

INITIAL STAGE OF DEFECT STRUCTURAL
EVOLUTION IN F82H AND ITS MODEL ALLOYS
BY IRRADIATION DAMAGE

Doctoral Dissertation

Graduate school of Engineering, Kyoto University

Shaosong Huang

2014

CONTENTS

Chapter 1	Introduction	1
1.1	Nuclear energy and materials.....	1
1.2	Ferritic/martensitic steels	2
1.2.1	Properties of Ferritic/martensitic steels.....	2
1.2.2	Application for fission reactors	3
1.2.3	Application for fusion reactors.....	3
1.2.4	Irradiation effects on ferritic/martensitic steels	6
1.3	Lattice defects of metals	8
1.3.1	Sort of lattice defects.....	8
1.3.2	Point defects	9
1.3.3	Migration of point defects	10
	• Vacancy migration.....	11
	• Interstitial migration.....	12
1.3.4	Dislocations (line defects)	13
1.3.5	Space defects	14
1.4	Irradiation damage.....	15
1.4.1	Atomic displacement.....	15
1.4.2	Defect production rate	17
1.4.3	Cascade damage.....	18
1.4.4	Irradiation effects	20
	• Irradiation embrittlement	20
	• Void swelling	20
1.5	Purpose of this study	21
	Reference (Chapter 1).....	25
Chapter 2	Experiments.....	29
2.1	Irradiation experiments	29
2.1.1	Specimen preparation	29
2.1.2	Electron irradiation.....	29
2.1.3	Neutron irradiation	31
	• Kyoto University Research Reactor	31

• BR2 Reactor	35
2.1.4 Ion irradiation	36
2.2 Transmission electron microscopy.....	37
2.2.1 Principle of transmission electron microscopy	37
2.2.2 Thinning TEM specimens	39
2.3 Positron annihilation spectroscopy	41
2.3.1 History of positron annihilation spectroscopy	41
2.3.2 Principle of positron annihilation	42
2.3.3 Positron annihilation lifetime (PAL) measurement	44
2.4 Mössbauer spectroscopy	50
2.4.1 Principle of Mössbauer spectroscopy	50
• Isomer Shift	51
• Quadrupole splitting	52
• Hyperfine magnetic splitting	53
2.4.2 Experimental	56
Reference (Chapter 2).....	58
Chapter 3 Defect evolution by isolate point defects in F82H steel and its model alloys	61
3.1 Role of point defects on the void swelling resistance.....	61
3.2 Electron irradiation	61
3.2.1 Microstructure of specimens before irradiation	62
• X ray diffraction.....	62
• TEM observation	64
• Positron annihilation spectroscopy	66
3.2.2 Microstructure of specimens after irradiation.....	67
• Electron irradiation at 77 K.....	67
• Electron irradiation at 673 K.....	68
• Isochronal annealing behavior	69
3.2.3 Effects of alloying elements	71
3.2.4 Effects of C	73
3.3 Conclusion.....	75
Reference (Chapter 3).....	76
Chapter 4 Defect evolution by cascade damage in F82H steel and its model alloy	77
4.1 Role of dislocations on the void swelling resistance in ferritic materials	77

4.2	Neutron irradiation	77
4.2.1	Neutron irradiation at 363 K.....	78
4.2.2	Neutron irradiation at 573 K.....	80
4.2.3	Defect evolution in neutron irradiated specimens compared with those in electron irradiated specimens.....	81
	• Cr effect.....	81
	• W, V and Ta effect.....	82
	• Effects of C and/or Cr with other elements.....	82
4.2.4	Isochronal annealing behavior of defects in specimens irradiated with neutrons at 363 K to 1.5×10^{-3} dpa.....	84
	• Defects evolution in Fe after isochronal annealing	84
	• Cr and W solute atom effects during isochronal annealing	85
	• C effects during isochronal annealing.....	87
4.3	Fe ion irradiation.....	88
4.3.1	Positron annihilation spectroscopy.....	88
4.3.2	Cross sectional transmission electron microscopy	89
4.4	Conclusions	94
	Reference (Chapter 4).....	96
Chapter 5	Short range ordering in irradiated F82H and its model alloys	97
5.1	Property of Fe-Cr alloys.....	97
5.2	Short range ordering	97
5.3	Spectrum analyses.....	98
5.4	Measures of short-range order	99
5.5	Defect effects.....	102
5.6	Solute atom effects.....	105
5.6.1	Cr effect	105
5.6.2	W and other solute atom effects.....	109
5.6.3	Metal carbides effect	109
5.7	Conclusions	112
	Reference (Chapter 5).....	113

Chapter 6 Summary.....	115.
Acknowledgements.....	117
List of publications	119

Chapter 1 Introduction

1.1 Nuclear energy and materials

The increasing world-wide demand for energy has urged on international cooperation to meet energy need for maintaining and improving the environment. Nuclear energy is a good choice for this demand, since it can be produced by efficient nuclear fission reaction without the environmental waste compared to the use of coal or petroleum products. Although renewable energy sources offer the possibility of clean energy, there are concerns about efficiency and reliability, however, the reliability of nuclear power has been demonstrated by the reactors operating today. The increasing concern on environment from reliable sources of energy has led our society to reconsider nuclear energy as part of a more diverse energy portfolio. Public acceptance of nuclear energy as a viable solution can be accomplished by responsible recycling of waste combined with an increase in the reactor efficiency as defined in [1]. Current plans to make fission reactors more efficient will require that future reactors operate at higher temperatures (up to 1473 K) in order to deeply burn fuel than current reactors [1]. This next generation of more efficient and safer reactors is called Generation IV reactors (Gen IV). The current steels (such as 316 stainless steel) used in reactors are incapable of hosting the increased irradiation over long periods of time, and at elevated temperatures. They exhibit considerable swelling under the higher temperatures and irradiation dose. Therefore new steels are required to build next generation nuclear reactors. Due to their larger corrosion and swelling resistance, Fe-Cr (iron-chromium) based ferritic steels are potential structural materials for next generation of nuclear reactors.

Furthermore, nuclear fusion is considered as a promised future energy. The extreme environment in fusion reactor will require a wide range of materials that are tailored for high performance in a hostile environment involving intense heat fluxes, high temperatures, potentially corrosive coolants, significant cyclic thermo-mechanical stresses, and intense fluxes of high-energy neutrons and electromagnetic radiation. The most promising candidate materials for such applications are low-activation ferritic/martensitic steels, typically containing about 9 wt. %Cr and smaller quantities of W, V and Ta.

1.2 Ferritic/martensitic steels

1.2.1 Properties of ferritic/martensitic steels

These kinds of steels have two phases of $\gamma + \alpha$ (or δ) at high temperature. With rapid cooling, $\gamma \rightarrow M$ (martensite) transition will occur; ferrite still remains. Phases at room

temperature are martensite and ferrite. The amount of ferrite ranges from several percent to couples of percent depends on the composition and heat treatment. These steels mainly refer Cr steels with no significant Ni content.

The development of Cr steels is reported to have originated in 1912 with the manufacture of a 12 wt.%Cr, 2-5 wt. %Mo steels for steam turbine blades by Krupp and Mannesmann in Germany [2,3]. However, in 1912-13 Brearley in the U.K., while attempting to develop high-temperature steels for gun barrels, accidentally discovered that martensitic steels containing 13 Cr and 0.2 C did not rust [4]; the stainless characteristics of high-Cr steels were also recognized by Haynes in the USA and by Strauss and Maurer in Germany at about the same time. The high-Cr, high-C martensitic steels were hard and had a sharp cutting edge and were subsequently developed commercially for applications such as cutlery knives and tableware in competition with austenitic stainless steels as well as for razors, scalpel blades, and heat-resisting tools and bearings [5].

The 9 and 12 Cr transformable steels with lower C (0.1 max) content and additions of Mo, W, V, Nb, N and other elements, possessing oxidation and corrosion resistance at elevated temperatures, have subsequently been developed. The development of Cr steels is highly depended on physical metallurgical basis especially for constitution. Fig.1-1 shows the Fe-Cr-C equilibrium diagram. The γ -Fe loop in the diagram is closed if the chromium content exceeds about 12 wt.%; however, the austenite-stabilizing elements(C, N, Ni, Mn, Cu, Co) extend the γ - phase field, while the ferrite-forming elements (Cr, Mo, Nb, V, W, Si, Ti, Al) contract it [6,7]. 7-12 Cr steels are either fully austenitic or have a duplex (austenite plus δ -ferrite) structure at austenitizing temperature in the range 1123 to 1473 K. The austenite phase transforms to martensite during air cooling or rapid quenching to ambient temperature, and the steels are subsequently tempered to obtain a good combination of strength, ductility, and toughness. These steels have been used or considered for use in petro-chemical and chemical plants, gas turbine engineering, aircraft and aerospace industries, electrical power plants, and as nuclear fission and fusion components.

