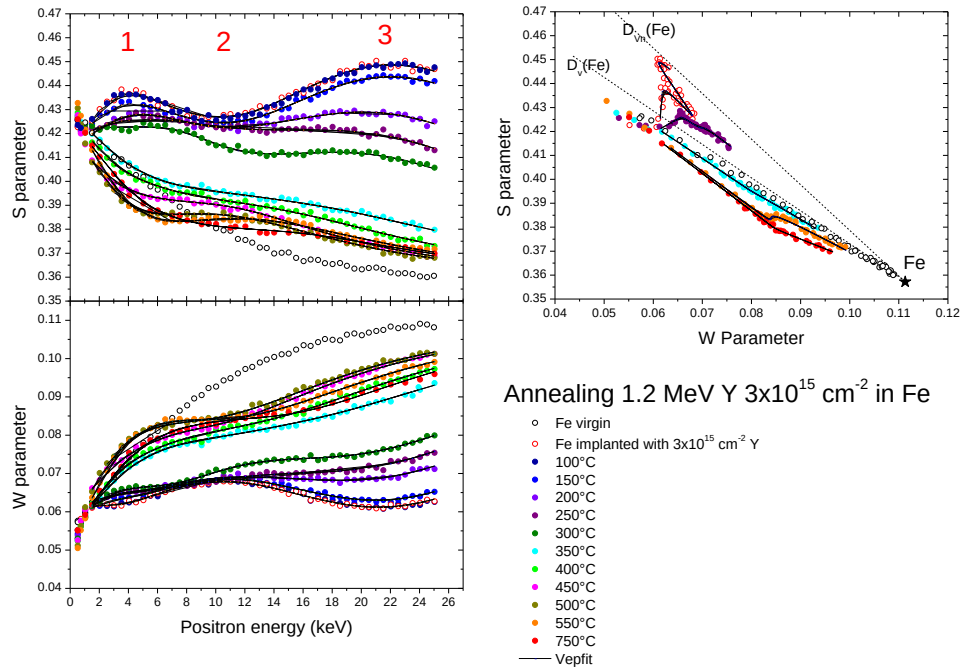


Figure IV-34: S(E), W(E) and S(W) for the Fe sample irradiated with 1.2 MeV Y at $3 \times 10^{15} \text{ cm}^{-2}$ and annealed at different temperature up to 750°C and Vepfit results.

The evolutions of S(E), W(E) and S(W) for the Fe sample implanted with 1.2 MeV Y at $3 \times 10^{15} \text{ cm}^{-2}$ and annealed at different temperatures up to 750°C are presented in Figure IV-34. For S(W) curves, only the cases of the as-implanted state and states after annealing at the four following temperatures 250°C, 350°C, 550°C and 750°C are plotted in order to get a clear illustration of the evolutions. The Vepfit results are also shown as the solid lines which show that the experimental results are well fitted.

There is no difference observed after annealing at 100°C compared to the as implanted sample. From 150°C annealing, the S(E) values in regions 1 and 3 -which are roughly indicated in the figure- begin to decrease whereas their decrease in region 2 where locates the Y peak is very limited. At 200°C and 250°C, the S(E) values decrease in regions 1 and 3 is much more pronounced and the decrease in region 2 is still weak. The first evident S(E) decrease in region 2 occurs at 300°C. At 350°, S(E) values continue to decrease in all the three regions and S(W) points are located below the $D_v(\text{Fe})$ line. S(E) values continue to decrease at 400°C. From 450°C, one plateau of S(E) values is formed in region 2. This plateau is more evident after 500°C and 550°C annealings and the S(E) values for these two annealings are very similar. After 750°C annealing, S(E) values slightly decrease and S(W) points remain below the $D_v(\text{Fe})$ line.

Vepfit results for all the annealed states up to 750°C are reported in Table IV.10. A damage structure of four layers is obtained for all the annealed states up to 550°C as in the as-implanted state. In contrary, a two layers damage structure is found for 750°C annealed state. The damage structures for 250°C, 350°C, 550°C and 750°C annealed states compared to the as-implanted state are shown in Figure IV-35.

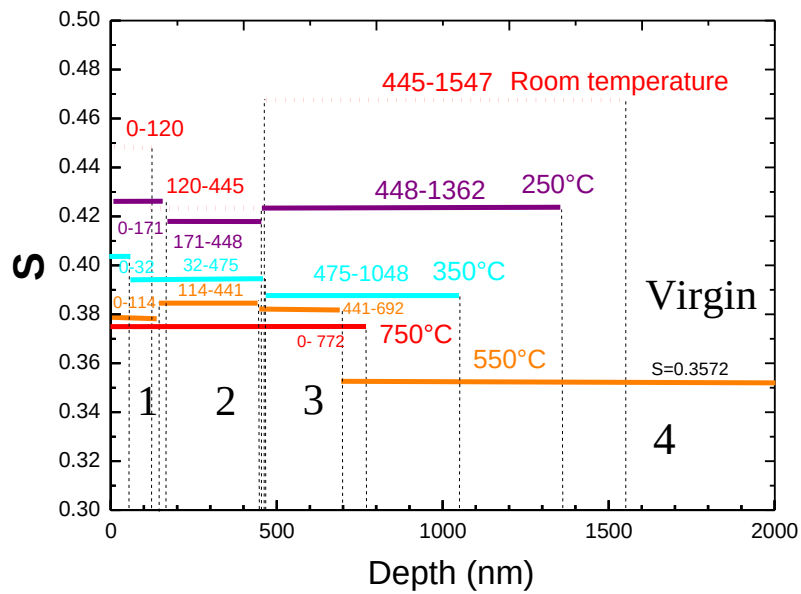


Figure IV-35: Damage depth structure of four layers obtained by Vepfit for the Fe sample irradiated with 1.2 MeV Y at $3 \times 10^{15} \text{ cm}^{-2}$ (red short dot line) and annealed at 250°C (purple), 350°C (cyan), 550°C (orange) and 750°C (red).

The S annihilation characteristics of the first three layers decrease respectively with the temperature. The layer 2 where locates the Y peak always stops at $\sim 455 \text{ nm}$ as in the as-implanted state. But the thickness of the layer 3 where the vacancy clusters exist decreases with the temperature. The post irradiation annealing behaviors are different for the first three layers. Thus, they are discussed respectively in section IV.2.3.

1.2 MeV 3×10^{15} $\text{cm}^{-2} \text{Y}$	Layer 1				Layer 2			
	S	W	L^+ (nm)	Thickness (nm)	S	W	L^+ (nm)	Thickness (nm)
RT	0.4493	0.0604	28	120	0.4209	0.0693	15	445
150°C	0.4345	0.0641	11	98	0.4206	0.0702	25	510
200°C	0.4299	0.0657	14	125	0.4179	0.0708	30	448
250°C	0.4264	0.0659	9	171	0.4186	0.0711	30	448
300°C	0.4228	0.0669	9	210	0.3964	0.0793	40	442
350°C	0.4029	0.0745	22	32	0.3937	0.0808	45	475
400°C	0.3971	0.0774	20	103	0.3896	0.0833	50	486
450°C	0.3907	0.0781	20	64	0.3901	0.0838	50	465
500°C	0.3831	0.0835	16	114	0.3877	0.0849	50	422
550°C	0.3792	0.0855	20	114	0.3862	0.0840	60	441
750°C	0.3787	0.0852	38	772	virgin	virgin	virgin	virgin
1.2 MeV 3×10^{15} $\text{cm}^{-2} \text{Y}$	Layer 3							
	S	W	L^+ (nm)	Thickness (nm)				
RT	0.4652	0.0543	10	1547				
150°C	0.4593	0.0575	15	1483				
200°C	0.4354	0.0665	20	1426				
250°C	0.4224	0.0708	25	1362				
300°C	0.4171	0.0737	30	1271				
350°C	0.3847	0.0892	55	1048				
400°C	0.3805	0.0920	60	823				
450°C	0.3661	0.1026	65	885				
500°C	0.3686	0.1005	100	726				
550°C	0.3837	0.0888	100	692				
750°C	/	/	/	/				

Table IV.10: Vepfit results for the Fe sample irradiated with 1.2 MeV Y at $3 \times 10^{15} \text{ cm}^{-2}$ and annealed at different temperature up to 750°C.

b) Effect of annealing in O implanted Fe samples

As presented in the section 1.2, the S(E) curves obtained for the O implanted samples at high fluences evolve with the storage time at room temperature. Thus, the effect of annealing at room temperature has been firstly studied in the following. Then the isochronal effect at different temperatures will be developed.

i) Storage at room temperature

Figure IV-36 shows S(E) and S(W) for the Fe samples irradiated by 650 keV O at the fluence of $2.2 \times 10^{15} \text{ cm}^{-2}$ and stored during 60 days and 236 days at room temperature. A damage structure of 3 layers is obtained by Vepfit and the obtained annihilation characteristics are reported in Table IV.11. The third layer corresponds to the Fe lattice and thus it is not reported. The S values obtained after 236 days storage increase compared to the ones obtained after 60 days. The S(W) point extracted for the layer 1 of the 236 days stored sample is closer to the $D_{\text{vn}}(\text{Fe})$ line and farer from the Fe lattice point than the one

obtained in the 60 days stored sample. It indicates that the concentration and size of vacancy clusters in layer 1 increase after 236 days storage. The $S(W)$ point of layer 2 in 60 days stored sample is situated on the $D_V(\text{Fe})$ line which means the detection of vacancy defects with free volume close to the single vacancy. The one in 236 days stored sample is slightly above the $D_V(\text{Fe})$ line and farer from the Fe lattice point. It indicates that the size of vacancy in layer 2 also slightly increases after 236 days storage. The thickness of layer 2 is 100 nm narrower in the 236 days stored sample compared to the one in 60 days stored sample. It indicates that a part of vacancy defects have migrated to the surface after 236 days storage. It will be discussed in section 2.2 and 2.3.

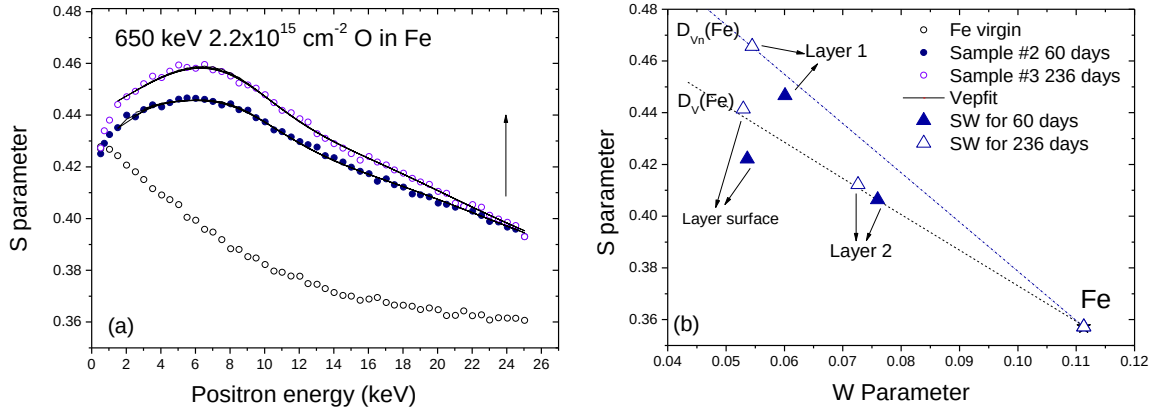


Figure IV-36: $S(E)$ and $S(W)$ for the Fe samples irradiated by 650 keV O at fluences $2.2 \times 10^{15} \text{ cm}^{-2}$ and stored during 60 days and 236 days at room temperature.

650 keV 2.2×10^{15} cm^{-2} O	Layer 1				Layer 2			
	S	W	L^+ (nm)	Thickness (nm)	S	W	L^+ (nm)	Thickness (nm)
60 days	0.4466	0.0601	10	264	0.4064	0.0760	10	957
236 days	0.4657	0.0545	43	265	0.4122	0.0726	15	866

Table IV.11: Vepfit results for implanted Fe with 650 keV O ions at $2.2 \times 10^{15} \text{ cm}^{-2}$ and stored during 60 days and 236 days at room temperature.

ii) Isochronal annealings at the temperature range from 100 to 550°C

In order to study the post-irradiation annealing behavior of V defects in O implanted Fe samples at higher temperature than room temperature, the annealing experiments were performed at temperatures from 100°C up to 550°C under vacuum during 1 hour with a step of 50°C for the samples stored at RT during ~ 235 days. The 100°C up to 550°C annealing experiments are performed in situ in the SPBDB machine developed by CEMHTI Orleans laboratory and the sample is measured with positron after each annealing except for the 450°C and 500°C annealings. The Fe sample implanted with 650 keV O at the fluence of $2.2 \times 10^{15} \text{ cm}^{-2}$ is chosen because it gives a relative deeper projection range (510 nm) which should facilitate the observation of O diffusion. In this case, the effect of oxygen on vacancy annealing behavior should be revealed more easily.

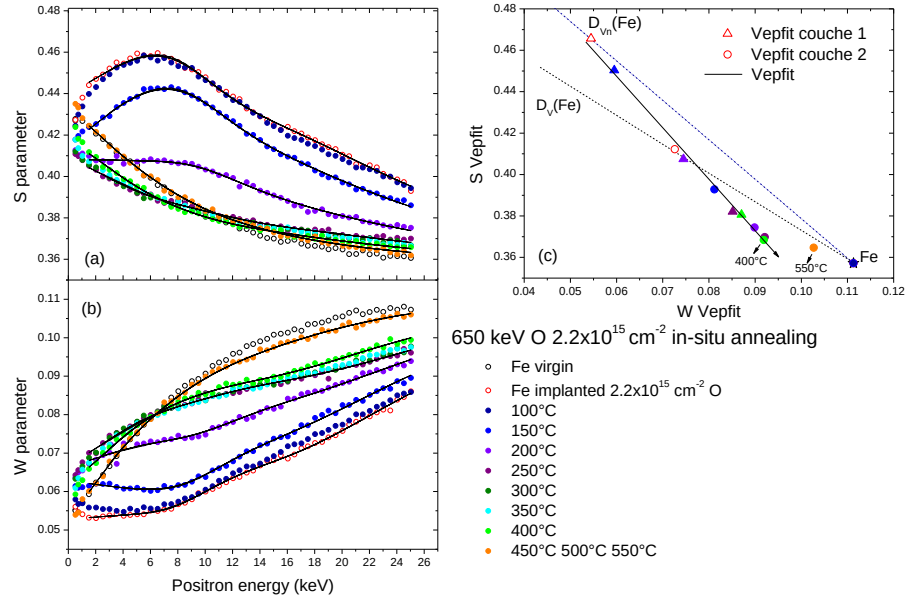


Figure IV-37: $S(E)$, $W(E)$ and $S(W)$ for the Fe sample irradiated with 650 keV O at $2.2 \times 10^{15} \text{ cm}^{-2}$ and annealed at different temperature up to 550°C and Vepfit results.