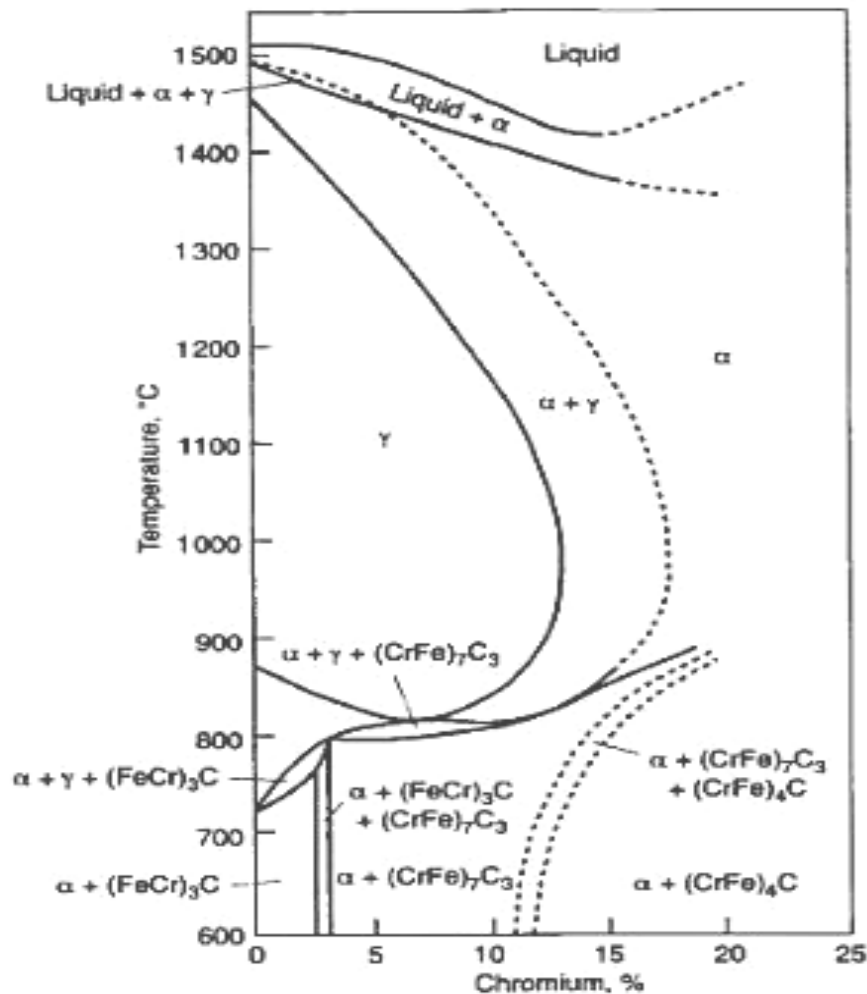


Fig.1-1 Effect of Cr on the constitution of Fe-Cr-C alloys containing 0.1C wt. % [8]; note that $(\text{CrFe})_4\text{C}$ is M_{23}C_6 carbides.

1.2.2 Application for fission reactors

High-chromium (9–12 wt.%Cr) ferritic/martensitic steels were first considered for elevated-temperature in-core applications (cladding, wrappers, and ducts) for fast reactors in the 1970s, because of their excellent thermal properties and irradiation resistance (low swelling) relative to austenitic stainless steels [9]. HT9, nominally Fe-12Cr-1Mo-0.5W-0.5Ni-0.25V-0.2C (all compositions are in wt. %), which was developed in Europe in the 1960s for the power-generation industry, was chosen as the material for investigation in the U.S. fast reactor program. Similar types of steel were chosen in Europe and Japan (EM-12, FV448, DIN 1.4914, and JFMS in France, United Kingdom, Germany, and Japan, respectively). A large amount of information was generated in the respective nuclear programs on the properties of these steels before and after irradiation [10].

1.2.3 Application for fusion reactors

When ferritic/martensitic steels were considered as structural materials for fusion reactors in the late 1970s, HT9 was the first one considered in the U.S. Program [10,11]. Similarly, the first such steels in the programs in Europe and Japan were the steels previously considered in their fast reactor programs mentioned above [10,12]. In the mid-1980s, the idea of low-activation materials was introduced into the international fusion programs [13-15]. The objective was to build reactors from materials that would either not activate when irradiated by neutrons or, if activated, develop low-level radiation or the radioactivity would decay quickly, allowing for improved safety of operation as well as hands-on maintenance [13,14]. Truly “low-activation” steels defined in this way is not possible, because they are limited by the decay of the products from transmutation of Fe atoms. “Reduced-activation” steels, where the activity decays in a relatively short time, thus allowing for shallow land burial, as opposed to deep geological storage, were considered to be possible, and their development was pursued.

Beginning in the mid-1980s, fusion reactor materials research programs in Japan, the European Union, and the United States began working toward developing “reduced-activation” ferritic/martensitic steels for use in a fusion energy demonstration reactor and subsequent power reactors [14-19]. The development evolved from calculations to determine which elements must be replaced in conventional Cr-Mo steels to obtain a rapid decay of induced radioactivity after irradiation in a fusion reactor [13, 14]. Such calculations indicated that the typical steel-alloying elements Mo, Nb, Ni, Cu, and N must be eliminated or minimized to obtain “reduced activation.” Proposals for reduced-activation ferritic steels involved the replacement of Mo in conventional Cr-Mo steels by W [15,16-19] and/or V [16, 19]. Fusion materials programs in Japan, the European Union, and the United States have developed Cr-V and Cr-W-V steels [15-21] to which Ta is sometimes added as a replacement for Nb [15,17,18].

Steels with 7–9 wt. %Cr were usually chosen due to the difficulty of eliminating Delta (δ)-ferrite in a 12 %Cr steel without increasing C or Mn for austenite stabilization. δ -ferrite can lower toughness, and Mn promotes χ -phase precipitation during irradiation, which can cause embrittlement. Low-Cr (2.25 %Cr) steels were also considered [14,19,20,21], but in the end, 7–9 %Cr steels were chosen for further study and development as shown in Table 1-1. In Japan, a Fe-8.0Cr-2.0W-0.2V-0.04Ta-0.10C (F82H) [17,22,23] and Fe-9Cr-2W -0.2V-0.07Ta-(JLF-1) [20,24,25] steel were chosen, in China, a Fe-9Cr-1.5W-0.2V-0.07Ta-0.10C (CLAM) and in Europe, a Fe-9.3Cr-1.0W-0.25V-0.04Cu-0.10C (OPTIFER Ia) and Fe-9.4Cr- 1.1Ge-0.30V-0.13C (OPTIFER II) were originally chosen and investigated [26]. The steel with the best properties in the U.S. was ORNL 9Cr-2WVTa steel [14, 21,27]. Based on the earlier work on the

reduced-activation steels, a new composition was more recently developed in Europe called EUROFER [28].

Table 1-1 Compositions of reduced-activation steels presently of interest in international fusion programs.

Programs	Steels	C	Si	Mn	Cr	W	V	Ta	N	B
Japan	F82H	0.10	0.2	0.50	8.0	2.0	0.20	0.04	<0.01	0.003
	JLF-1	0.10	0.08	0.45	9.0	2.0	0.20	0.07	0.05	
China	CLAM	0.10	0.01	0.45	9.0	1.5	0.20	0.07	0.02	
	OPTIFER Ia	0.10	0.06	0.50	9.30	1.0	0.25		0.015	0.006
Europe	OPTIFER II	0.125	0.04	0.50	9.40		0.25		0.015	0.006
	EUROFER	0.11	0.05	0.50	8.5	1.0	0.25	0.08	0.03	0.005
	ORNL9Cr-									
USA	2WVTa	0.10	0.30	0.40	9.0	2.0	0.25	0.07		

Development of structural materials for fusion energy is guided by the operational conditions expected in fusion power plants, and by lifetime and safety requirements associated with economics and environmental concerns. The operational conditions necessitate the use of structural materials at high temperatures in order to achieve high thermodynamic efficiency, as well as at low temperatures dictated by normal shutdown and start-up operations along with maintenance of plant components. Exposure to energetic neutron irradiation can induce dramatic damages in materials. The five key phenomena of highest significance for establishing viable operating temperatures and doses of structural materials are in references [29,30]: 1. Low temperature irradiation hardening and embrittlement, which typically emerges for displacement damage levels above 0.001–0.1 displacements per atom (dpa) at temperatures below $\sim 0.4 T_M$, where T_M is the melting point temperature; 2. Potential matrix and/or grain boundary embrittlement due to irradiation-enhanced or –induced precipitation due to coupled solute–defect processes that are typically most prevalent at doses above 1–10 dpa at intermediate temperatures of 0.3–0.6 T_M ; 3. Plastic deformation due to irradiation creep (acting in addition to thermal creep processes) that is most significant for doses above 10 dpa at irradiation temperatures below 0.45 T_M ; 4. Volumetric swelling due to void formation when the damage levels is more than 10 dpa at intermediate temperatures of 0.3–0.6 T_M ; 5. High temperature He embrittlement of grain boundaries, which is considered as a major issue in mechanically stressed materials for transmutant He concentration levels above ~ 10 –100 appm (>1 –10 dpa) at exposure temperatures above 0.5 T_M . In most structural materials, the first and last of these five phenomena define the lower and upper bounds for viable operating temperatures, and the other three listed phenomena typically determine the maximum viable

operating lifetime. The key challenges for developing improved irradiation-resistant structural materials are centered on two major topics: 1. Expanding the operation temperature window; 2. Expanding the viable operational lifetime of structural materials. Fig.1-2 shows the Operational design window for the FW/B of a conceptual fusion power plant.

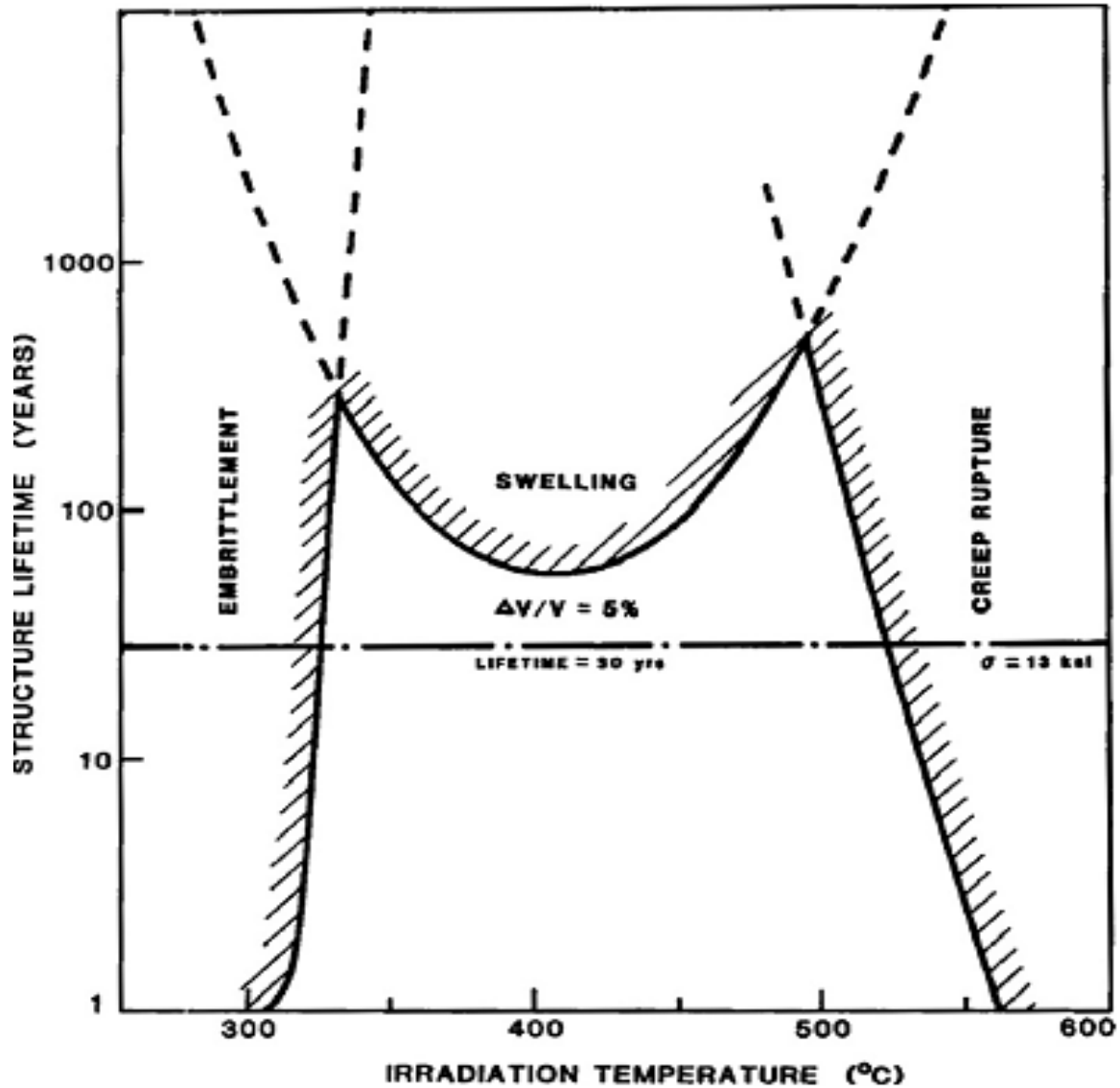


Fig.1-2 Operational design window for the FW/B of a conceptual fusion power plant (magnetic mirror design), where early versions of ferritic/martensitic steels were proposed [31].

1.2.4. Irradiation effects on ferritic/martensitic steels

High-energy neutron irradiation in a fast reactor or fusion reactor displaces atoms from their normal matrix positions and form vacancies and interstitials. It is the disposition of the “displacement damage,” measured as displacements per atom (dpa) that affects the mechanical properties (discussed below). The general damage process in microstructure associated with

irradiation dose and temperature involves the agglomeration of vacancies and interstitials into voids and interstitial type dislocation loops that cause swelling. Loops form below 673–723 K. Loop size increases and loop number density decreases with increasing temperature, eventually becoming unstable [32].

In ferritic/martensitic steels, agglomeration of vacancies can lead to void swelling up to about 773 K. Ferritic steels attracted attention at the beginning for the fast reactor program due to their low swelling compared to conventional austenitic stainless steels (e.g., type 304 or 316 stainless steels) when irradiated in the Experimental Breeder Reactor (EBR-II) (Fig.1-3). Swelling is defined as $\Delta V/V_0$, where ΔV and V_0 are volume change and original volume, respectively. At the maximum swelling temperature of around 673–693 K, less than 2 wt. %swelling was observed for HT9 and modified 9Cr-1Mo (T91) irradiated to 200 dpa in the Fast Flux Test Facility (FFTF) [32]. Irradiation-induced precipitates also affect properties [32-34]. Precipitates formed in the 9–12 %Cr steels during irradiation include α' [33], G-phase [33], M_6C [34], and χ -phase [32, 33]. For most of the 9–12 %Cr-Mo steels investigated, Laves phase, which forms during thermal aging at ≈ 673 to 873K[32,34], can cause embrittlement; it does not form if irradiation is above ≈ 873 K [32,33]. Displacement damage produced by the neutron irradiation will lead to transmutation reactions of neutrons with metal atoms to produce a new atom (usually another metal atom with a smaller atomic number) and a gas atom—He or H. The new non-gaseous atom is generally thought not to affect the properties of the steel, although this atom is the source of the radioactivity that “activates” the structural material and provided the impetus for the search for a “low-activation” material in the fusion program. The effect of the H was generally thought to be minimal, because most of it was expected to migrate out of the lattice at reactor operating temperatures. However, ion [35] and proton [36,37] irradiations have produced evidence for retention of considerable amounts of the H, but it is not expected to be an issue in martensitic steels above about 250°C [37]. For a fusion reactor, where the He: dpa ratio is about 10, indications are that He can affect swelling, although the 9–12 %Cr steels still remain low swelling. The He: dpa ratio for ferritic/martensitic steels in most fission reactors is about two orders-of-magnitude lower and has a minimal effect on swelling.

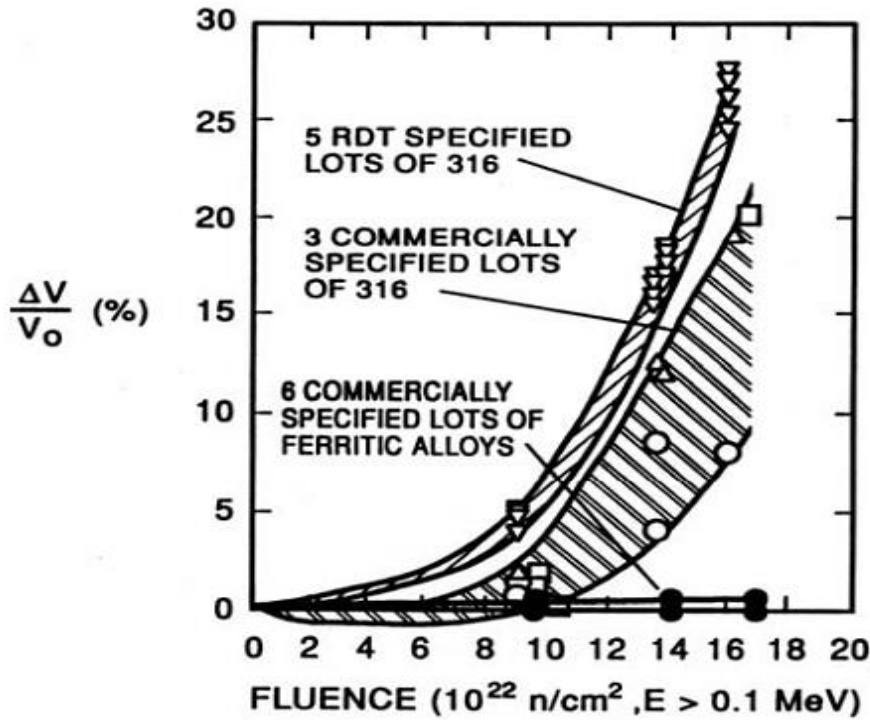


Fig.1-3 Swelling behavior of six commercial heats of ferritic/martensitic steels compared to type 316 stainless steel after irradiation in EBR-II at 693K to ≈ 80 dpa (from D. S. Gelles, unpublished research).

For materials used in reactor plants, exposure to high dose neutron irradiation can induce dramatic change in their properties due to irradiation induced defects, e.g. low temperature irradiation hardening, embrittlement and void swelling generated in nuclear materials during the irradiation. These make the nuclear power plants less reliable and shorten the lifetime of their usage. In this situation, knowledge of properties of defects and their evolution in corresponding materials is very important. In the following sections, the main properties of the defects will be described.