The evolutions of $S(E)$, $W(E)$ and $S(W)$ for the Fe sample implanted with 650 keV O at the fluence of $2.2 \times 10^{15} \text{ cm}^{-2}$ and annealed at different temperatures up to 550°C are presented in Figure IV-37. The Vepfit results are also shown as the solid lines in $S(E)$ and $W(E)$ plots and show that the experimental results are well fitted. A damage structure of three layers is obtained by Vepfit for all the annealed states up to 550°C as in the as-implanted state shown in Figure IV-38. The Vepfit results are reported in Table IV.12. Only the results for the first two layers are presented and the third layer corresponds to the Fe lattice. The $S(W)$ characteristics in layer 1 and 2 obtained by Vepfit are illustrated in figure IV.37-c).

There is no difference observed after annealing at 100°C compared to the as implanted sample. $S(E)$ values begin to decrease from 150°C to 250°C. The decrease of $S(E)$ values from 300°C to 400°C are very slight. It is noted that the S annihilation characteristics of the first two layers decrease respectively with the temperature. The $S(W)$ points change of layer 1 and 2 up to 400°C follows the same line which indicates that only one regime exists. The $S(E)$ values at low positron energies increase after 550°C annealing which indicates an increase of positron diffusion length. The effective diffusion length of positrons obtained for 550°C annealed sample is $\sim 150 \pm 3 \text{ nm}$ and the corresponding $S(W)$ point moves towards the Fe lattice point. These results indicate that almost all the defects are recovered after 550°C annealing.

The largest quantity of O atoms is located in layer 2 and a small quantity is located in layer 1 in the as-implanted state. After 550°C annealing, the O depth profile is measured by SIMS as presented in section IV.2.2. The layer 2 depth increases at 150°C, 250°C and 400°C. And it decreases at 400°C and 550°C. It should also be noted that the layer 1 depth becomes very limited after 550°C. The post irradiation annealing behaviors are studied respectively for the first two layers as presented in section 2.3.

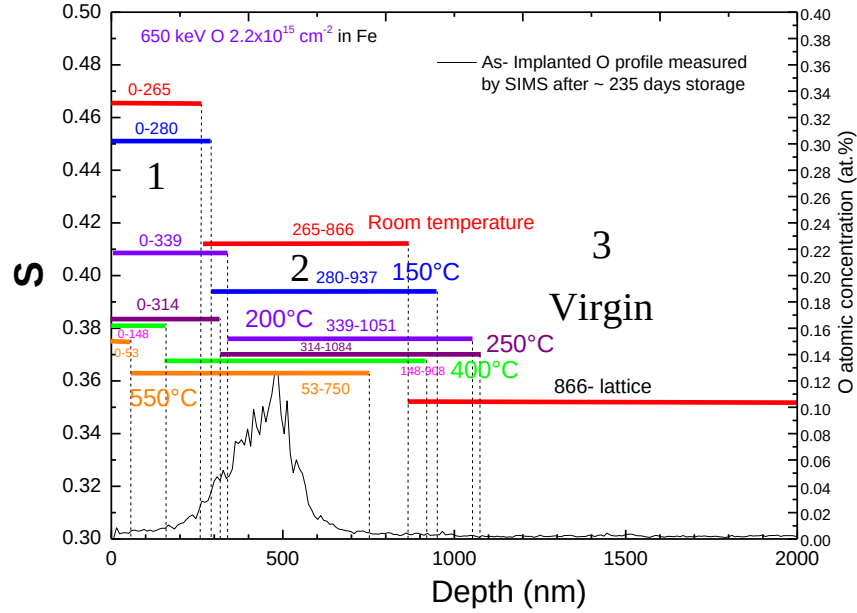


Figure IV-38: A damage structure of three layers obtained by Vepfit for the Fe sample irradiated with 650 keV O at $2.2 \times 10^{15} \text{ cm}^{-2}$ (red) and annealed at 150°C (blue), 200°C (violet), 250°C (purple), 400°C (green) and 550°C (orange).

650 keV 2.2×10^{15} cm^{-2} O	Layer 1				Layer 2			
	S	W	L^+ (nm)	Thickness (nm)	S	W	L^+ (nm)	Thickness (nm)
RT after 236 days	0.4657	0.0545	43	265	0.4122	0.0726	15	866
150°C	0.4503	0.0595	45	280	0.3928	0.0812	50	937
200°C	0.4074	0.0745	50	339	0.3744	0.0899	60	1051
250°C	0.3821	0.0852	60	314	0.3698	0.0921	80	1084
400°C	0.3806	0.0871	61	148	0.3684	0.0919	135	908
550°C	0.3768	0.1031	63	53	0.3647	0.1027	150	750

Table IV.12: Vepfit results for the Fe sample irradiated with 650 keV O at $2.2 \times 10^{15} \text{ cm}^{-2}$ after ~ 235 days storage at room temperature and annealed at different temperature up to 550°C.

IV.2.2. Y, O depth profiles after annealing measured by SIMS

a) Y depth profile after annealing

The Y concentration profile for the 1.2 MeV Y implanted Fe sample at the fluence of $3 \times 10^{15} \text{ cm}^{-2}$ has also been measured by SIMS after annealing at 550°C. As shown in Figure IV-39, the width of the Y profile after 550°C annealing is the same as the one measured in the as-implanted state. The slight shift of profiles peak is due to the depth resolution of SIMS measurements. Thus, it is concluded that the Y concentration profile does not change after 550°C annealing.

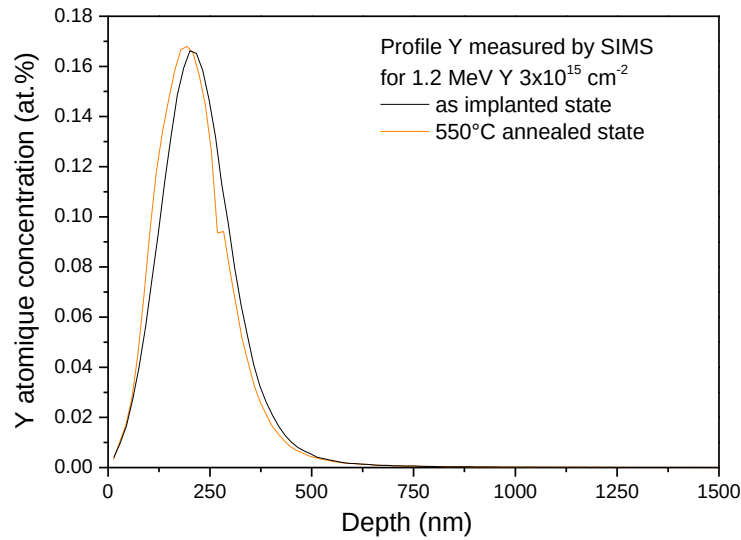


Figure IV-39: Y concentration profiles in as implanted state and 550°C annealed state for the 1.2 MeV Y implanted Fe sample at fluence $3 \times 10^{15} \text{ cm}^{-2}$ measured by SIMS.

The diffusion coefficient of Y in Fe is expected to be low (see Figure IV-29) and the migration energy of V_nY complex ($n=2-4$) has been calculated by Caroline Barouh ^[197] as showed in Figure IV-40. These values are higher than 1.8 eV. This result confirms the low diffusion capacity of Y in bcc Fe, even in the presence of vacancy. There is correlation between theoretical and experimental results: the no evolution of the Y peak after 550°C annealing is in agreement with the high migration energy of the vacancy yttrium complexes.

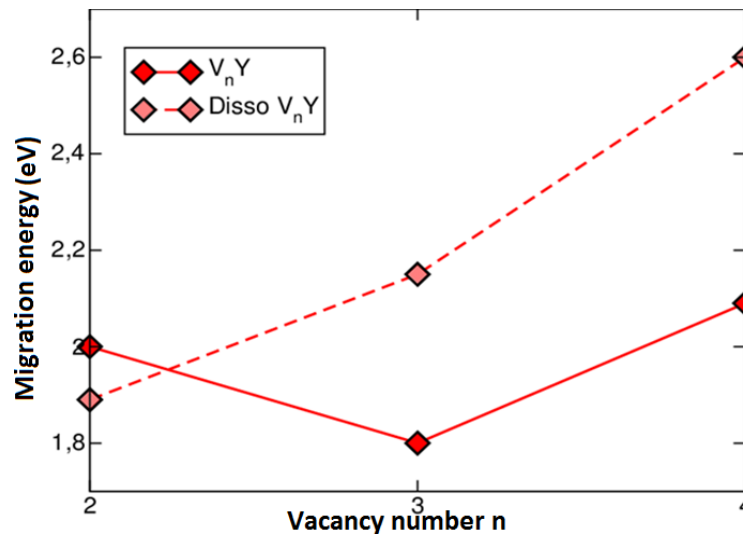


Figure IV-40: The migration and dissociation energy of V_nY ($n=2-4$) complex calculated by Caroline Barouh, PhD in CEA Saclay ^[197].

b) O depth profile after annealing

The evolution of S(E) curves with the storage time at room temperature for O implanted samples at high fluence has been observed. It indicates that the O depth profile in Fe could evolve with the storage time at room temperature. To check the quantity of O remains in Fe after ~ 235 days storage at room temperature, one Fe sample implanted by double beams 1.2 MeV Y and 285 keV O has been measured by SIMS and is used as the reference sample. It is supposed that the presence of Y atoms could retain the total implanted O atoms in Fe sample because of the high binding energy between O and Y ($E_{b-2NN}(O_{int}-Y_{sub})$: 0.73 eV^[83] 0.85 eV^[127] 1.01 eV^[126]). Double beam implantations, 1.2 MeV $2 \times 10^{15} \text{ cm}^{-2}$ Y and 285 keV $2.7 \times 10^{15} \text{ cm}^{-2}$ O, are performed with the 3 MV Tandetron accelerator at laboratory HZDR Dresden. The profile of O in this sample is measured by SIMS and the implanted O fluence is considered to be the desired one, $2.7 \times 10^{15} \text{ cm}^{-2}$. The general error of implantation fluence is lower than 10%. The relative sensitivity factors (RSFs) for O could be obtained and used to quantify the O fluence in other Fe sample. With this RSFs value, the real O fluence in 285 keV $2.7 \times 10^{15} \text{ cm}^{-2}$ O implanted Fe is measured to be $2.35 \times 10^{15} \text{ cm}^{-2}$ after a RT storage of more than 235 days. The difference between the desired fluence and the measured one is 13% which is higher than the implantation fluence error. As shown in Figure IV-41, the O profile in O implanted Fe is closer to the surface compared to the one obtained in double beam Y, O implanted Fe which indicates the migration of O towards the surface during the storage time. This measurement suggests that one part of O atoms is lost at the surface.

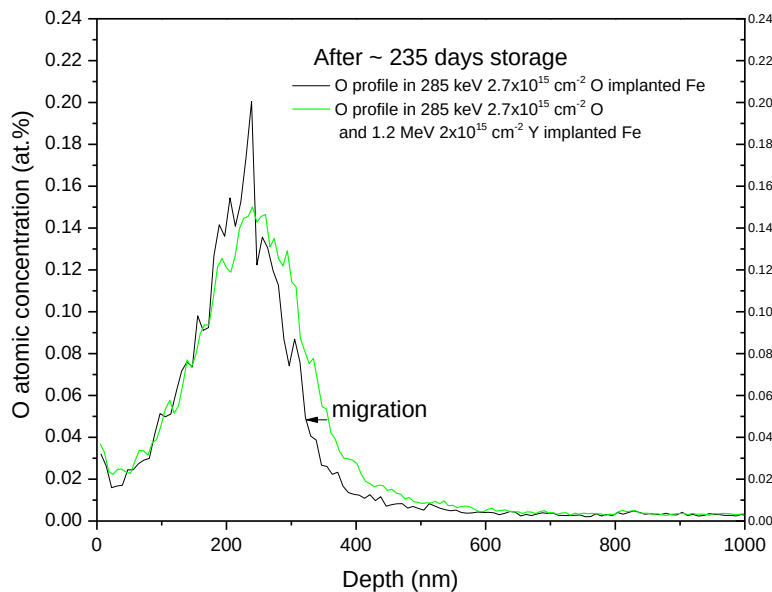


Figure IV-41: O concentration profiles in 285 keV $2.7 \times 10^{15} \text{ cm}^{-2}$ O implanted Fe and double beams, 285 keV $2.7 \times 10^{15} \text{ cm}^{-2}$ O and 1.2 MeV $2 \times 10^{15} \text{ cm}^{-2}$ Y, implanted Fe measured by SIMS after ~ 235 days storage.

Figure IV-42(a) shows that the surface of the Fe sample implanted with 285 keV O at the fluence of $2.7 \times 10^{15} \text{ cm}^{-2}$ is oxidized after ~ 240 days storage at room temperature. This surface oxidation confirms the O migration towards the sample surface which serves as a potential well. This oxidation is not

observed for He, Y, Ti implanted Fe samples, even for the sample implanted with 700 keV Ti at the fluence of $5 \times 10^{14} \text{ cm}^{-2}$ which gives a similar damage dose (0.57 dpa) as the one calculated for implantation with 285 keV O at the fluence of $2.7 \times 10^{15} \text{ cm}^{-2}$ (0.75 dpa). In addition, no S(E) evolution and no oxidation is observed with the storage time at room temperature in low O fluence implanted Fe samples. The oxygen concentration (300 appm) in these samples could be not enough to produce or observe evolutions.

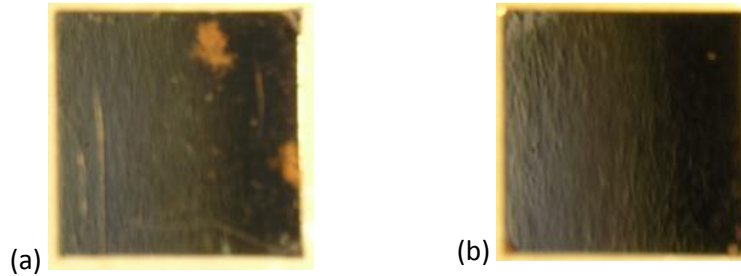


Figure IV-42: The surface state of Fe samples observed by optical microscopy after implantations with (a) 285 keV $2.7 \times 10^{15} \text{ cm}^{-2}$ O (0.75 dpa) (b) 700 keV $5 \times 10^{14} \text{ cm}^{-2}$ Ti (0.57 dpa) after ~ 240 days storage at room temperature.