1.3 Lattice defects of metals

1.3.1 Different lattice defects

According to their dimensional nature, the lattice defects can be divided into the following groups.

- (i) Point defects (zero-dimensional) $\cdots$ Interstitials (Interstitial atoms), Vacancies, Impurities.
- (ii) Line defects (one-dimensional) $\cdots$ Dislocations (edge, screw, mixture).
- (iii) Plane defects (two-dimensional) $\cdots$ Grain boundaries, Dislocation loops (Interstitial- and vacancy-type), etc.
- (iv) Space defects (three-dimensional) $\cdots$ Voids and Bubbles (Cavities), Precipitates.

In a real crystal, several lattice defects exist under the mutual interaction of each defect and the mechanical and physical properties are influenced by their interaction. For example, dislocations and grain boundaries act as absorption sinks for point defects and point defects are also produced by the intersection of two screw dislocations. Point defects are the most elementary lattice defects. However, in irradiation effects, point defects are the most fundamental defects. No matter how complex the irradiation effects, to the end, they are induced by point defects generated during the irradiation. Point defects migrate in the crystal lattice through the thermal vibration of atoms and form point-defect clusters, such as dislocation loops and voids.

1.3.2 Point defects

Elementary point defects are usually classified into interstitials, vacancies and impurities. In some definition, small clusters of point defects, such as di-vacancies, di-interstitials and vacancy-impurity complexes, etc, are also enclosed into this catalogue. However, when complexes evolve to larger clusters as dislocation loops and voids, they are included in one- or two- dimensional defects. When non-equilibrium concentrations of point defects are introduced excess by an external cause, for example irradiation damage, the process by which point defects grow into clusters is also important for understanding the crystal defects.

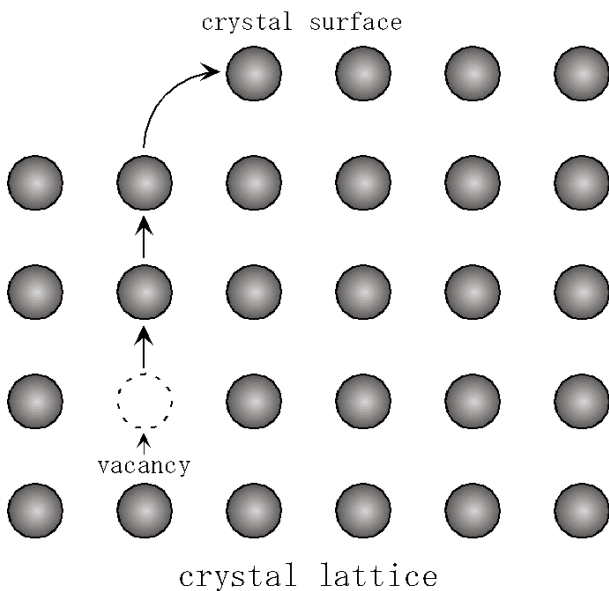


Fig.1-4 Schottky defect.

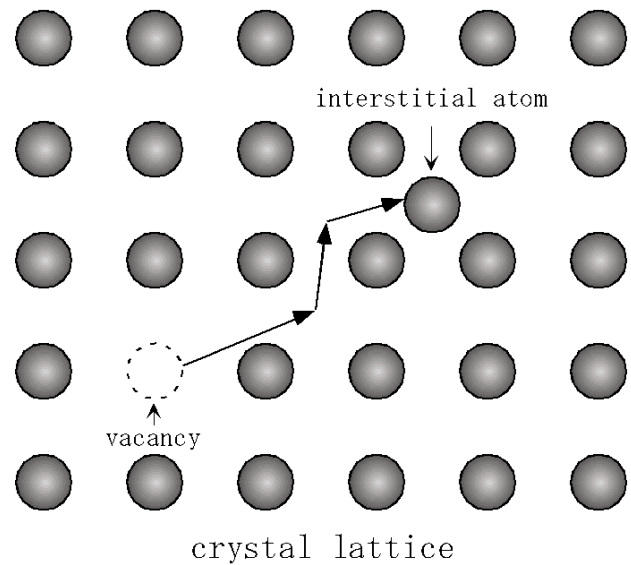


Fig.1-5 Frenkel defect (Frenkel pair).

Both vacancies and interstitials are often called intrinsic lattice defects to distinguish them from extrinsic lattice defects, such as impurities. These intrinsic defects are produced when an atom is removed from a proper lattice site to an improper site. As can be seen from Fig.1-4, an

atom is removed from the interior to a site on the crystal surface and a vacancy remains at the site of the removed atom. This vacancy is called a Schottky defect and it was first studied in ionic crystals. In Fig.1-5, another type of point defect is shown. An atom is removed to somewhere in an interstice of the crystal lattice and the configuration of this lattice contains a vacancy and an interstitial. These defects are called Frenkel defects and the pair of a vacancy and an interstitial is the Frenkel pair. Frenkel pairs are mainly produced by irradiation damage from neutrons, ions, electrons, etc. In the case of irradiation damage due to high-energy neutrons or ions, small clusters of point defects are also created directly, and it is called the cascade damage.

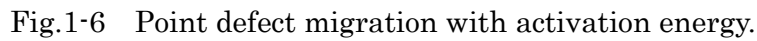
On the other hand, impurities occupy interstitial or substitutional sites. The most typical example of an interstitial solid solution is the solution of C or N in Fe. On the other hand, the most typical example of a substitutional solid solution is the solution of donor or acceptor atoms in crystalline Si.

1.3.3 Migration of point defects

The migration of point defects is important for investigating the clustering of point defects in metals when a non-equilibrium concentration of point defects is produced by an external cause, such as irradiation damage. The random (Brownian) motion of point defects is usually described by the diffusion coefficient D , which is a function of temperature. In the case of point defects in metals, the diffusion coefficient D is generally given by the migration frequency M , the geometrical factor g and the lattice constant a ,

$$D = g \times a^2 \times M. \quad \dots (1. 1)$$

The equation for the migration frequency M can be obtained as follows. A model of point defect migration with activation energy is shown in Fig.1-6. In this one-dimensional model, the activation energy for migration E^m corresponds to the potential barrier at point 3 in order to get from the equilibrium position 1 to the neighboring equilibrium position 2. Position 3 is a saddle point on the potential surface.



(i) Adiabatic approximation is assumed for calculating the potential energy.

(iii) The probability of the particle being in a state with energy E^m is calculated using an equilibrium statistical mechanism.

The equation for migration frequency M is obtained under the above assumptions and Arrhenius's law as [38,39]

where the frequency factor corresponds to the vibration of lattice atoms and is usually taken as $10^{12} \sim 10^{14} \text{ sec}^{-1}$ [40].

Point defects can become mobile depending on their configuration. In the case of vacancy migration, atoms simply exchange places with neighbors. In Fig.1-7, a model of vacancy migration in the $\{110\}$ -plane of the bcc lattice is shown. As can be seen from this figure, vacancy migration requires the disconnection of atomic bonds from neighboring atoms. The binding energy of atomic bonds is comparatively high and the activation energy for vacancy migration is ordinarily higher than that for interstitial migration. On the other hand, a di-vacancy is more mobile than a single vacancy.

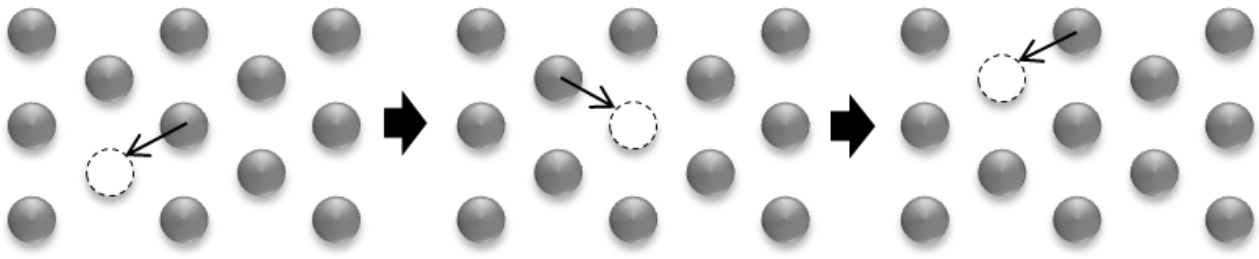


Fig.1-7 Model of vacancy migration in the $\{110\}$ -plane of bcc metals.

• *Interstitial migration*

The activation energy for interstitial migration is typically much less than that for vacancy migration. This is due to the structure of interstitials. In metals, such as Al, Cu, Ni, Mo, Fe and Zn, it is known that interstitials exist in a split configuration. Fig.1-8 shows the split, which is called a dumbbell configuration, in the $\{110\}$ plane of bcc metal. It appears from this figure that two atoms share the same lattice site in this structure. The split interstitial axis of the fcc lattice is orientated in the $\langle 100 \rangle$ direction, that of the bcc lattice in the $\langle 110 \rangle$ direction, and that of hcp lattice parallel to the c axis.