O concentration profiles after ~ 235 days storage at room temperature and 550°C annealing for the Fe sample implanted with 650 keV O at the fluence of $2.2 \times 10^{15} \text{ cm}^{-2}$ have been measured by SIMS. As shown in Figure IV-43, the O profile after 550°C annealing is different from the one measured before annealing. This result confirms the relative high diffusion capacity of O compared to that of Y in bcc Fe. The O quantity after 550°C annealing, is obtained using the relative sensitivity factors (RSFs) determined in the sample after ~ 235 days storage at room temperature which is supposed to contain $2.2 \times 10^{15} \text{ cm}^{-2}$ O. With this RSFs value, the O quantity in 550°C annealed sample is measured to be $2.1 \times 10^{15} \text{ cm}^{-2}$. The difference between the O amount before and after 550°C annealing is 5% which is lower than the implantation fluence error. Thus, no oxygen is lost after 550°C annealing. But the depth profile is drastically different, the height of the peak is 2.61 times higher and the FWHM is 2.16 times lower. The maximum of the O peak is shifted toward the surface of approximately 20 nm after 550°C annealing. It is concluded that the O atoms become concentrated around the peak after 550°C annealing indicating that oxygen migrates at short distance during annealing.

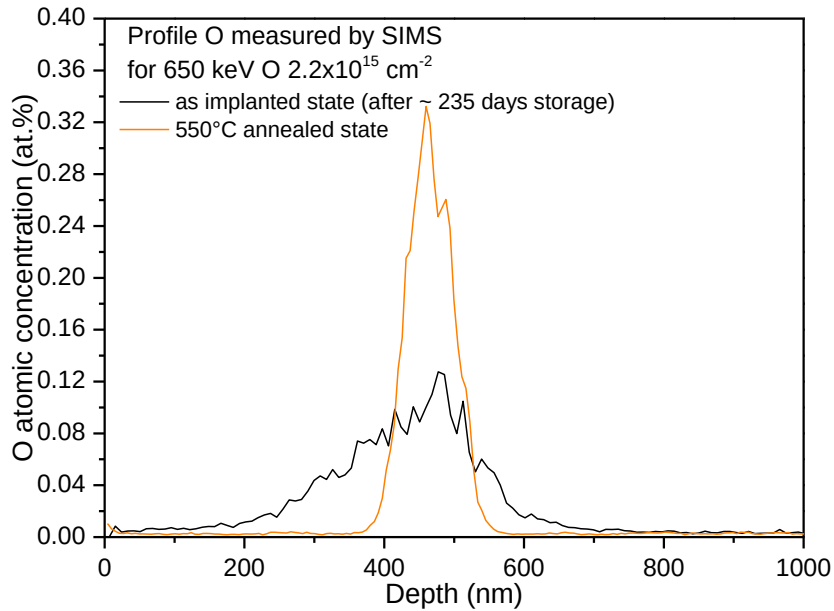


Figure IV-43: O concentration profiles in as implanted state after ~ 235 days storage at room temperature and 550°C annealed state for the 650 keV O implanted Fe sample at fluence $2.2 \times 10^{15} \text{ cm}^{-2}$ measured by SIMS.

IV.2.3. Y effect on annealing behavior of vacancy defects

a) Y effect on the temperature evolution of vacancy defects

For sample implanted with 1.2 MeV Y at the fluence of $3 \times 10^{15} \text{ cm}^{-2}$, a damage structure of four layers is detected for all annealed states as for the as-implanted sample. The vacancy clusters are observed for the three first layers and the fourth layer corresponds to the Fe lattice. The positron annihilation characteristics and the layer widths of the three layers evolve respectively with the annealing temperature.

In this section, the post irradiation annealing behavior is discussed in the following by distinguishing the 3 layers.

Layer 3

The layer 3 where large vacancy clusters and very limited amount of Y atoms exist have been detected is firstly studied. Figure IV-44 shows the S_3 values of the third layer S_3 obtained by Vepfit as a function of the annealing temperature and of the W_3 values. The Figure IV-44 (a) shows that S_3 begins to decrease at 150°C and the corresponding $S_3(W_3)$ point plotted in figure IV.44(b) stays on the $D_{Vn}(\text{Fe})$ line and moves to the Fe lattice point. It means that the concentration of Fe vacancy clusters is reduced. S_3 values continue to decrease for annealing performed at 200°C, 250°C and 300°C when the corresponding $S_3(W_3)$ points move towards the $D_V(\text{Fe})$ line. It indicates that the concentration and size of large vacancy clusters are reduced. At 350°C, the $S_3(W_3)$ point is slightly below the $D_V(\text{Fe})$ line indicating that a large part of vacancy clusters is recovered. But the $S_3(W_3)$ point is still far from the Fe lattice point indicating

another type of positron traps still exists in the sample. The $S_3(W_3)$ points continue to move towards the Fe lattice point at 400°C and 450°C indicating the trap concentration decreases. At 500°C and 550°C the S_3 values begin to increase again and the corresponding $S_3(W_3)$ points go far away from the Fe lattice point. It is difficult to know if this change is real or if it is due to the limitations of the fitting procedure. In our procedure the defects gradient is only modeled with a low number of homogeneous layers and hardly reflects the probable more complex existing gradient. Thus a thinner layer with a higher S can be equivalent in total number of traps to a larger layer with a lower S . Sometimes like in the case of the Y implanted samples, it is difficult to distinguish between these two possibilities. Thus, the interpretation of the increase of the S values obtained for the annealing at 500°C and 550°C is questionable and uncertain. If we consider that the model used to fit represent the global gradient in the sample, it could correspond to an increase of the concentration of traps accompanied with a decrease of the thickness of the layer 3 with the temperature increase. It indicates that defects have been removed in the deeper region of layer 3. The $S_3(W_3)$ points change follows two lines as illustrated in figure IV.44(b) which means two regimes of evolution exist.

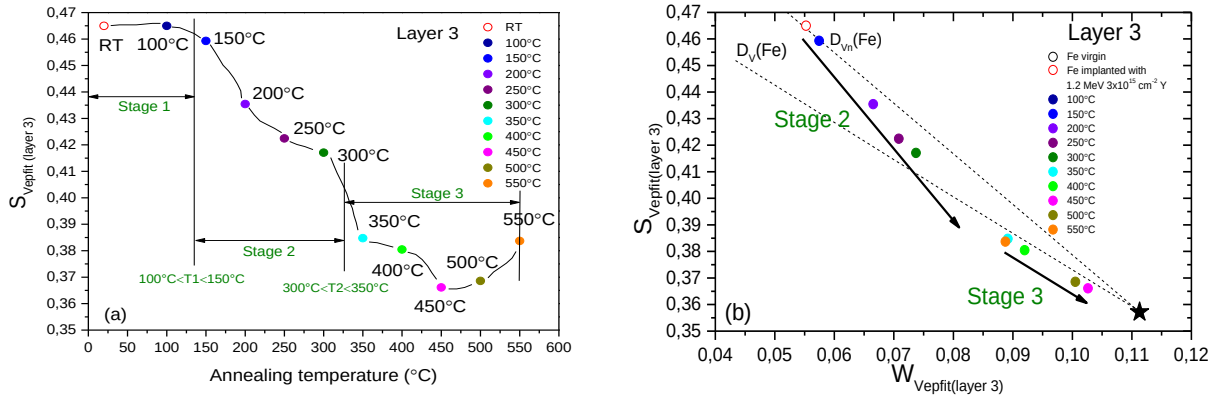


Figure IV-44: S values of the third layer obtained by Vepfit as a function of (a) the annealing temperature and (b) W values of the third layer for implanted Fe with 1.2 MeV Y ions at $3 \times 10^{15} \text{ cm}^{-2}$.

Thus several annealing stages are observed. In the stage 1: from room temperature up to T1 ($100^\circ\text{C} < T1 < 150^\circ\text{C}$), no change of S_3 and W_3 values is observed. A second stage from T1 up to T2 ($300^\circ\text{C} < T2 < 350^\circ\text{C}$), in this temperature range the vacancy concentration continues to decrease. The stage 3 appears from T2 when a large part of the vacancy defects is recovered. From this temperature the $S_3(W_3)$ points are below the $D_v(\text{Fe})$ line which indicates that the positrons detect new traps with free volume lower than the single vacancy or special chemical environment.

Layer 1

The post irradiation annealing behavior in layer 1 is then studied. Before annealing we have seen that large vacancy clusters and a small part of Y atoms exist in this layer. Figure IV-45 shows the S values determined in layer 1 S_1 obtained by Vepfit as a function of the annealing temperature and of the W_1 values.

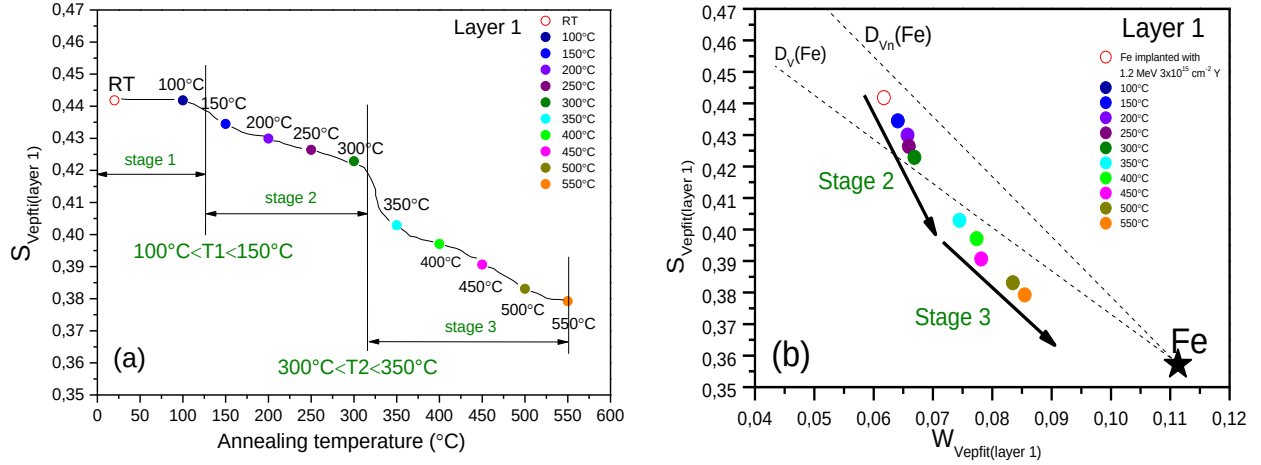


Figure IV-45: S values of the first layer obtained by Vepfit as a function of (a) the annealing temperature and (b) W values of the first layer for implanted Fe with 1.2 MeV Y ions at $3 \times 10^{15} \text{ cm}^{-2}$.

Like in layer 3 several stages can be distinguished. In the stage 1 (from room temperature up to T_1 ($100^{\circ}\text{C} < T_1 < 150^{\circ}\text{C}$)), no change of S_1 and W_1 values is observed. From T_1 up to T_2 ($300^{\circ}\text{C} < T_2 < 350^{\circ}\text{C}$), corresponding to the second stage (stage 2), S_1 values decrease regularly and the $S_1(W_1)$ points evolution indicates the decrease of the concentration or size of the vacancy clusters. A third stage is observed from T_2 , corresponding to the recovery of a large part of the vacancy clusters. From 400°C up to 550°C the $S_1(W_1)$ points are below the $D_V(\text{Fe})$ line which indicates that the positrons detect new traps with free volume lower than the single vacancy or special chemical environment.

Layer 2

Finally, the post irradiation annealing behavior in layer 2 where locates the highest quantity of $Y_n - V_m$ complexes is studied in the following. Figure IV-46 shows the S_2 values obtained by Vepfit in the second layer as a function of the annealing temperature and of the W_2 values of the same layer.

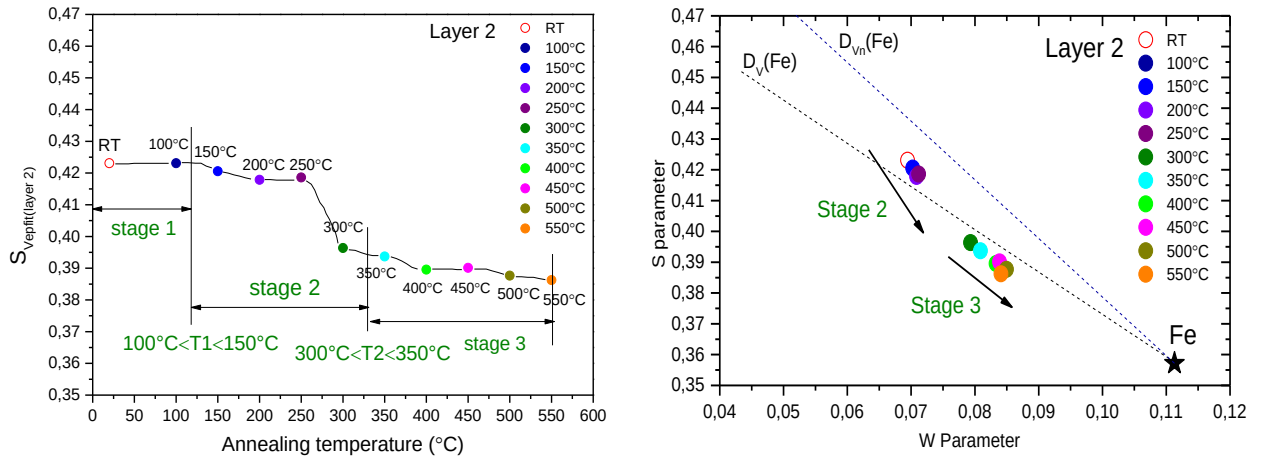


Figure IV-46: S values of the second layer obtained by Vepfit as a function of (a) the annealing temperature and (b) W values of the second layer for implanted Fe with 1.2 MeV Y ions at $3 \times 10^{15} \text{ cm}^{-2}$.

Three annealing stages are observed in layer 2. In the stage 1 (from room temperature up to T1 ($100^{\circ}\text{C} < T_1 < 150^{\circ}\text{C}$)) there is no change of the S_2 and W_2 values. From T1 up to T2 ($300^{\circ}\text{C} < T_2 < 350^{\circ}\text{C}$), corresponding to the second stage (stage 2), S_2 decreases slightly and the corresponding $S_2(W_2)$ points move towards the $D_V(\text{Fe})$ line. It means the concentration and/or size of vacancy clusters decrease regularly but slightly up to 250°C . From T2, the large vacancy clusters are no more the main positron traps and new traps are detected with free volume lower than the single vacancy or special chemical environment.

In conclusion, same general behavior is observed for the 3 layers with 3 major annealing stages.

The post irradiation annealing behaviors of defects in the three layers are compared with each other. All the curves of S as the function of temperature and S as a function of W are reported in Figure IV-47.