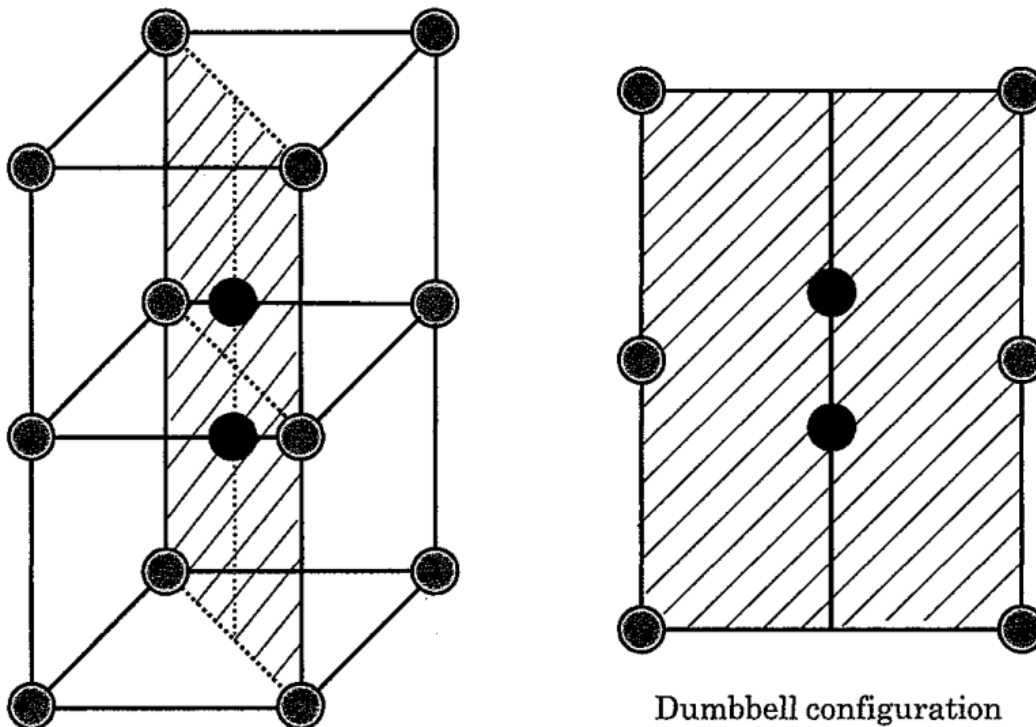


Fig.1-8 Model of the split interstitial configuration (dumbbell configuration) in the $\{110\}$ plane of bcc metals.

Furthermore, the configuration of the interstitial has another type, which is called crowdion. This is a linear arrangement with interstitials along the close-packed direction of

atomic phases (fcc: $\langle 110 \rangle$ direction, bcc: $\langle 111 \rangle$ direction). In Fig.1-9, a model of the crowdion configuration in the $\langle 111 \rangle$ direction of the bcc lattice is shown. The crowdion is more mobile than the dumbbell because of configuration. The activation energy for migration of the crowdion is estimated to be less than 0.1 eV. The crowdion configuration of the interstitial is obtained under irradiation, at low temperature [41]. At a higher temperature, the crowdion configuration will convert easily into the split configuration.

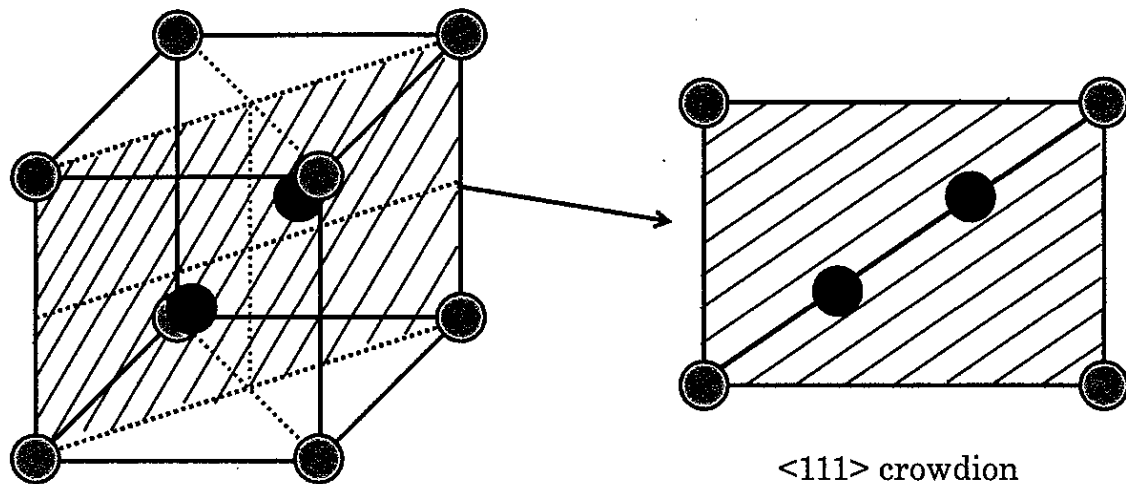


Fig.1-9 Model of the crowdion configuration in the $\langle 111 \rangle$ direction of fcc metals.

1.3.4 Dislocations (line defects)

The plastic deformation of crystals is mainly caused by slip deformation. In real crystals, thermal vibrations of the lattice actually help to start the slip and the crystal lattice has boundaries between slipped and un-slipped regions as shown in Fig.1-10. This line imperfection is called a dislocation.

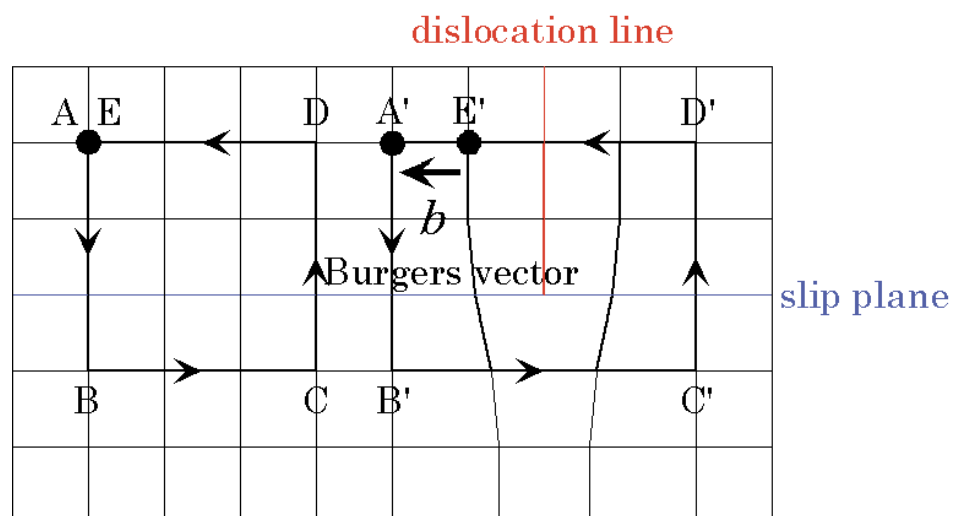


Fig.1-10 Simple configuration of the edge dislocation line with the Burgers vector in the crystal lattice.

The crystal part that slip has passed should return to original lined up crystal structure, otherwise it will stay at unstable state, so the slip movement vector (Burgers vector) must be crystal lattice vector , if not, a two dimensional mixed area will be produced after slip.

Sets the unit vector of dislocation line to δl and Burgers vector to $\mathbf{b}$. When Burgers vector is perpendicular to the dislocation line, it is edge dislocation. While, when Burgers vector is parallel to the dislocation line, it is screw dislocation. The plane that δl and $\mathbf{b}$ composite is dislocation slip plane. Dislocation moving out of its slip plane is called dislocation climb, and also named as non-conservation motion. This movement accompanies releasing or absorbing of point defects (mainly vacancies). The driving force for dislocation climb is the movement of vacancies through a crystal lattice.

In the process of irradiation damage, dislocation loops is mainly form. First point defects accumulate to form a plate, then via dislocation reaction, the plate change to dislocation loop.

In bcc crystal, $\langle 110 \rangle$ type dumbbell interstitials accumulate along the most condensed plane $\{110\}$, forming a fault with a burgers vector $(1/2)\langle 110 \rangle$ and then via one of the following dislocation reaction to form dislocation loop.

$$\frac{1}{2}[110] + \frac{1}{2}[001] \rightarrow \frac{1}{2}[111] \quad \dots (1. 3)$$

$$\frac{1}{2}[110] + \frac{1}{2}[1\bar{1}0] \rightarrow \frac{1}{2}[100] \quad \dots (1. 4)$$

As the fault energy is higher in bcc structure than that in fcc structure, the dislocation reaction that resulting disappearance of fault is easier happened in bcc structure. $b = (1/2)\langle 111 \rangle$ and $b = \langle 100 \rangle$ are two possible kind of dislocation loops, not only for interstitial type but also for vacancy type dislocation loop. Note that, the priority of formation of these two kinds of dislocation loops is very important for the irradiation damage in this kind of crystal materials. Determination of burgers vector of irradiation induced dislocation loop is very important to study the void swelling resistance property in bcc structure materials. Studies show that the unique swelling resistance in ferritic steels (with bcc structure) is due to the formation of $b = \langle 100 \rangle$ type dislocation type. However, from the point of view of energy, the energy of $b = \langle 100 \rangle$ type dislocation loop is higher than $b = (1/2)\langle 111 \rangle$ type dislocation loop. The related mechanism has not been understood yet.

1.3.5 Space defects

Space defects are also mainly classified into two types, voids and precipitates. A void is a three-dimensional aggregation of vacancies. Voids with gases, such as H_2 , He, Kr, etc., are called bubbles. Voids and bubbles are often called cavities as a generic definition. The growth of

voids result into the swelling of metals and it is a major issue for nuclear materials to develop resistance to swelling.

The formation of voids requires a large amount of irradiation with high energy particles at temperatures from $0.2T_M$ to $0.55T_M$ for almost all metals. The formation mechanism can be explained as following. In the case of irradiation in this temperature range, the density of dislocations increases with the growth of interstitial type dislocation loops at first. Dislocations absorb interstitials preferentially, which is called the bias. If a super saturation amount of vacancies is remained, they aggregate to make voids. Once formed, voids grow gradually because of their small bias effect for point defects [42,43]. It was also confirmed that the void densities are often enhanced at and near dislocations and grain boundaries [44]. The formation of a void is also influenced strongly by the generation of impurities during irradiation. Inert gases, such as He produced by (n, α) reactions with neutrons, make the void stable and the role of He for the void nucleation is of a concern for nuclear materials' development [45,46].

A precipitate is an aggregation of atoms that segregate from the parent phase of an alloy when they are not soluble. Precipitation is also important for the change of properties in metals under irradiation. A large number of vacancies and interstitials exist in irradiated metals and the density of these point defects near proper sinks induces solute segregation in the vicinity of sinks. The formation of precipitates in many alloys under irradiation causes the embrittlement of materials and is an important problem for nuclear materials.

1.4 Irradiation damage

1.4.1 Atomic displacement

Atoms on lattices can be displaced by collisions with high energy incident particles. If the energy of a displacement atom is low, recombination of a displacement atom with a vacancy may happen due to the thermal vibration of crystal lattices. However, if the energy exceeds the specific energy, the atom can be displaced permanently from its normal lattice site, resulting in a vacancy and an interstitial (Frenkel pair). This is the most elementary model of irradiation damage. This energy is called displacement threshold energy, and the displacement threshold energy depends on the kind of metals and effective values for typical metals are 40 eV for Fe, Cr, Ni, V, 30 eV for Ti, Cu, 25eV for Al, Pb, and 90eV for Ta, W [47].

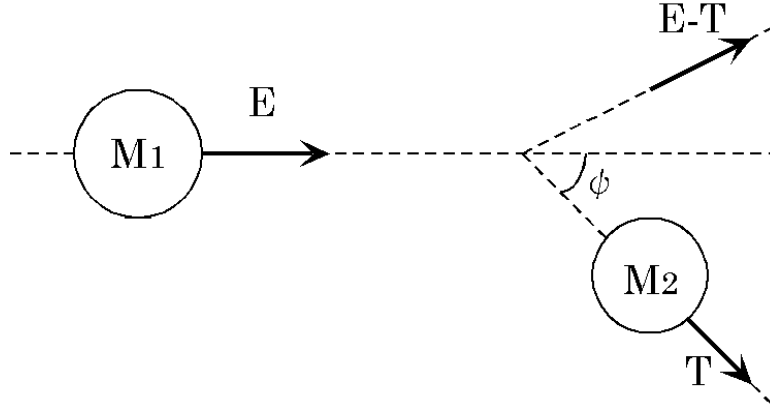


Fig.1-11 Schematic viewing of a simple collision between an incident particle and a constituent atom (laboratory system).

The interaction between irradiation and solids is thought of as a collision of two rigid bodies, the incident particle and the constituent atom, as shown in Fig.1-11. The transfer of energy to a target atom for head-on collisions is given by the classical formula,

$$T_{\max} = \frac{4M_1M_2}{(M_1 + M_2)^2} E \quad \cdots(1. 5)$$

where E is the energy of the projectile, and M_1 and M_2 are the mass of the projectile and the target atom, respectively. Therefore, the minimum energy for making a Frenkel pair by the incident particle $E_{\min}$ is written as follows,

$$E_{\min} = \frac{(M_1 + M_2)^2}{4M_1M_2} E_d \quad \cdots(1. 6)$$

where E_d is the displacement energy. In the case of electron irradiation, however, the relativistic effect must be taken into the equation (1.8). The relational expression between E_d and $E_{\min}$ is rewritten as follows,

$$E_d = 2 \frac{m}{M_2} \frac{E_{\min}}{mc^2} (E_{\min} + 2mc^2) \quad \cdots(1. 7)$$

where m is the electron mass and c is the speed of light.

Table 1-2 shows the $E_{\min}$ of each particle for Al, Fe and Mo when the E_d is 25 eV [48]. In general, atomic displacement by irradiation damage occurs above 0.5 MeV for electron irradiation, above 0.1 MeV for neutron or proton irradiation, and at about several tens of eV for heavy ion irradiation.

Table 1-2 Minimum energies of each incident particle for displacement in Al, Fe and Mo (displacement energy: 25 eV) [48].

Target Incident	Al	Fe	Mo
Electron (MeV)	0.56	0.81	1.06
Neutron, Proton (keV)	181	393	613
He ion	56	100	163
Ni ion	29	25	27
Ar ion	26	26	30
Xe ion	44	30	26

1.4.2 Defect production rate

The first displaced atom is generally called the primary knock-on atom (pka). If the energy of a pka E_p is higher than $2E_d$, secondary atomic displacements will be caused by elastic collisions. The number of displaced atoms, or vacancy-interstitial pairs, N_d is given by the Kinchin and Pease's simple model [49].

$$\begin{aligned}
 N_d &= 0 & E_p < E_d \\
 N_d &= 1 & E_d \leq E_p < 2E_d \\
 N_d &= \frac{\beta E_p}{2E_d} & 2E_d \leq E_p
 \end{aligned}
 \quad \dots (1.8)$$

β is the damage efficiency with a recommended value of 0.8, which accounts for the deviation from a hard sphere ($\beta=1$) of interatomic potential [50].

The probability of displacement is estimated from the displacement cross-section. The displacement cross-section depends on the sort of particle and the energy of an incident particle. Notably, the displacement by neutron irradiation over 1 MeV is not isotropic due to the increase of forward scattering. As the energy of a neutron increases much more, non-elastic collisions and other nuclear transformation reactions, such as (n,p), (n, α) and (n,2n), will occur frequently.

The case of the production of pka produced by neutrons of energy with E_n will be taken up. The cross section $\sigma_d^i(E_n)$ is given by [51]

$$\sigma_d^i E_n = \sigma^i(E_n) \int_{E_d}^{E_{p,\max}} P(E_n, E_p) N_d dE_p, \quad \dots (1.9)$$

where $E_{p,max}$ is the maximum pka energy, $\sigma^i(E_n)$ is the cross section by the E_n energy neutron and $P(E_n, E_p)$ is the probability of pka production whose energy is from E_p to E_p+dE_p by neutrons of E_n energy. As each collision occurs individually, the total displacement cross section by neutrons of E_n energy is given as follows,

$$\sigma_d(E_n) = \sum_i \sigma_d^i(E_n). \quad \dots(1.10)$$

To estimate the rate of defect production under irradiation, the unit dpa (displacement per atom) is often used. The general equation for calculating the defect production rate n (dpa/s) is given by

$$n = \int_0^\infty \sigma_d(E_n) \phi(E_n, t) dE_n, \quad \dots(1.11)$$

where $\phi(E_n, t)$ is the neutron flux from E_n to E_n+dE_n energy. In practice, the neutron flux can be regarded as constant during irradiation and the mean cross section for the energy spectrum of neutrons is usually used for the simplification of the calculation as,

$$n = \phi_{tot} \cdot \bar{\sigma}_d \quad \dots(1.12)$$

and

$$\bar{\sigma}_d = \frac{\int_0^\infty \sigma_d(E_n) \phi(E_n) dE_n}{\int_0^\infty \phi(E_n) dE_n}, \quad \dots(1.13)$$

where ϕ_{tot} is the total fluence of neutrons and $\bar{\sigma}_d$ is the mean cross section. In the case of actual irradiation experiments, the region of neutron energy which causes atomic displacements effectively can be fixed. The effective range of neutron energy for irradiation damage is usually defined as from 0.1 to 20 MeV or from 1 to 20 MeV.

1.4.3 Cascade damage

A pka which obtains a higher recoil energy than 100 keV acts as a projectile in the lattice and releases its primary recoil energy through collisions with other lattice atoms. In this way, the pka initiates a collision cascade.

Fig.1-12 is a two-dimensional model of cascade damage in the $\{110\}$ plane of a bcc metal. Interstitials are also produced by simple events where an atom is knocked from its site and reaches thermal energy in an interstitial position. On the other hand, interstitials are also produced by replacement collision sequences, which are form crowdions. Here vacancies are created by placing the corresponding atom on the next lattice site. The displaced atom at that lattice site nudges the next site and so on. When the sequence of replacement collisions stops

because of a loss of energy, the last atom nudged from its lattice site becomes an interstitial. This is the mechanism by which a vacancy is formed far from its interstitial. In cascade damage, there exists a vacancy-rich "core" (subtle area) surrounded by a "shell" of interstitials. Interstitials make interstitial-type dislocation loops grow faster due to the rapid migration frequency and result in a vacancy-rich area. This vacancy-rich area will be the cause of void growth as the core after dislocations grow sufficiently. Notably, He atoms crowd into such a vacancy-rich area promote void growth.