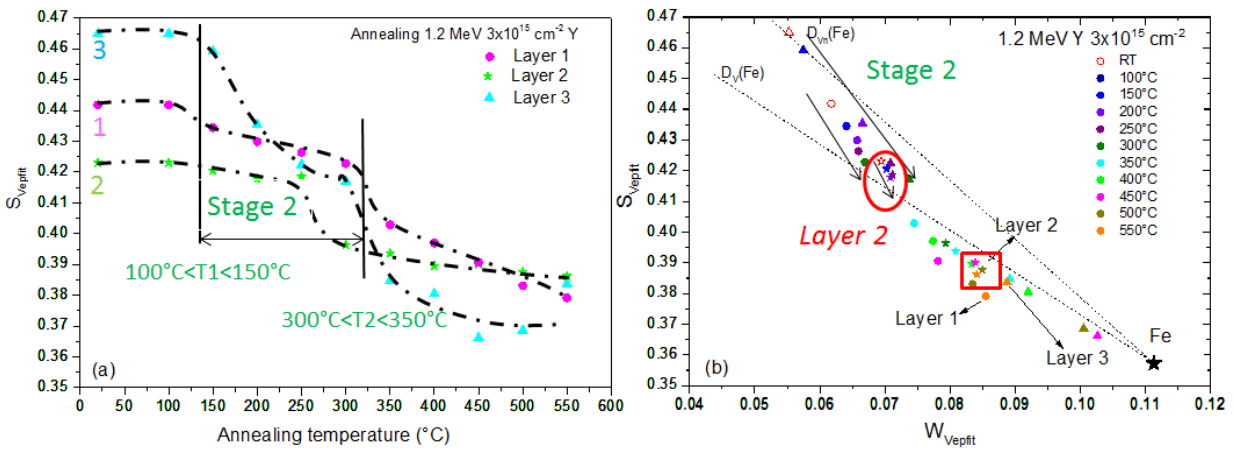


Figure IV-47: S values of the three layers for implanted Fe with 1.2 MeV Y ions at $3 \times 10^{15} \text{ cm}^{-2}$ as a function of (a) the annealing temperature and (b) W values of the three layers.

In the stage 2, the size and concentration of vacancy clusters continue to decrease from T1 ($100^{\circ}\text{C} < T_1 < 150^{\circ}\text{C}$) up to T2 ($300^{\circ}\text{C} < T_2 < 350^{\circ}\text{C}$). The large vacancy clusters recovery is due to their dissociation and migration. It is noted that the decrease rate of S is faster for the layer 3 than for the two other layers. It can be due to the difference in the vacancy clusters distribution induced in the different layers. Especially for the layer 2 this decrease is very low ($\Delta S_2 = S_2(150^{\circ}\text{C}) - S_2(100^{\circ}\text{C}) = 0.0045$) where the proportion of large vacancy clusters is the lowest due to the presence of Y as discussed in the section 1.6 of this chapter. The S change is much larger in layer 3 where the Y concentration is the lowest even after annealing.

For the 3 layers a new type of defects traps the positrons in stage 3. It has a lower free volume than the single vacancy or a special chemical environment. One of the candidates can be dislocation as it has been already discussed in the case of He irradiated samples (see chapter III section 3.1). However the distribution of positron traps detected in this stage 3 differs in the 3 layers. The highest S values are obtained in the temperature range from 450°C to 550°C for the layer 2 where Y amount is the highest and then in the layer 1 where the Y amount is not negligible (see figure IV.27). Considering the dislocations, their population is expected to be the highest in layer 2 and 1 where the damage dose is the

highest. It suggests that a competition exists with other type of defects with higher S than in dislocations in layer 2 compared to layer 1. These competing defects could be $Y-V_3$ and $Y-V_4$ complex whose dissociation energy is respectively ~ 2.93 eV and ~ 2.57 eV as calculated by C.Barouh^[197]. They would not dissociate before 662°C and 727°C .

Some defects are still present even after annealing at 750°C as shown in Figure IV-48. A damage structure of two layers is obtained by Vepfit for the Y implanted sample after 750°C annealing. The $S(W)$ point of the first layer which spreads up to the depth of ~ 772 nm is below the $D_V(\text{Fe})$ line and far from the Fe lattice one. The effective positron diffusion length in this layer L^+ is ~ 38 nm which indicates that the defects recovery has not been completed at 750°C . It should be noted that 750°C annealing is able to eliminate all the defects existing in the as-polished and laminated Fe samples before implantation. Thus, it means that Y atoms presence limits this defect recovery. These stable defects should not be $Y-V_n$ ($2 < n < 6$) complexes which have a maximum dissociation energy ~ 2.93 eV as calculated by C.Barouh^[197]. With this energy, these complexes would all dissociate at about 730°C and release the vacancy defects. Moreover the dislocations density is expected to be low at this temperature as shown experimentally^[183]. Thus, the nature of this stable defect is not yet clear. Among the candidates, the precipitates will have to be envisaged. Positron lifetime and transmission electron microscopy or APT experiments could help to determine the nature of these traps. It has to be noticed that the Y depth profile will have to be measured after this 750°C annealing.

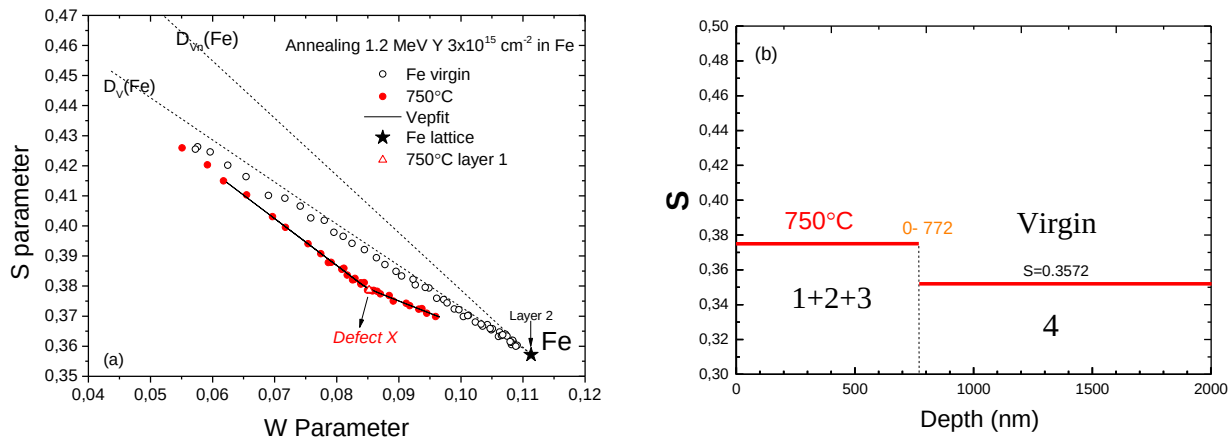


Figure IV-48: (a) $S(W)$ and (b) a damage structure of two layers for the Fe sample irradiated with 1.2 MeV Y at $3 \times 10^{15} \text{ cm}^{-2}$ and annealed at 750°C .

The simulation work realized by C.J. ORTIZ et al.^[189] aroused our attention. In this work, they have studied the evolution of damage produced by collision cascades in Fe by both kinetic Monte Carlo (KMC) and rate theory (RT) approaches. Figure IV-49 shows the evolution of I_n and V_n cluster mean size during isochronal annealing for a 30 keV Fe irradiation for a dose of 10^{-4} dpa according to KMC and RT models. Both models illustrate the growth of interstitial and vacancy clusters in the temperature range 100- 700 K. The authors ascribed these results to the intracascade clustering induced by the high damage energy, 30 keV in this case. It should be noted that the PKA energy $W_{1/2}$ in 1.2 MeV Y implanted Fe sample is calculated to be ~ 50 keV which is much higher (see details in section IV.1.1). Thus, their vacancy cluster size is possible to increase with the annealing temperature according to this simulation. But the increase

of vacancy cluster size with the annealing temperature is not detected by our positron experiments. One reason for this lack of detection could be due to the positron detection limit. It is possible that the larger vacancy cluster is created in 1.2 Y implanted sample during the annealing by agglomerating the small vacancy clusters. But finally they are not detected by positron because of their concentration is lower than the positron detection limit (for vacancy clusters with size of 10 vacancies, the detection limit is 0.0118 appm, see details in chapter II section 3.2). Thus, this possibility could not be excluded.

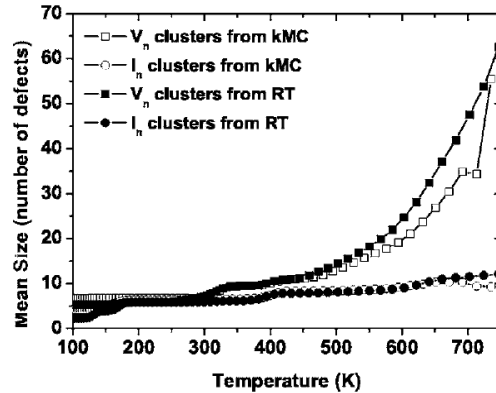


Figure IV-49: Evolution of I_n and V_n cluster mean size during isochronal annealing for a 30 keV Fe irradiation for a dose of 10^{-4} dpa according to KMC (open symbols) and RT (full symbols) models^[189].

b) Conclusions

In conclusion, same general behavior is observed for the 3 layers with 3 major annealing stages. If we focus on the vacancy clusters evolution in the presence of Y atoms –that means in the layer 2 where the Y concentration is the highest- with the annealing temperature the following mechanisms can be proposed:

- After Y implantation, vacancy clusters V_n , the Y_m-V_n complexes and also dislocations are created.
- After 150°C annealing, one fraction of vacancy clusters V_n with large size dissociate, migrate and recombine with interstitials.
- After 300°C annealing, the remained vacancy clusters V_n with small size also recombine with interstitials. The Y_m-V_n complexes and dislocations are still detected.
- After 550°C annealing, one fraction of the Y_m-V_n complexes is recovered but the other complexes like $Y-V_3$ and $Y-V_4$ could still resist at this temperature. The dislocations still exist.
- After 750°C annealing, the $Y-V_3$ and $Y-V_4$ complexes also dissociate and recombine. In addition, the dislocations disappear at this temperature. But another positron trap whose nature is not yet clear is still detected by positrons. Their nature has to be studied using positron lifetime, TEM or APT techniques.

IV.2.4. O effect on annealing behavior of vacancy defects

a) Storage at room temperature

As presented in section 2.1, the vacancy concentration and size increase in the sample implanted with 650 keV O at the fluence of $2.2 \times 10^{15} \text{ cm}^{-2}$ after ~235 days storage at room temperature. The evolution of O depth profile in Fe after ~ 235 days storage at room temperature is also observed as presented in section 2.2 and a part of O has migrated towards the sample surface.

These results could be explained as followed. First the high binding energy for V- O_{int} complex ($E_{\text{b-1NN}}(\text{O}_{\text{int}}\text{-V}) = 1.65 \text{ eV}^{[126]} \text{ } 1.45 \text{ eV}^{[81]}$; $E_{\text{b-2NN}}(\text{O}_{\text{int}}\text{-V}) = 0.75 \text{ eV}^{[126]} \text{ } 0.60 \text{ eV}^{[81]}$) slows down the V migration. And these complexes can exist after irradiation in the layer where the O amount is high enough (1274 appm at Rp for 650 keV O at the fluence of $2.2 \times 10^{15} \text{ cm}^{-2}$). It is interesting to notice that the evolution of vacancy has not been observed in He irradiated Fe samples during their storage at room temperature because vacancy migration is completed after the irradiation -the migration temperature of V in bcc Fe is below the room temperature (-53 to 5°C) as suggested by Takaki et al. ^[107]. The diffusivity of O in the interstitial site has been estimated experimentally to be about twenty one orders of magnitude higher than that of tracer Fe atoms at 273 K as shown in Figure IV-50 ^[63, 64]. In addition, the migration energy of OV_n ($n=0\text{-}3$) complexes has been calculated by Caroline Barouh ^[197]. As shown in Figure IV-51, the migration energy of O-V_3 is as low as the one calculated for the pure Fe vacancy which indicates that the migration of O-V_3 at room temperature is possible. This O-V_3 complex migration would change in the same time the vacancy defects distribution and the O depth profile in Fe. It is also interesting to notice that the dissociation energy of the O-V_3 complexes is about 1 eV so they should not dissociate at room temperature. If these O-V_3 complexes diffuse toward the surface it could lead to agglomeration of larger defects. It should lead to the decrease of positron trapping at these O-V_3 complexes that have lower S value compared to the one for larger vacancy clusters and the increase of annihilation fraction in high S traps (larger vacancy clusters). This process leads to an increase of S and of the S/W slope. It is exactly what is observed in the layer 1 of the sample implanted with 650 keV O at the fluence of $2.2 \times 10^{15} \text{ cm}^{-2}$ when the storage time increases from 60 to ~ 235 days. These increases are accompanied with an increase of oxygen concentration in the region 1 nearer to sample surface as observed in the SIMS measurements.

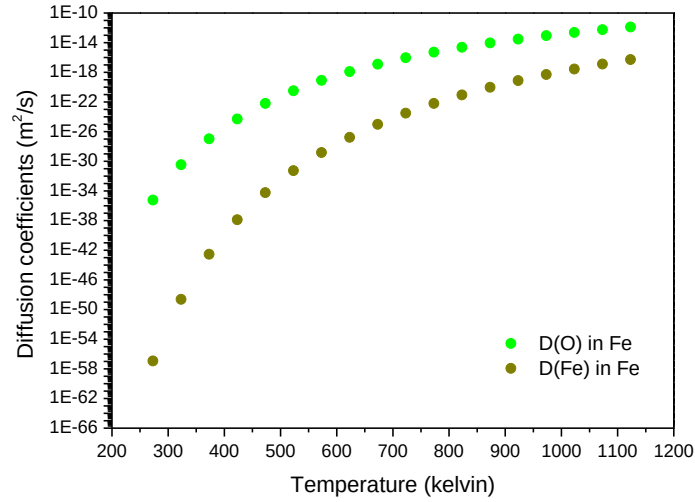


Figure IV-50: The iron and oxygen diffusion coefficient in iron by fitting a classical nucleation-growth-coarsening model to small-angle neutron scattering data ^[63, 64].

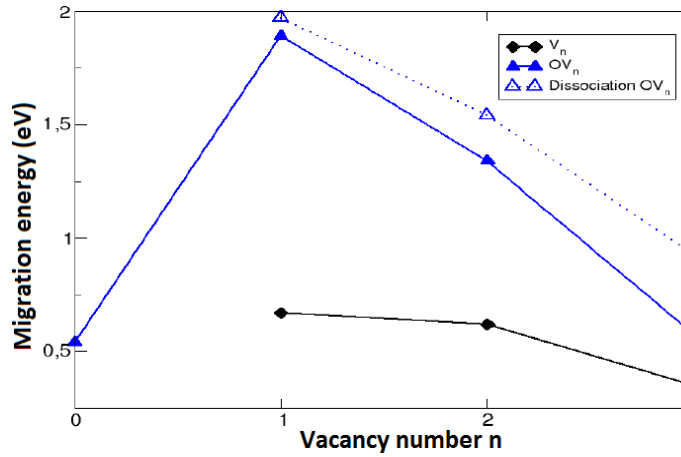


Figure IV-51: The migration and dissociation energy of OV_n (n=0- 3) complex calculated by Caroline Barouh ^[197], PhD in CEA Saclay

b) Isochronal annealing in the temperature range from 100°C to 550°C

The post- irradiation annealing behavior of V defects in O implanted Fe samples at higher temperature than room temperature is studied in the following. As presented in section 2.1, three layers are found for the O implanted sample and the third layer corresponds to the Fe lattice.

The post irradiation annealing behavior in layer 1 is firstly studied. Large vacancy clusters and a small part of O atoms exist in this layer. Figure IV-52 shows S_1 values of the first layer obtained by Vepfit as a function of the annealing temperature up to 400°C and of the W_1 values. The layer 1 of the 550°C annealed state is not compared here because of its small thickness.

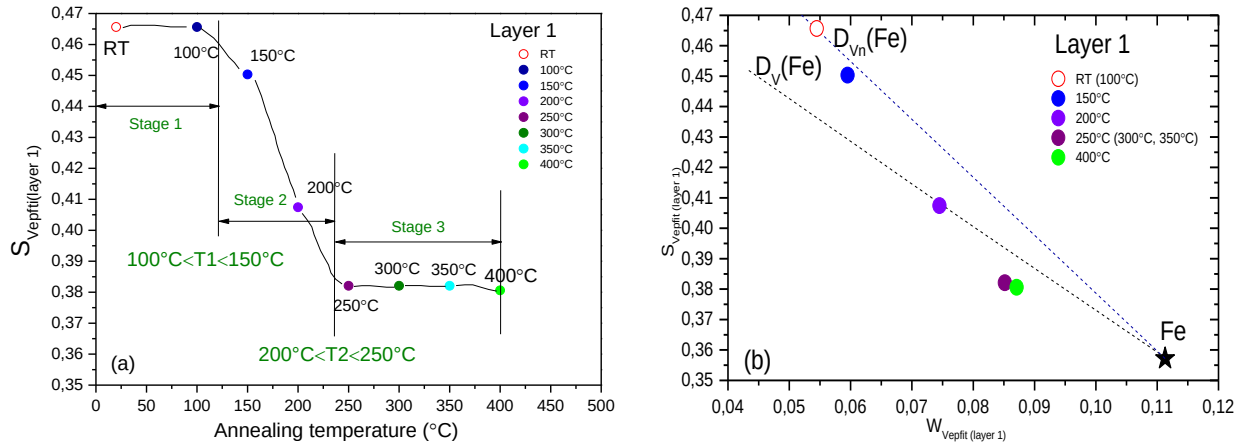


Figure IV-52: S values of the first layer obtained by Vepfit as a function of (a) the annealing temperature up to 400°C and (b) W values of the first layer for implanted Fe with 650 keV O ions at $2.2 \times 10^{15} \text{ cm}^{-2}$.

The figure IV-52(a) shows that S begins to decrease at T1 and the corresponding $S_1(W_1)$ point plotted in figure IV-52(b) moves towards the $D_{\text{V}}(\text{Fe})$ line and the Fe lattice point. It means that the size and concentration of Fe vacancy clusters is reduced. At T2, the S_1 value continues to decrease and the $S_1(W_1)$ point is below the $D_{\text{V}}(\text{Fe})$ line indicating that a large part of vacancy clusters is recovered. In addition, it suggests the presence of another positron trap. At 300°C and 350°C, S_1 values and $S_1(W_1)$ points do not change. S_1 value continues to decrease and $S_1(W_1)$ point moves towards the Fe lattice point for annealing at 400°C.

As shown in Figure IV-52 (a), the stage 1 is defined from room temperature to T1 ($100^{\circ}\text{C} < T_1 < 150^{\circ}\text{C}$) where the vacancy concentration or size does not change. The stage 2 is observed from T1 to T2 ($200^{\circ}\text{C} < T_2 < 250^{\circ}\text{C}$) where the vacancy concentration or size begins to decrease. And at the stage 3, from T2, a large part of the vacancy defects is recovered.

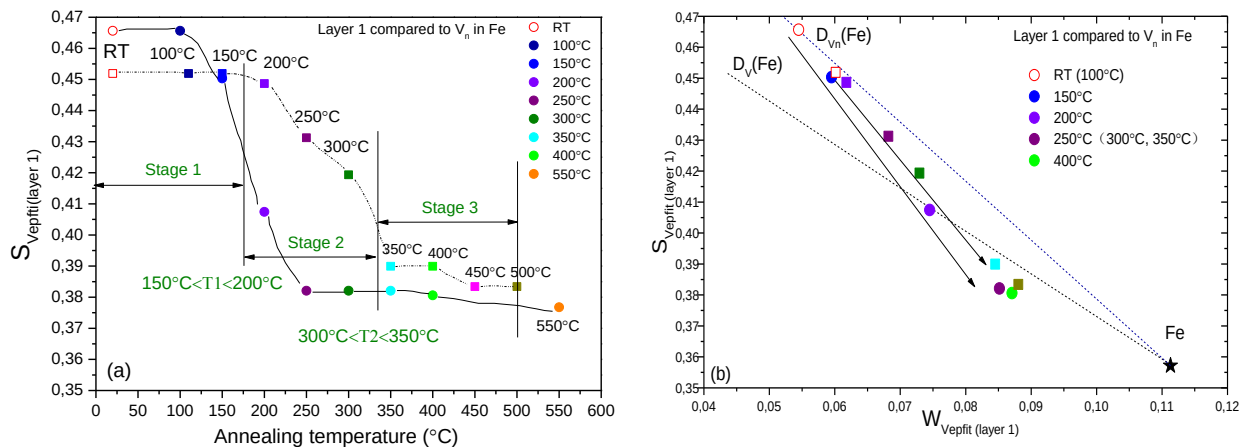


Figure IV-53: S values of the first layer (round symbols) for implanted Fe with 650 keV O ions at $2.2 \times 10^{15} \text{ cm}^{-2}$ compared to the ones for vacancy clusters in Fe irradiated with 1.5 MeV at $1 \times 10^{16} \text{ cm}^{-2}$ He (square symbols) as a function of (a) the annealing temperature and (b) W values of the first layer.

The post irradiation annealing behavior in layer 1 of the O implanted sample is compared to the one of vacancy clusters in Fe irradiated with 1.5 MeV at $1 \times 10^{16} \text{ cm}^{-2}$ He as shown in Figure IV-53. The stage 2 begins from 100°C in layer 1 of O implanted sample whereas it appears at 150°C for the vacancy clusters in He irradiated Fe. The stage 3 is also shifted to lower temperature in the layer 1 of the O implanted sample. It occurs at 200°C against 300°C in He irradiated Fe. The vacancy distribution difference in both O and He irradiations could explain these recovery differences of the large vacancy clusters. It could be related to the size of the pure vacancy defects and /or to the presence of nV-mO complexes. It is interesting to notice that the O profile measured at 550°C is drastically narrower compared to the one obtained before annealing. The O concentration in layer 1 becomes negligible after annealing at 550°C. It indicates that the nV-mO complexes have migrated and /or been dissociated during annealing since O_{int} has a migration energy of about 0.5 eV thus is expected to diffuse already at room temperature.

In conclusion, the recovery of vacancy clusters is observed at lower temperature in the layer 1 of the O implanted sample, it could be explained by the presence of $O_n - V_m$ complexes that could migrate and/or dissociate at low temperature and accelerate the vacancy recovery.

The post irradiation annealing behavior in layer 2 is then studied. The $O_n - V_m$ complex with low free volume, like O- single vacancy complex, is supposed to be the predominant defects detected in this layer due to the O concentration/dpa high ratio. Figure IV-54 shows the S_2 values in the second layer obtained by Vepfit as a function of the annealing temperature up to 550°C and of the W_2 values.

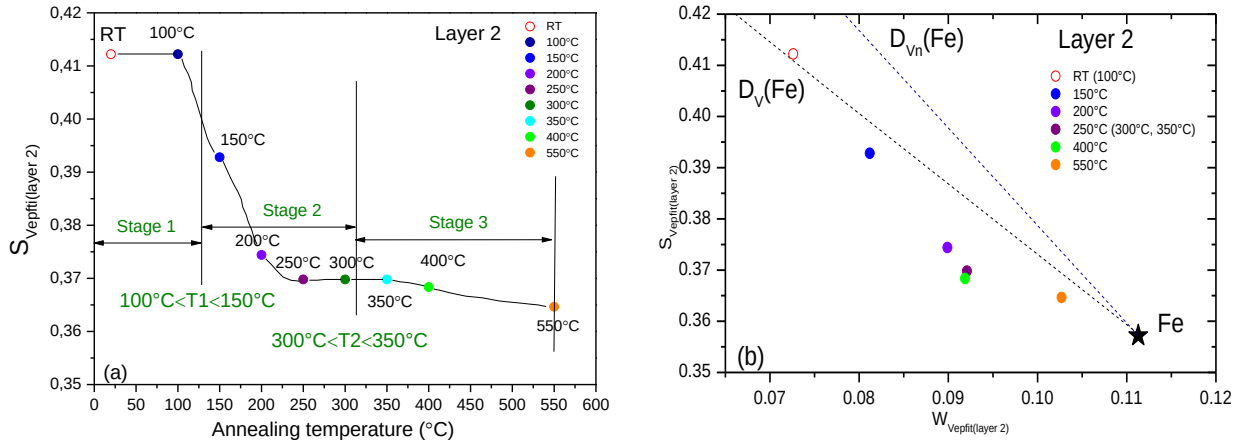


Figure IV-54: S value of the second layer obtained by Vepfit as a function of (a) the annealing temperature (b) W value of the second layer for implanted Fe with 650 keV O ions at $2.2 \times 10^{15} \text{ cm}^{-2}$.

S_2 begins to decrease from T_1 ($100^\circ\text{C} < T_1 < 150^\circ\text{C}$) and the corresponding $S_2(W_2)$ point is located below the $D_V(\text{Fe})$ line and moves away this line. It means that the concentration of single vacancy type defects is reduced. The concentration reduction could be caused by the migration of V- O small complexes. S_2 continues to decrease at 200°C and 250°C and $S_2(W_2)$ points are below the $D_V(\text{Fe})$ line approaching the Fe lattice point. It indicates the presence of another positron trap. From 300°C to 400°C, the S_2 and $S_2(W_2)$ changes are very slight. At 550°C the $S_2(W_2)$ point approaches the Fe lattice characteristics without reaching it. But the effective diffusion length of positron obtained at this

temperature is $\sim 150 \pm 3$ nm. These results indicate that a large part of the defects are recovered after 550°C annealing.

If we compare these results with the evolution of single vacancy induced in Fe irradiated with 1.5 MeV $2 \times 10^{14} \text{ cm}^{-2}$ He as shown in **Figure IV-55**, it is noted that their general behavior is almost the same.

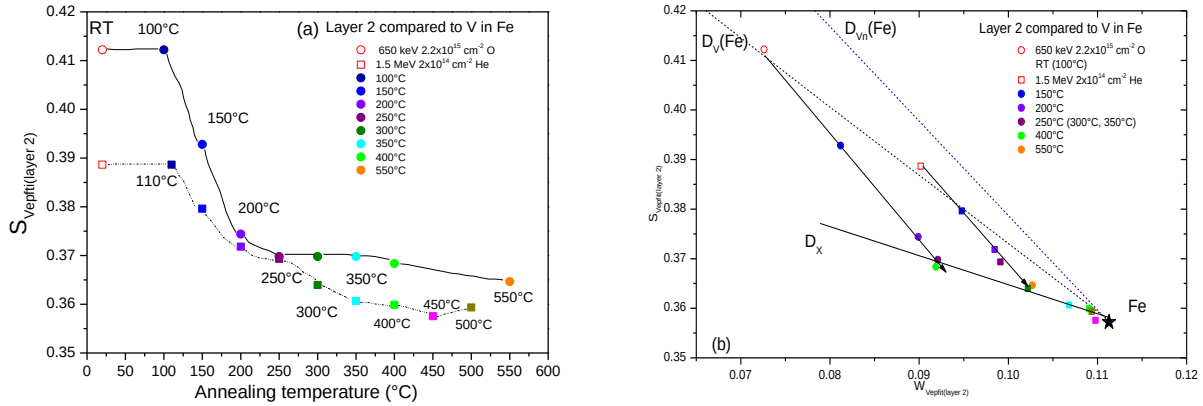


Figure IV-55: S values of the second layer (round symbols) for implanted Fe with 650 keV O ions at $2.2 \times 10^{15} \text{ cm}^{-2}$ compared to the ones for single vacancy in Fe irradiated with 1.5 MeV $2 \times 10^{14} \text{ cm}^{-2}$ He (square symbols) as a function of (a) the annealing temperature and (b) W values of the second layer.

The $S(W)$ points changes follow respectively two lines which have the same slope. Thus, it suggests that same mechanisms drive their evolution. It is interesting to notice that $S(W)$ points measured between 300 and 500°C for He irradiated sample and from 250°C to 550°C in O implanted sample are approximately aligned on the same straight line D_X . It could indicate that the same type of defects are detected, with various concentration, the lowest obtained for the He irradiated case. They could be defects with an apparent free volume lower than the single vacancy or with a special chemical environment different from Fe. As discussed in chapter III section 3.1, it could be dislocations but even if this hypothesis cannot be discarded without checking their absence by TEM, the low damage dose induced in He irradiations makes it less probable. These defects seem to be related to oxygen atoms since the O concentration is still high in the layer 2 of the O implanted sample even after the annealing at 550°C (see O profile in **Figure IV-43**). The $S(W)$ point obtained after the annealing at 550°C is close to the Fe lattice one and ΔS (S measured – S lattice = 0.0075) is low. S value depends on the trapping rate which is the product of concentration and specific trapping coefficient of the defects and increases with the trapping rate. Thus to a low S value corresponds a low trapping rate. For the single vacancy case an equivalent ΔS (0.0075) corresponds to a vacancy concentration of about $1 \times 10^{17} \text{ cm}^{-3}$ (see details in chapter 2 section 3.2). This concentration is approximately 3 orders of magnitude lower than the average oxygen concentration measured by SIMS in the region where these defects are detected. So we can conclude that if the defects which are detected by positrons are related to oxygen, they should contain a large fraction of O atoms. These defects seem to be the result of the oxygen gathering observed in SIMS. The $S(W)$ point location obtained in the oxygen rich layer which is below the $D_V(\text{Fe})$ line suggests that these defects are more probably dislocations or iron oxides. It has to be noticed that the oxygen

concentration is 20 appm in the virgin sample. So such enriched defects can also exist in He irradiated Fe samples after annealing at 500°C.

c) Conclusions

The vacancy clusters evolution in the presence of O atoms with the annealing temperature can be summarized as follows.

- After O implantation, vacancy clusters V_n , the O_m-V_n complexes and also dislocations are created. During the storage at room temperature, the complexes such as $O-V_3$ can diffuse toward the surface and lead to agglomeration of larger defects and a release of O with oxidation of the surface.
- After 150°C annealing, one fraction of vacancy clusters V_n with large size dissociate, migrate and recombine with interstitials. Some O_m-V_n complexes also migrate and/or dissociate.
- After 250°C annealing, the remained vacancy clusters V_n with small size also recombines with interstitials. The rest O_m-V_n complexes migrate and/or dissociate.
- Up to 550°C, the dislocations and O enriched defects exist in the system.