Cascades for recoil energies in the order of 10^5 eV were computer-simulated using binary collision codes in previous works. According to the model by Seeger *et al.* [52], the vacancies are frequently clustered and are surrounded by interstitials. In addition, the defect density strongly fluctuates and the structure can be expressed as a complex of subcascades. This feature is typical for high-energy cascades. The defect cascade can be imaged by electron microscopy [53,54] and field ion microscopy [55,56]. However, both studies reflect the state of a cascade after a passage of time that is very long compared with that necessary to produce the initial displacement ($10^{-13} \sim 10^{-11}$ sec). The observation of a single event or a few events of cascade damage is of strong concern for the study of irradiation damage.

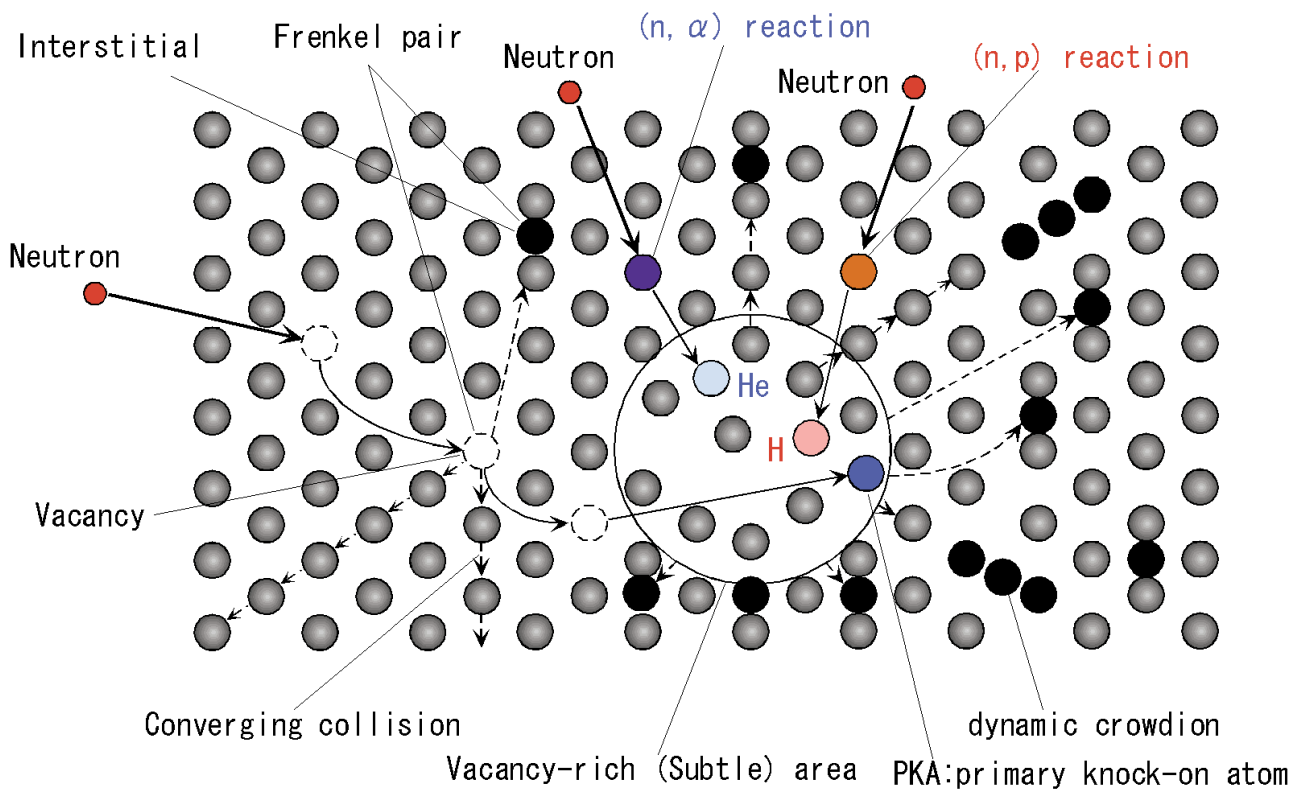


Fig.1-12 Schematic illustration of a two-dimensional model for cascade damage in the $\langle 110 \rangle$ -plane of bcc metals.

1.4.4 Irradiation Effects

In this section, the basic changes in materials properties caused by irradiation will be described. The first is irradiation embrittlement and the second is void swelling.

- *Irradiation embrittlement*

Most of materials are hardened after high-dose irradiation and lost ductility cause of the accumulation of point defects and lattice defects, especially the growth of dislocations and their network. The irradiation embrittlement of austenitic stainless steels and inconels for nuclear materials was first reported in 1959 [57]. It was reported that a lower ductility was observed in tensile and stress-rupture tests after irradiation. Systematic results later demonstrated that small amounts of He atoms generated by (n, α) nuclear transformation of B led to a significant reduction in the total elongation at fracture [58].

The most important problem related to irradiation embrittlement for structural materials is the shift of the ductile-to-brittle transition temperature (DBTT) of low-alloy steels used for reactor pressure vessels (RPV). After long-term irradiation, the DBTT can shift to near 373K which is risky for the RPV steel. The RPV steel may fracture due to thermal stress upon a rapid cooling if an emergency shuts down of the nuclear reactor is carried out due to an unexpected trouble. Irradiation embrittlement is also important in the first wall of a fusion reactor.

- *Void swelling*

For most metals, void formation can be caused by a large amount of irradiation with high energy particles at temperatures from $0.2 T_M$ to $0.55 T_M$. Void swelling is the volume change of materials with the accumulation of residual voids (cavities). The void swelling and the formation of voids in the bulk material of a stainless steel was initially detected in structural core parts of the Dounreay Fast Reactor of Scotland in 1967 [59]. Early conferences on nuclear material were convened to bring together researchers to exchange a rapidly expanding volume of data and theoretical analyses on the void swelling problem [60,61]. How the crystal structure affects swelling is not fully understand. For example, ferritic steels (bcc-structure) are generally more resistant than austenitic steels (fcc-structure) but the detail mechanism has not been clarified sufficiently [62].

Gaseous impurities are now accepted as necessary prerequisites for the stabilization of the void structure, especially He gas. But the effects of H and He atoms on the void formation are not completely clear and further study is necessary for the realization of a fusion reactor because the production rates of H and He atoms from nuclear reactions are much higher than in the environment of a fission reactor.

1.5 Purpose of this study

Due to the prediction [63] and discovery [64] of swelling in metals under neutron irradiation a lot of effort has been made to understand the reasons for the different response of different materials to these conditions. This is important for the fabrication of irradiation-resistant materials for fission and fusion reactors, as the associated swelling and dimensional instability can present design and operational difficulties for reactor core components. The modern theory assumes the formation of interstitial clusters directly in displacement cascades, revealed both experimentally [65] and in molecular dynamics (MD) simulations [66,67], and their one-dimensional (1-D) mobility [67], the existence of which was predicted in [68] for the explanation of void–lattice formation [69,70]. Up to now, the theory has been developed for pure metals and assumes a high mobility of at least a fraction of interstitial clusters. It succeeds in explaining several observations in fcc metals, for example, higher swelling rates near grain boundaries and in materials with smaller grain size [71,72], and under neutron irradiation compared to electron irradiation [73]. Both effects contradict the BEK theory [74], which assumes single vacancies and interstitials to be the only mobile defects, but can be explained by the annihilation of rapidly migrating interstitials clusters at dislocations and grain boundaries and by the much longer mean-free path of 1-D versus 3-D migrating defects. However, the understanding of much smaller swelling rates in bcc alloys compared to fcc alloys and of the sensitivity of the developing microstructure to material composition is still poor. The perception that the generic bcc crystal structure confers immunity on all bcc metals and alloys against the high swelling rates characteristic of fcc metals and alloys was called into doubt. This occurred when various vanadium-binary alloys were found to swell at very large rates, sometimes in excess of those observed in fcc systems [75,76]. This suggests that chemical and segregation processes can easily overwhelm crystallographic influences.

One research [77] addressed the question of whether we can use the steady-state swelling and creep rates of fcc and bcc Fe-base alloys at high damage levels to draw conclusions associated with the relative defect production, survivability, and agglomeration of point defects in the two crystal systems. Results showed that the differences in steady-state swelling rates of Fe-based fcc and bcc alloys are not so very large, with the observed difference in swelling reflecting primarily the influence of crystal structure, composition, displacement rate, micro-chemical evolution and temperature history to determine the duration of the transient regime of swelling.

The research on Fe-Cr binaries shows that the major influence of Cr level lies in the duration of the incubation period with peak swelling arising as a consequence of the shortest

transient regime at ~ 10 wt.%Cr. The formation of the α' phase is thought to be associated with the reduction in swelling at higher Cr levels [78,79]. Commercial ferritic/martensitic stainless steels also exhibit the same behavior as the Fe-Cr binaries. As shown in Fig.1-13(b), both of these swelling ranges are relatively consistent with the Fe-(9, 12) Cr behavior shown in Fig.1-13(a) with some additional influence of solutes to extend the transient. The dependence of swelling in HT9 on applied stress is yet another indication of the inherent instability associated with the end of the transient regime.