If we focus on the region where the oxygen concentration is the highest the major defects are small O-V complexes. They can dissociate and migrate when temperature becomes higher than 150°C leading to their recovery. Free Oxygen atoms becomes mobile and can agglomerate in oxygen enriched defects that can be dislocations or iron oxide precipitates.

IV.2.5. Conclusions

In this section, the evolution of vacancy defects distribution after annealing in Y and O implanted samples has been studied.

The annealing experiments were performed at temperatures from 100°C up to 750°C under vacuum during 1 hour with a step of 50°C for 1.2 MeV Y implanted sample at the fluence of $3 \times 10^{15} \text{ cm}^{-2}$. Several evolution steps have been observed. After 150°C annealing, one fraction of vacancy clusters V_n dissociate, migrate and recombine with interstitials. After 300°C annealing, the remained vacancy clusters V_n with small size also recombines with interstitials and the Y_m-V_n complexes and dislocations are still detected. After 550°C annealing, one fraction of the Y_m-V_n complexes is recovered but the other complexes like $Y-V_3$ and $Y-V_4$ could still resist at this temperature as dislocations. After 750°C annealing, the $Y-V_3$ and $Y-V_4$ complexes also dissociate and recombine. In addition, the dislocations disappear at this temperature. But another positron trap whose nature is not yet clear is still detected by positrons.

The effect of annealing at room temperature has been firstly studied for O implanted sample. The Fe samples irradiated by 650 keV O at the fluence of $2.2 \times 10^{15} \text{ cm}^{-2}$ and stored during 60 days and 236 days at room temperature have been compared. The size and concentration of vacancy defects increase after 236 days storage and one part of vacancy defects have migrated to the surface as one fraction of O atoms is lost at the surface during the 236 days storage. One part of O atoms is lost at the surface after ~ 235 days storage. The low migration energy of O- V_n complexes such as $O-V_3$ could explain these evolutions.

The annealing experiments were also performed at temperatures from 100°C up to 550°C under vacuum during 1 hour with a step of 50°C for the sample implanted with 650 keV O at the fluence of $2.2 \times 10^{15} \text{ cm}^{-2}$ stored at RT during ~ 235 days. Several evolution steps have been observed. After 150°C annealing, one fraction of vacancy clusters V_n dissociate, migrate and recombine with interstitials. Some O_m - V_n complexes also migrate and/or dissociate. After 250°C annealing, the remaining vacancy clusters V_n with small size also recombine with interstitials as the remaining O_m - V_n complexes migrate and/or dissociate. After annealing at 550°C, dislocations and O enriched defects whose nature is not yet clear are still detected.

IV.3. An atomic scale mechanism proposed for the ODS nanoparticles nucleation

From the results obtained in this thesis, the interactions between Y, Ti, O atoms and vacancy in bcc Fe and also interaction of Cr with vacancy in bcc FeCr can be summarized as follows:

- It has been demonstrated that Y is strongly bounded with the vacancy which confirms the theoretical calculations of the binding energy ($E_{b-1NN}(V-Y_{sub}) = 1.45 \text{ eV}$ ^[195]). The diffusion capacity of Y atoms is low even if many vacancies are presented. Y atoms do not diffuse after 550°C annealing. The low diffusion capacity of Y in bcc Fe is correlated to the high migration energy ($\sim 2 \text{ eV}$) of V_nY complex ($n=2-4$) calculated by C.Barouh ^[197]. After 550°C annealing, one fraction of the Y_m - V_n complexes is recovered but the other complexes like $Y-V_3$ and $Y-V_4$ could still resist at this temperature. After 750°C annealing, the $Y-V_3$ and $Y-V_4$ complexes also dissociate and recombine.
- Our experiments have shown that O is bounded with the vacancy which confirms the theoretical calculations ($E_{b-1NN}(O_{int}-V) = 1.65 \text{ eV}$ ^[126] 1.45 eV ^[81], $E_{b-2NN}(O_{int}-V) = 0.75 \text{ eV}$ ^[126] 0.60 eV ^[81]). The diffusion capacity of O atoms is high. V_m - O_n complex, for example OV_3 , migrates at room temperature. One part of implanted O fluence is lost to the surface after ~ 235 days room temperature storage. The O concentration profile in Fe has changed after 550°C annealing. This confirms the dissociation energy of O- V_n complexes as calculated by C.Barouh ^[197]. In addition, it is observed that the Y atoms could inhibit this V_m - O_n complex migration at room temperature. It could be correlated to the high calculated binding energy between O and Y ($E_{b-2NN}(O_{int}-Y_{sub})$: 0.73 eV ^[83] 0.85 eV ^[127] 1.01 eV ^[126]).
- Ti is less bounded with the vacancy and it suggests that the fraction of mV - nTi complexes is lower than the case of Y. It confirms the relatively lower binding energy between vacancy and Ti ($E_{b-1NN}(V-Ti_{sub}) = 0.26 \text{ eV}$ ^[65, 126]) compared to the one between V- Y ($E_{b-1NN}(V-Y_{sub}) = 1.45 \text{ eV}$ ^[195]) obtained by calculations.
- Cr is not bounded with the vacancy. It confirms the very weak V-Cr interactions, $E_{b-1NN}(V-Cr) = 0.057 \text{ eV}$ and $E_{b-2NN}(V-Cr) = 0.007 \text{ eV}$ ^[186], obtained by calculations. It also corresponds to the high binding energy of Cr with SIA ($0.3-0.4 \text{ eV}$) per crowdion in the cluster ^[186]. The presence of Cr atoms slows down the vacancy clusters recovery due to their binding with the Fe interstitials. They are recovered at 450°C instead of 350°C.

With these conclusions, a schematic mechanism is proposed for the first steps of the ODS nanoparticles nucleation at the atomic scale:

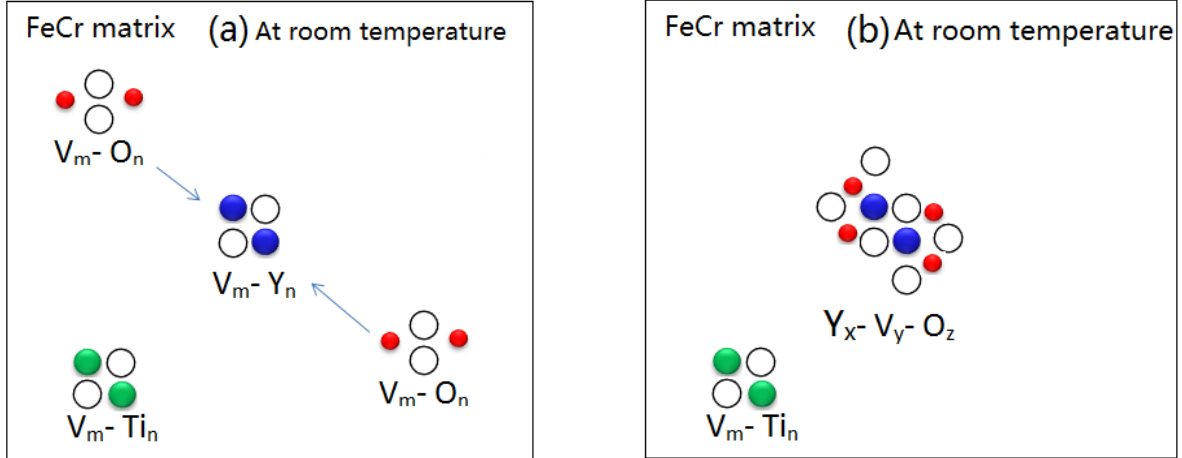


Figure IV-56: The first step of nanoparticles formation mechanism: the V_m-O_n complex migrates to V_m-Y_n complex and forms $Y_x-V_y-O_z$ complex at room temperature. Blue ball represents Y atom; green ball represents Ti atom; red ball represents O atom; black vacant ball represents vacancy.

- Step 1: During mechanical alloying (MA) process, the Y, Ti, O atoms and vacancy defects are introduced into FeCr matrix (see Figure IV-56 for an illustration). The complexes V_m-Y_n , V_m-O_n and V_m-Ti_n could be respectively formed. It is noted that the fraction of V_m-Ti_n complex should be lower than that of V_m-Y_n , V_m-O_n because of their weaker binding with vacancies. At room temperature, some of the V_m-O_n complexes like OV_3 could migrate because of their high diffusion capacity. In contrary, the V_m-Y_n complex could serve as a nucleation site because of its relative lower diffusion capacity. The Y atoms could also inhibit the V_m-O_n complex migration if $Y_x-V_y-O_z$ complexes are formed at room temperature as shown in figure (b). In conclusion, the V_m-Y_n is the earliest germ for the nucleation oxide nanoparticles.

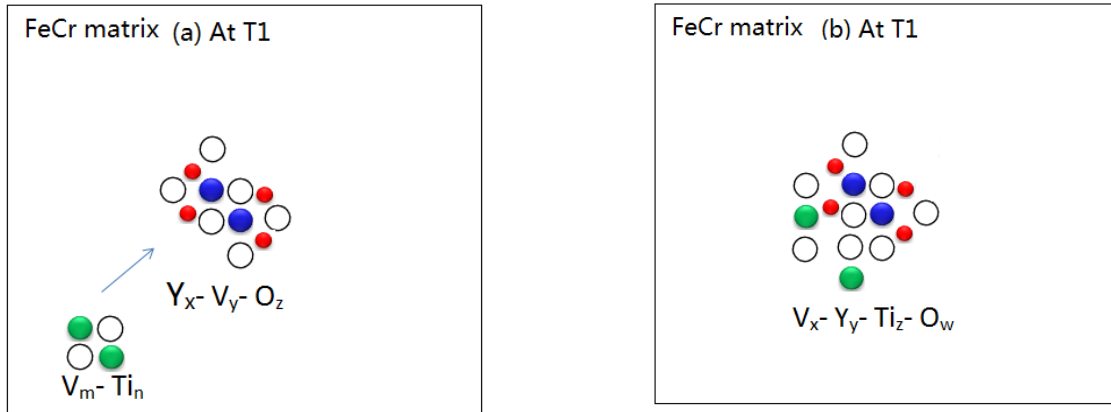


Figure IV-57: The second step of nanoparticles formation mechanism: the V_m-Ti_n complex migrates to $Y_x-V_y-O_z$ complex and forms $V_x-Y_y-Ti_z-O_w$ complex at temperature T1. Blue ball represents Y atom; green ball represents Ti atom; red ball represents O atom; black vacant ball represents vacancy.

- Step 2: As illustrated in Figure IV-57, the V_m - Ti_n complex (or Ti_x - V_y - O_z complex if it is formed) could migrate at temperature T_1 ($T_1 > RT$) and the V_x - Y_y - Ti_z - O_w complex is formed. It is supposed that the Ti diffusion coefficient is higher than the Y diffusion coefficient which is concluded by the experiments ^[63, 64, 199]. Unfortunately, the post irradiation annealing experiments have not been performed for the Ti implanted Fe sample because of the limited thesis duration. This study will be interesting for validating the Ti diffusion capacity.

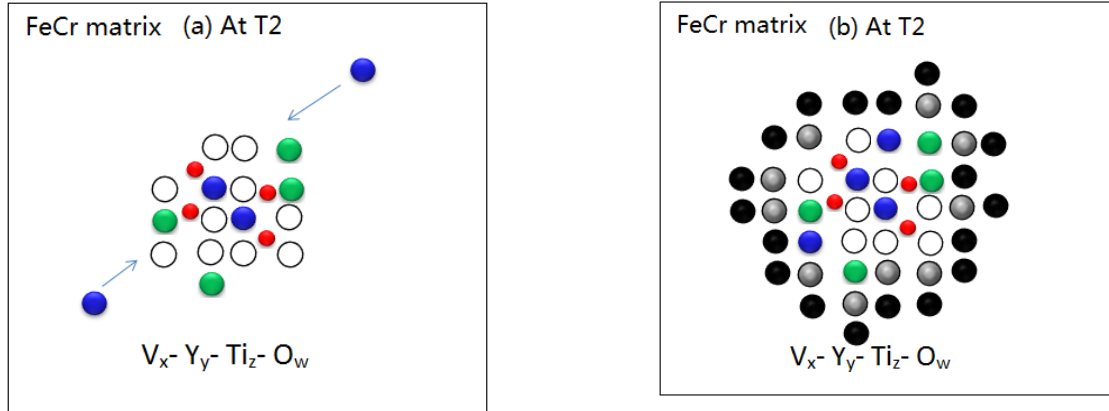


Figure IV-58: The third step of nanoparticles formation mechanism: the Y atoms migrate to V_x - Y_y - Ti_z - O_w complex and forms V_x - Y_y - Ti_z - O_w (which has a higher Y/Ti ratio) complex at temperature T_2 ($T_2 > T_1$). Blue ball represents Y atom; green ball represents Ti atom; red ball represents O atom; black vacant ball represents vacancy; gray ball represents Cr atoms; black full ball represents Fe lattice atoms.

- Step 3: As shown in Figure IV-58, the Y atoms migrate (or V_m - Y_n or Y_x - V_y - O_z or V_x - Y_y - Ti_z - O_w) at temperature T_2 ($T_2 > T_1$ and also $T_2 > 550^\circ\text{C}$) and the V_x - Y_y - Ti_z - O_w complex which has a higher Y/Ti ratio than the one formed in the second step is formed. The vacancy quantities in the complex could be reduced because of the high temperature T_2 . It corresponds to the study by H.Sakasegawa et al. ^[59] that Y/Ti ratio and size for $Y_xTi_yO_z$ particles increase after annealing at 1473 K for one hour. It is known that the size increase of nanoparticles in ODS steel would degrade the materials strength. Thus, it would be important to control the Y diffusion to prevent the nanoparticles size increase.

The positive binding of Cr atoms with the Fe interstitials observed in this thesis suggests that the Cr shell of the nanoparticle could be formed. In addition, the negative binding energy between Cr and Y, Ti ($E_{b-1NN}(\text{Cr-Y}) = -0.16 \text{ eV}$; $E_{b-1NN}(\text{Cr-Ti}) = -0.15 \text{ eV}$) ^[126] helps the formation of this shell/core structure. The second shell of Ti could also be formed because of its binding with Fe atoms and its repelling from Y atoms (Y-Ti interaction is repulsive at least up to the fifth nearest neighbor ^[83]). But these effects could be compensated by its binding with vacancy and O ($E_{b-1NN}(\text{O}_{int}\text{-Ti}_{sub}) = 0.26 \text{ eV}$ ^[126] 0.27 eV ^[127]; $E_{b-2NN}(\text{O}_{int}\text{-Ti}_{sub}) = 0.16 \text{ eV}$ ^[126] 0.55 eV ^[127]).

IV.4. Conclusions

The interaction between vacancy and yttrium, titanium and oxygen in bcc Fe has been studied in this chapter.

In section IV.1, the creation of vacancy defects by implantations with heavy ions Y, Ti and O has been investigated.

Vacancy clusters are detected in all implanted Fe samples whatever the nature of the ion, their energy, fluence and the irradiation temperature. The vacancy concentration or size is the highest for the low fluences and the depth distribution shows channelling of the ions and vacancy migration during implantation. For high fluences there is a layer where the vacancy defects are smaller which corresponds to the solutes Y, Ti, and O implantation peak as measured by SIMS or calculated by SRIM. It indicates the Y, Ti and O elements influence the defects formation. It could be due to the interaction that are possible between vacancy and the solute which can lead to their binding and a reduced migration and consequently agglomeration of vacancies in this layer where some V_n-X_m ($X=Y, Ti, O$) can be detected. This effect is less pronounced for Ti for which the binding energy with vacancy is the lowest.

In section IV.2, the evolution of the vacancy defects distribution as a function of annealing has been studied in the Y, and O implanted samples. It depends on the post-irradiation distribution of vacancy defects and on the concentration of solutes.

In samples implanted with Y at high fluence, several evolution steps have been observed but no diffusion of Y occurs up to 550°C. After 150°C annealing, one fraction of vacancy clusters V_n dissociate, migrate and recombine with interstitials. After 300°C annealing, the remaining vacancy clusters V_n with small size also recombines with interstitials and the Y_m-V_n complexes and dislocations are still detected. After 550°C annealing, one fraction of the Y_m-V_n complexes is recovered but the complexes like $Y-V_3$ and $Y-V_4$ could still resist at this temperature. The dislocations still exist in the damaged zone. After 750°C annealing, the $Y-V_3$ and $Y-V_4$ complexes also could dissociate and recombine. In addition, the dislocations disappear at this temperature. But another positron trap whose nature is not yet clear is still detected.

This study has revealed an evolution during the storage at room temperature for the sample implanted with O at high fluence which is not observed for the other irradiation or implantations conditions. The vacancy distribution changes up to approximately 235 days of storage and it is accompanied with a low diffusion of O towards the surface which leads to its oxidation. It has been explained by the possible migration of $O-V_n$ complexes such as $O-V_3$ complexes for which the migration energy has been calculated as low as the one calculated for pure Fe vacancy. The annealing experiments performed at temperatures from 100°C up to 550°C in sample implanted with O at high fluence and stored during 235 days have shown several evolution steps. After 150°C annealing, one fraction of vacancy clusters V_n dissociate, migrate and recombine with interstitials. Some O_m-V_n complexes also migrate and/or dissociate themselves. After 250°C annealing, the remaining vacancy clusters V_n with small size also recombines with interstitials and the remaining O_m-V_n complexes migrate and/or dissociate themselves. After annealing at 550°C, the dislocations and O enriched defects whose nature is not yet clear are detected in the damaged layer.

Finally, a schematic model has been proposed to explain the first steps of the ODS nanoparticles nucleation by using the results obtained in this thesis and other information found in literature.

- Step 1: During mechanical alloying (MA) process, the complexes V_m-Y_n , V_m-O_n and V_m-Ti_n could be respectively formed. The fraction of V_m-Ti_n complex should be the lowest. At room temperature, the V_m-O_n complex like $O-V_3$ could migrate because of its high diffusion capacity. In contrary, the V_m-Y_n complex could serve as a nucleation site because of its low diffusion capacity at room temperature. The Y atoms could also inhibit the V_m-O_n complex migration if $Y_x-V_y-O_z$ complexes are formed. In conclusion, the V_m-Y_n is the earliest germ for the nucleation oxide nanoparticles.
- Step 2: It is proposed that the V_m-Ti_n complex could migrate at temperature T_1 ($T_1 > RT$) and the $V_x-Y_y-Ti_z-O_w$ complex could be formed.
- Step 3: The Y atoms which are not involved in the O-Y-V complexes can migrate at temperature T_2 ($T_2 > T_1$ and also $T_2 > 550^\circ C$) and the $V_x-Y_y-Ti_z-O_w$ complex which has a higher Y/Ti ratio and bigger size than the one formed in the second step is formed. The vacancy quantities in the complex could be reduced because of the high temperature T_2 . It is known that the size increase of nanoparticles in ODS steel would degrade the materials strength. Thus, it would be important to control the Y diffusion to prevent the nanoparticles size increase.

Cr shell of the nanoparticle could be formed because of its binding to Fe interstitials. In addition, the negative binding energy between Cr and Y, Ti could help the formation of the shell/core structure. The second shell of Ti could also be formed because of its binding with Fe atoms and its repelling against Y atoms. But these effects could be compensated by its binding with vacancy and O.

General conclusion

The present thesis is an experimental study of the interaction of vacancy defects with Y, O and Ti solute to better understand their role in the nanoparticles formation in ODS steels. The ODS steels are expected to be used for claddings, targets and some other core and fuel structures of Gen-IV reactors because of their outstanding properties at high temperature and under irradiation.

It is known that the excellent properties of ODS steels are induced by the fine dispersion of nanoparticles. But the atomic scale clustering mechanism of these nanoparticles is not yet cleared. Although there are some simulation works which try to shed light on the nucleation route, the lack of experimental data for fundamental properties of nanoparticle constitutions (vacancy, Y, Ti, O) makes these works difficult to be validated. For example, several parameters, like the binding energies between Y, Ti, O, Cr and vacancy, the Y, Ti, O migration energies, have been calculated but needs to be verified experimentally. These fundamental properties would be important to control the nanoparticles composition, structure and nucleation route in order to guarantee the materials high quality.

In this work, the quality of virgin samples has been firstly optimized to allow the study of the defects induced by implantations/irradiations. The irradiations and implantations have been performed to introduce the vacancy defects and also Y, Ti, O atoms in the bcc Fe matrix for studying their interactions. After the implantations, slow positron beam Doppler broadening (SPBDB) technique is used for characterizing vacancy defects. It gives the information about defects distribution in depth, their natures and also chemical effect of Y, Ti, O on vacancies. Secondary Ion Mass Spectrometry (SIMS) is used to measure the Y, Ti, O concentration depth profiles to better understand positron results. Annealings have been performed after the implantations. The samples are measured by PAS and SIMS after each annealing to study the annealing effect.

In order to know the behavior of vacancy defects in Fe and FeCr, He irradiations have been realized. The single vacancy has been created at low He fluences (from 1×10^{-5} to 2×10^{-4} dpa). The single vacancies detected in the study are probably bound to C or/and to O. The annealing experiments have shown several stages: The concentration of Fe single vacancy begins to decrease at 150°C due to the dissociation of V-C complex and the recombination of the free vacancies with the interstitials. From 200°C positrons detect at least two types of defects: Fe single vacancy that could be V-O complexes and another one with free volume lower than single vacancy. This new defect could be dislocation. After annealing at 500°C, a large part of the defects have been eliminated. Vacancy clusters are detected at high He fluences (from 5×10^{-4} to 1×10^{-1} dpa). The concentration of Fe vacancy clusters begins to reduce at 200°C which could be due to the migration of vacancy clusters and recombination with the interstitials. The size and/or concentration of vacancy clusters decreases at 250°C. This observation could be explained by the fact that the vacancy clusters dissociate from temperature close to 250°C. At 350°C, a major fraction of vacancy clusters are recovered. After annealing at 500°C defects are still detected that could be dislocations or vacancy-impurity complexes. In the case of bcc FeCr matrix, single vacancies are the main detected defects at low fluences (from 6×10^{-5} to 6×10^{-4} dpa) in FeCr sample. The concentration of single vacancy in Fe-12Cr is reduced already at 110°C which is at lower temperature than in pure Fe. This elimination could be due to the SIAs long-range migration. The V concentration continues to decrease at 150°C. This stage can be explained by the V-C pairs dissociation as in the case of Fe. In FeCr

samples irradiated at high fluences (from 6×10^{-3} to 7.8×10^{-2} dpa), vacancy clusters are detected and their size or concentration decrease monotonously with Cr content at the same damage dose. It could be due to the strong interactions between Cr atoms with self-interstitials (SIA) which reduces the mobility of these interstitial clusters and consequently increasing the vacancy recombination on these sinks. The vacancy clusters size and concentration begin to decrease at 250°C. It could be due to the vacancy clusters dissociation. On the contrary, the annealing stage observed at 200°C in Fe doesn't occur in Fe12Cr sample. It suggests that the temperature of vacancy clusters migration in Fe12Cr is higher than that in pure Fe. A large part of the vacancy clusters are recovered at 450°C which is 100°C higher than in the case of Fe. This shift in vacancy recovery could also be explained by the higher migration temperature of vacancy clusters in Fe12Cr.

Once the vacancy defects properties have been revealed, the Y, Ti, O implantations have been performed to study the Y, Ti, O- vacancy interactions in Fe matrix. The implantations with heavy ions Y, Ti and O have induced vacancy clusters in Fe which are formed by single vacancies and small clusters migration during implantations. Their size and concentration distribution depends on the nature and energy of the ions. For the heaviest ions Y and Ti, damage is detected deeper than expected from the SRIM calculations with the most pronounced effect for the heaviest ions Y. In all cases, the defects depth distribution shows a lower size of vacancy defects in the region where the concentration of the incident ions Y, Ti and O is the highest. This effect of the ions on the damage formation is more pronounced for respectively O, Y and Ti. This behaviour is correlated to the binding energy that has been calculated for V-X type complexes which is the highest for O then Y and finally low but still positive for Ti. The process reduce the mobility and agglomeration probability of the vacancy defects.

The evolution of the vacancy defects distribution as a function of annealing has been studied in the Y, and O implanted samples. It depends on the post-irradiation distribution of vacancy defects and on the concentration of solutes.

In samples implanted with Y at high fluence, several evolution steps have been observed but no diffusion of Y occurs up to 550°C. After 150°C annealing, one fraction of vacancy clusters V_n with large size dissociate, migrate and recombine with interstitials. After 300°C annealing, the remained vacancy clusters V_n with small size also recombines with interstitials and the Y_m - V_n complexes and dislocations are still detected. After 550°C annealing, one fraction of the Y_m - V_n complexes is recovered but the complexes like Y - V_3 and Y - V_4 could still resist at this temperature. The dislocations still exist in the damaged zone. After 750°C annealing, the Y - V_3 and Y - V_4 complexes also dissociate and recombine. In addition, the dislocations disappear at this temperature. But another positron trap whose nature is not yet clear is still detected.

This study has revealed an evolution during the storage at room temperature for the sample implanted with O at high fluence which is not observed for the other irradiation or implantations conditions. The vacancy distribution changes up to approximately 235 days of storage and it is accompanied with a diffusion of O towards the surface which leads to its oxidation. It has been explained by the possible migration of O - V_3 complexes for which the migration energy has been calculated as low as the one calculated for pure Fe vacancy. The annealing experiments performed at temperatures from 100°C up to 550°C in sample implanted with O at high fluence and stored during 235 days have shown

several evolution steps. After 150°C annealing, one fraction of vacancy clusters V_n with large size dissociate, migrate and recombine with interstitials. Some O_m - V_n complexes also migrate and/or dissociate. After 250°C annealing, the remaining vacancy clusters V_n with small size also recombines with interstitials and the remaining O_m - V_n complexes migrate and/or dissociate. After annealing at 550°C, the dislocations and O enriched defects whose nature is not yet clear are detected in the damaged layer.

Finally, a schematic model has been proposed to explain the first steps of the ODS nanoparticles nucleation by using the results obtained in this thesis and other information found in literature.

- Step 1: During mechanical alloying (MA) process, the complexes V_m - Y_n , V_m - O_n and V_m - Ti_n could be respectively formed. The fraction of V_m - Ti_n complex should be the lowest. At room temperature, the V_m - O_n complex like O - V_3 could migrate because of its high diffusion capacity. In contrary, the V_m - Y_n complex could serve as a nucleation site because of its low diffusion capacity at room temperature. The Y atoms could also inhibit the V_m - O_n complex migration if Y_x - V_y - O_z complexes are formed. In conclusion, the V_m - Y_n is the earliest germ for the nucleation oxide nanoparticles.
- Step 2: It is proposed that the V_m - Ti_n complex could migrate at temperature T_1 ($T_1 > RT$) and the V_x - Y_y - Ti_z - O_w complex could be formed.
- Step 3: The Y atoms which are not involved in the O - Y - V complexes can migrate at temperature T_2 ($T_2 > T_1$ and also $T_2 > 550^\circ C$) and the V_x - Y_y - Ti_z - O_w complex which has a higher Y/Ti ratio and bigger size than the one formed in the second step is formed. The vacancy quantities in the complex could be reduced because of the high temperature T_2 . It is known that the size increase of nanoparticles in ODS steel would degrade the materials strength. Thus, it would be important to control the Y diffusion to prevent the nanoparticles size increase.

Cr shell of the nanoparticle could be formed because of its binding to Fe interstitials. In addition, the negative binding energy between Cr and Y, Ti could help the formation of the shell/core structure. The second shell of Ti could also be formed because of its binding with Fe atoms and its repelling against Y atoms. But these effects could be compensated by its binding with vacancy and O.

Perspectives

Several complementary experimental studies would have to be performed to complete the present thesis and help to confirm some results or to answer some highlighted questions. The positron lifetime experiments could be realized to check the evolution of the vacancy defects size which would be important to confirm the obtained conclusions for Y, Ti, O- V interactions. The transmission electron microscopy (TEM) will be helpful to confirm the presence of dislocations after irradiation and annealing. The annealing post-irradiation could be performed in Ti- implanted sample to study the Ti effect on annealing behavior of vacancy defects. It would be also important to determine the Ti diffusion capacity during annealing. It would also be interesting to perform the annealing post- irradiation for the double beams Y- O implanted sample to obtain information on the ternary Y- O- V complex interaction.

It would be very interesting to measure the Y depth concentration profile in Y implanted sample after the annealing at 750°C to check that Y is still concentrated in sample and to perform APT experiments to see if it could be trapped in precipitates.

Once the Y, Ti, O and vacancy interactions in bcc Fe matrix are clearly revealed, it would also be interesting to see how the Cr presence could change their interactions in bcc FeCr matrix. It would help to know the role of Cr in the nanoparticle shell/core structure.

All these experimental work would find a valuable issue if it is complement with theoretical study as it has been done and would have to be reinforced. For example the calculation of the annihilation characteristics of different vacancy defects decorated with O, Y and Ti would help to determine the nature of the defects observed experimentally. The use of cluster dynamics simulations could also help to better understand the microstructural evolution as a function temperature and irradiation conditions. It would be interesting to check how these simulations are able to predict the experimental results. Then these models should help to establish trends in the effect of solute/vacancy ratio and the proportion of the different solutes to form a uniform distribution of fine oxide nanoclusters which are desired to guarantee the excellent properties of the ODS steels in nuclear severe conditions.

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Annexes

Annex A1: Electron- bombardment furnace

The furnace used is an electron-bombardment furnace developed in laboratory CNRS-Orleans/CEMHTI. Samples are placed on a SiC sample holder which is posed above a tungsten filament. The electric current passing the filament heats the sample holder by Joule effect. For further increasing the temperature, one voltage could be imposed between the filament, accelerating electrons towards the sample holder. This phenomenon of electron- bombardment enables attaining the high temperature. In the case of 750°C annealing of Fe, one 1.2 keV voltage is imposed to reach this temperature. The pumping system assures that the vacuum before heating is less than 5×10^{-6} mbar. The temperature is measured by using a pyrometer which focuses on the SiC sample holder in the case of Fe annealing. The good thermal contact between SiC sample holder and the Fe sample ensures that the temperatures of these two objects are similar. The emissivity used for the SiC sample holder is 0.8.

Annex A2: Electrochemical polishing

The electrochemical polishing process used for FeCr samples preparations is presented here. As shown in Figure 0-1, the FeCr sample is linked to the anode of a current generator and the cathode is connected to a graphite rod. The sample and the graphite rod are immersed into the electrolyte bath (~ 250 ml) which is composed of 2% of perchloric acid and 98% of ethylene glycol monobutyl ether. The generator voltage is set to be ~ 60V which gives a current ~ 0.18- 0.2A in the electrolyte. The electrolyte is agitated by a magnet bar to ensure its homogeneity. After the electrochemical polishing, the samples were cleaned in acetone and ethanol by ultrasonics.

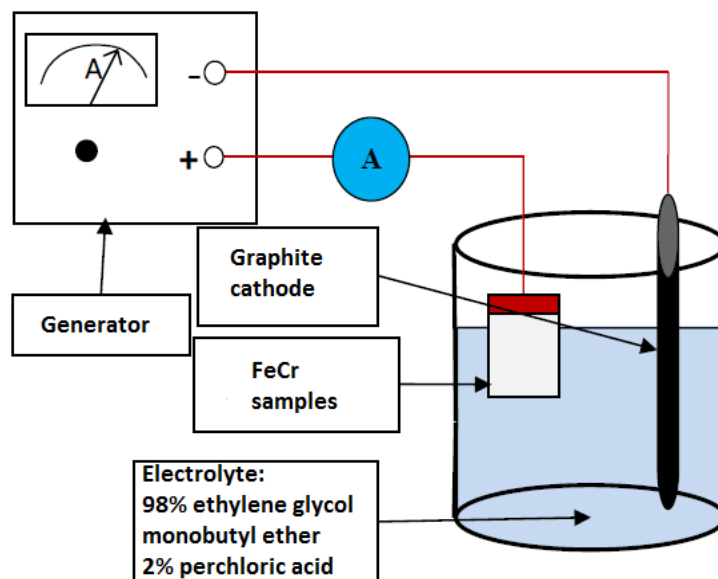


Figure 0-1: Schema of electrochemical polishing device used for FeCr sample.

Annex A3: The behavior of V in Fe3Cr, Fe5Cr and Fe9Cr (low He fluence: $1 \times 10^{14} \text{ cm}^{-2}$)

Annealings at temperature from 110°C up to 250°C have been realized for Fe- 3Cr, Fe- 5Cr and Fe- 9Cr samples irradiated with 2MeV He ions at $1 \times 10^{14} \text{ cm}^{-2}$ as shown in Figure 0-2, Figure 0-3 and Figure 0-4.

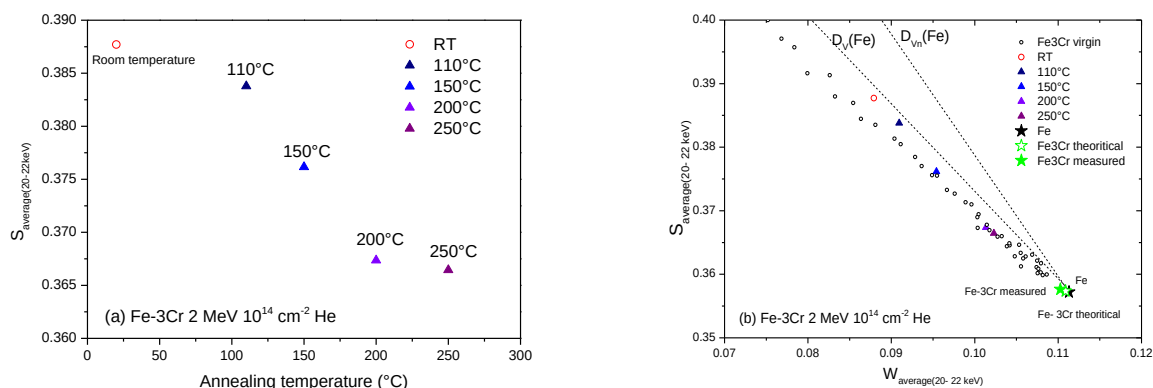


Figure 0-2: $S_{\text{average}(20-22\text{keV})}$ values as a function of (a) the annealing temperature and (b) $W_{\text{average}(20-22\text{keV})}$ for irradiated Fe3Cr with 2 MeV He ions at $1 \times 10^{14} \text{ cm}^{-2}$ up to 250°C.

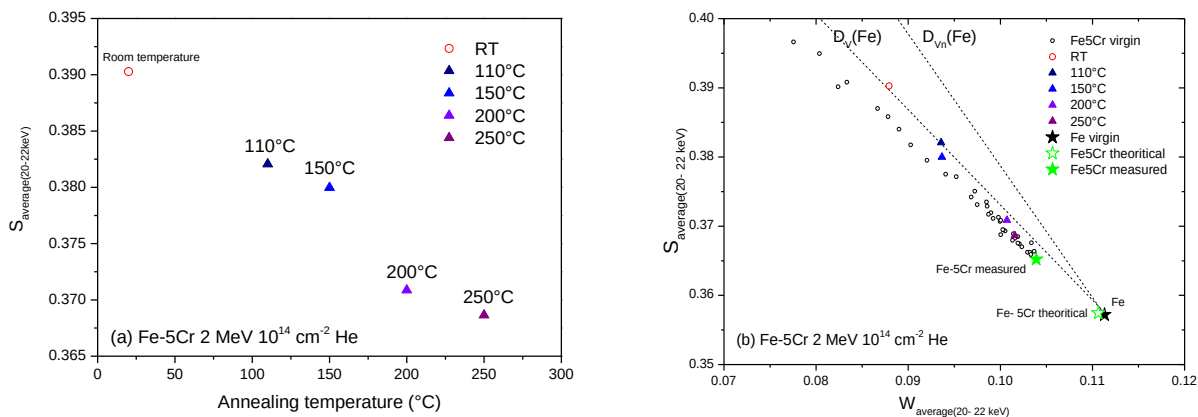


Figure 0-3: $S_{\text{average}(20-22\text{keV})}$ values as a function of (a) the annealing temperature and (b) $W_{\text{average}(20-22\text{keV})}$ for irradiated Fe5Cr with 2 MeV He ions at $1 \times 10^{14} \text{ cm}^{-2}$ up to 250°C.

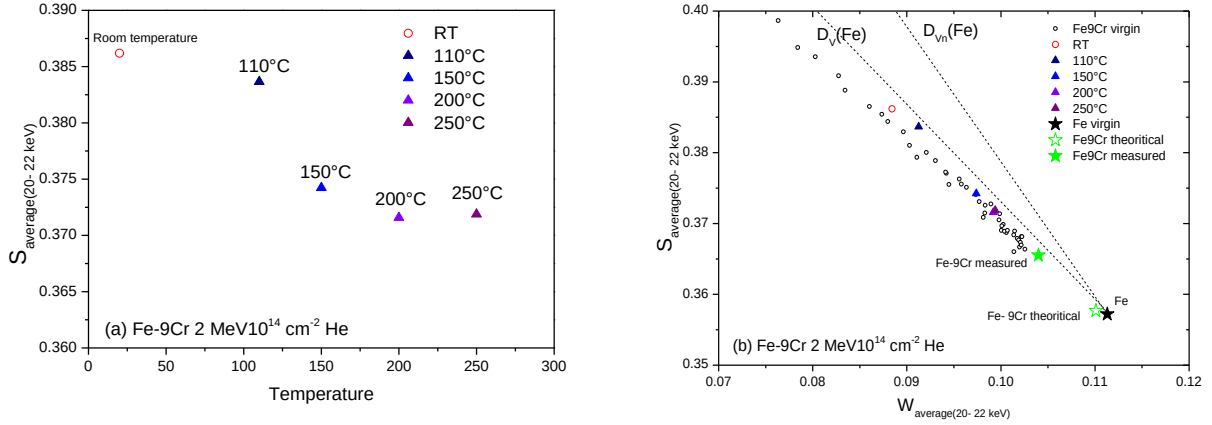


Figure 0-4: $S_{\text{average}(20-22 \text{ keV})}$ values as a function of (a) the annealing temperature and (b) $W_{\text{average}(20-22 \text{ keV})}$ for irradiated Fe9Cr with 2 MeV He ions at $1 \times 10^{14} \text{ cm}^{-2}$ up to 250°C.

Annex A4: The behavior of V_n in Fe3Cr (high He fluence: $1.3 \times 10^{17} \text{ cm}^{-2}$)

Annealings at temperature from 110°C up to 250°C have been realized for Fe- 3Cr samples irradiated with 2MeV He ions at $1.3 \times 10^{17} \text{ cm}^{-2}$ as show in Figure 0-5.

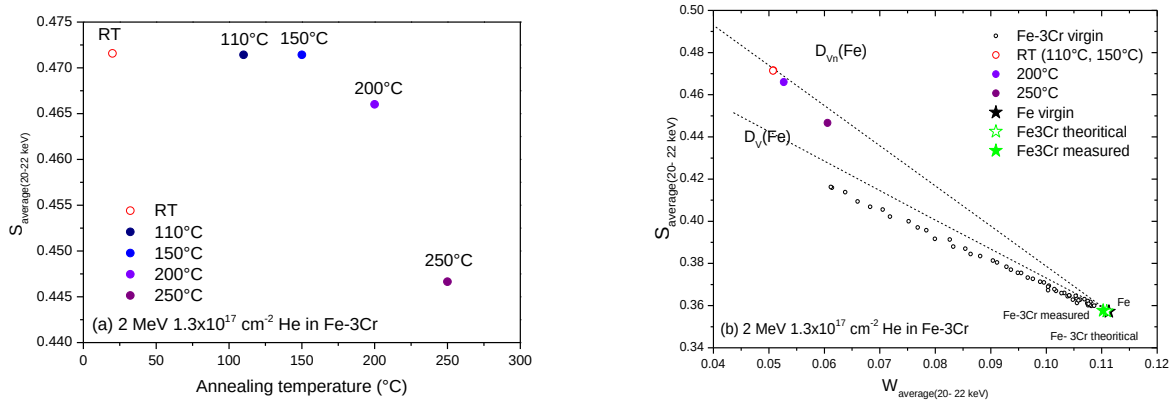


Figure 0-5: $S_{\text{average}(20-22 \text{ keV})}$ values as a function of (a) the annealing temperature and (b) $W_{\text{average}(20-22 \text{ keV})}$ for irradiated Fe3Cr with 2 MeV He ions at $1.3 \times 10^{17} \text{ cm}^{-2}$ up to 250°C.

Chenwei HE

Experimental study of the interaction of vacancy defects with Y, O and Ti solutes to better understand their roles in the nanoparticles formation in ODS steels

The severe operating conditions of the future nuclear reactor, Generation-IV, -high temperature and high irradiation damage-, require the adapted materials development. Oxide-dispersion strengthened (ODS) alloy is one of the most potential candidates expected to be used for fuel cladding material because of their outstanding swelling and creep properties. Their excellent properties are induced by the fine dispersion of oxide nanoparticles (Y, O, Ti), obtained by mechanical alloying of steel and oxide powders and which has to be better mastered. But the atomic scale clustering mechanism of these nanoparticles is not yet cleared. In this context, the present thesis using positron annihilation spectroscopy (PAS) and secondary ion mass spectrometry (SIMS) sheds light on the interaction of vacancy defects with Y, O and Ti solutes to better understand their roles in the nanoparticles formation.

The He irradiations have been performed to reveal the vacancy defects properties and Y, Ti, O implantations realized to study the Y, Ti, O- vacancy interactions in bcc Fe matrix. In all cases, the defects depth distribution shows a lower size of vacancy defects in the region where the concentration of the incident ions Y, Ti and O is the highest. This effect of the ions on the damage formation is more pronounced for respectively O, Y and Ti. It is explained by the formation of V-X (X=O, Y, Ti) complexes which reduce the mobility and agglomeration probability of the vacancy defects. The annealing of the Y and O implanted samples reveals that some O-vacancy complexes are mobile at room temperature and Y doesn't diffuse up to 550°C whilst Y-vacancy complexes remain as it is expected from theory. A model of the first steps of the ODS nanoparticles nucleation is proposed by using the results obtained in this thesis.

L'étude expérimentale de l'interaction entre défauts lacunaires et l'Y, O, Ti pour comprendre leur rôles dans la formation des nanoparticules d'alliages ODS

Les conditions sévères de fonctionnement des réacteurs du futur, Génération-IV, -haute température et fortes irradiations- nécessitent le développement de matériaux adaptés. Les aciers ODS (Oxide Dispersion Strengthened) sont des candidats très compétitifs pour le gainage du combustible en raison de leurs excellentes propriétés de gonflement et de fluage. Ces atouts majeurs sont induits par la fine dispersion de nanoparticules d'oxydes (Y, O, Ti) obtenue par co-broyage de poudres de la matrice et d'oxyde dont les conditions sont à optimiser pour maîtriser la distribution en taille et composition de ces nanoparticules. Dans l'objectif de mieux comprendre le mécanisme de formation de ces nanoparticules à l'échelle atomique, la présente thèse met à profit l'utilisation de la spectroscopie d'annihilation de positons (PAS) et de la spectrométrie de masse d'ions secondaires pour étudier l'interaction des défauts lacunaires avec des solutés Y, O et Ti et évaluer leur rôle dans la formation des nanoparticules.

Les irradiations avec des ions He ont été effectuées pour révéler les propriétés des défauts lacunaires et les implantations d'Y, Ti, O ont été réalisées pour étudier les interactions de ces éléments Y, Ti, O avec les lacunes dans la matrice de fer. La distribution des défauts en profondeur indique la présence de défauts lacunaires avec une taille plus petite dans la région où la concentration d'Y, Ti, O est la plus élevée. Cet effet est plus prononcé pour O, Y et Ti respectivement. Il est expliqué par la formation de V-X (X=O, Y, Ti) complexes qui réduisent la probabilité de la mobilité et d'agglomération des défauts lacunaires. Les recuits des échantillons implantés Y et O révèlent que des complexes O-lacune sont mobiles à température ambiante, et que l'yttrium ne diffuse pas jusqu'à 550°C alors que des complexes Y-lacunes sont encore détectés comme cela est attendu par des résultats théoriques. Un modèle des premières étapes de la nucléation des nanoparticules est proposé en utilisant les résultats obtenus dans cette thèse.



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