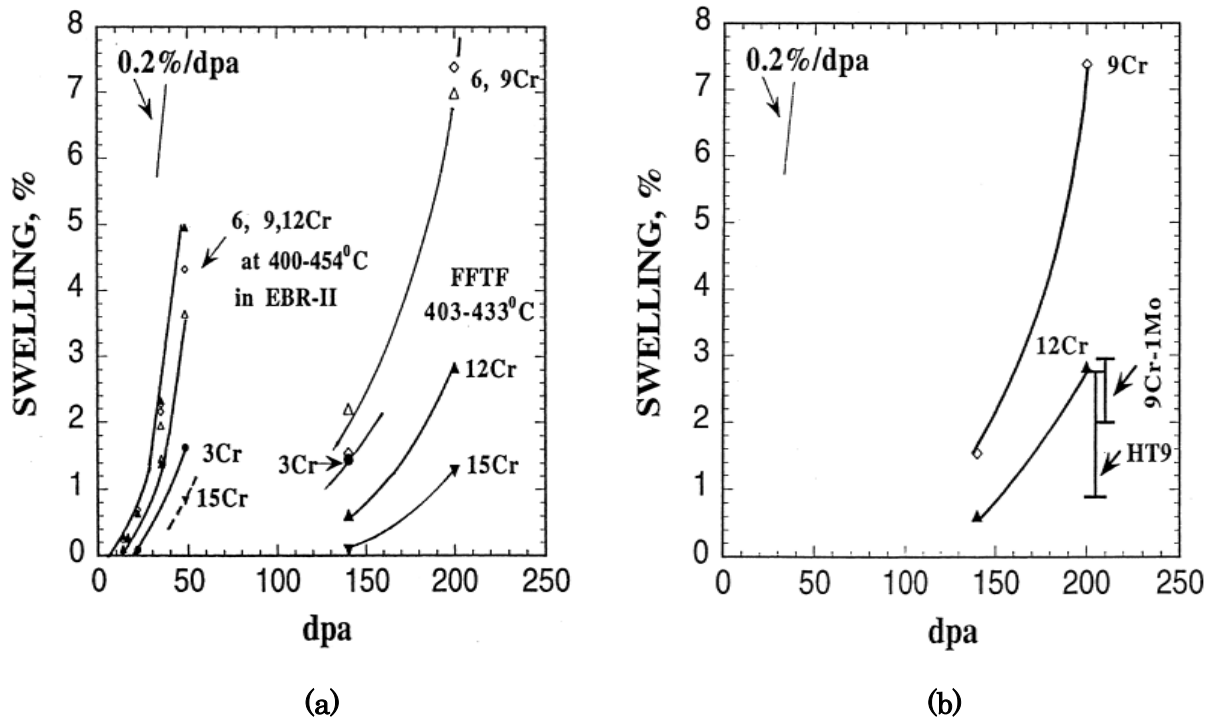


Fig.1-13 (a) Comparison of swelling of Fe-Cr alloys in EBR-II and FFTF-MOTA; (b) swelling observed in HT9 and 9Cr-1Mo in FFTF-MOTA [80,81].

The lower swelling observed in bcc steels compared to fcc steels is shown to be primarily a consequence of much longer transient regimes prior to the onset of steady-state swelling. The development of universal swelling rate is preceded by a transient regime whose duration is primarily dominated first by the initial alloy composition, and second by the subsequent irradiation-induced micro-chemical evolution of the alloy matrix.

An understanding of the related void swelling resistance is important for the fabrication of improved irradiation-resistant materials for fission or fusion reactors. However, the physical basis of the swelling resistance of these materials is not yet well understood [62]. The void swelling results from survivability and aggregation of irradiation-induced point defects. Knowledge of these microscopic mechanisms is indispensable for a reliable prediction and

modeling of the void swelling. Therefore, to get physical basis of the swelling, the properties of irradiation-induced point defects are required to study first.

In this study, defect evolution by different irradiations in F82H steel and its model alloys are investigated by positron annihilation spectroscopy, Mossbauer spectroscopy and transmission electron microscopy to reveal the void swelling resistance mechanism in ferritic/martensitic steels. The composition of this paper is as following.

(1) Chapter 2 "Experimental procedures"

Specimen preparation of F82H type ferritic/martensitic steel and its model alloys, experimental techniques and facilities used for irradiation were introduced.

(2) Chapter 3 "Defect evolution by isolate point defects in F82H steel and its model alloys"

Point defects properties and their elevated temperature evolution are of importance to study defect behavior in reduced activation ferritic/martensitic steels. In this chapter, Frenkel pairs were deliberately introduced with 30 MeV electrons using an electron accelerator in the Research Reactor Institute, Kyoto University to F82H steel and a serial designed model alloys to systematically analyze additive solute atoms and their synergistic effects. The positron annihilation lifetime spectroscopy (PALS) has been applied to model alloys to clarify the characteristics of point defect evolution under irradiation.

(3) Chapter 4 "Defect evolution by cascade damage in F82H steel and its model alloys "

Neutron irradiation is the real environment in nuclear power plant. The cascade caused by high energy neutron can make a different microstructural evolution in corresponding materials than those by electron irradiation. In this study, PALS investigations were conducted on alloys of F82H-type ferritic/martensitic steels before and after irradiation. The defects evolution in neutron irradiated alloys was studied as a comparison with those by electron irradiation to further check additive solute atoms and their synergistic effects on vacancy cluster evolution. To check the defect structure evolution at high irradiation dose in these model alloys, Fe ion irradiation was also conducted.

(4) Chapter 5 "Short range ordering in irradiated F82H and its model alloys"

The application of additional methods to assess such behavior is essential for better understanding of these damage mechanisms at microstructural level. Very few techniques are capable for detection of defects at the atomic level; moreover, it is extremely difficult to study the interaction of defects and the contribution of alloying elements to the kinetics of irradiation damage at the experimental base. The Mössbauer spectroscopy (MS) is a very suitable tool to

study a local environment of the Mössbauer atoms. Solute atoms in the vicinity of the Mössbauer probe change the Mössbauer spectral parameters. An existence of vacancy or large solute atom in the nearest neighborhood of the Mössbauer probe leads broadening of line-width of spectral components as a result of magnetic field distribution caused by local lattice distortion. In this chapter, MS was conducted on F82H and its model alloys before and after irradiation. The obtained hyperfine parameters were analyzed by combining with the previous PAS data.

Reference (Chapter 1)

- [1] *A Technology Roadmap for Generation IV Nuclear Energy Systems*, GIF-002-00, U.S. DOE Nuclear Energy Research Advisory Committee and the Generation IV International Forum, December (2002) .
- [2] Z. Briggs and T.D. Parker, *The Super 12% Cr steels Climax Molybdenum Co.*, New York (1965).
- [3] Anon, *Super 12% Cr Steels-An Update*, Climax Molybdenum Co., New York, (1983).
- [4] H.Brearkey, *Knotted String-Autobiography of a Steelmaker* Longmans, London, (1941).
- [5] J.H.G. Moneypenny, *Stainless Iron and Steel*, Chapman and Hall, London, (1926).
- [6] V.G. Rivlin and G.V. Raynor, *Int. Met. Reviews* 1 (1980) 21.
- [7] D. Pckner and I. M. Bernstein (Eds), *Handbook of Stainless Steels* McGraw-Hill, New York, (1977).
- [8] W. Tofaute, A.Sponheuer, and H.Bennek, *Arvhiv fur Eisenhot-tenwesen* 8 (1935) 499.
- [9] R. T. King et al., *Symposium on Structural Material for Service at Elevated Temperatures in Nuclear Power Generation*, ed. A. O. Schaefer, Am. Soc. Mech. Eng., New York (1975)375. [10] R. L. Klueh and D. R. Harries, *High-Ch romium Ferritic and Martensitic Steels for Nuclear Applications*, ASTM, West Conshohocken, Pa. 2001.
- [11] S. N. Rosenwasser, et al., *J. Nucl. Mater.*, 85-86 (1979) 177.
- [12] R. L. Klueh, K. Ehrlich, and F. Abe, *J. Nucl. Mater.*, 191-194 (1992) 116.
- [13] R. W. Conn et al., *Panel Report on Low Activation Materials for Fusion Applications*, UCLA Report PPG-778, University of California at Los Angeles (1983).
- [14] G. J. Butterworth and O. N. Jarv is, *J. Nucl. Mater.*, 122-123 (1984) 982.
- [15] R. L. Klueh and E. E. Bloom, *Nucl. Eng. Design/Fusion* 2 (1985) 383.
- [16] D. Dulieu, K. W. Tupholme, and G. J. Butterworth, *J. Nucl. Mater.*, 141-143 (1986) 1097.
- [17] M. Tamura, H. Hayakawa, M. Tanimura, A. Hishinuma, and T. Kondo, *J. Nucl. Mater.*, 141-143 (1986) 1067.
- [18] T. Noda, F. Abe, H. Araki, and M. Okada, *J. Nucl. Mater.*, 141-143 (1986) 1102.
- [19] D. S. Gelles, *Reduced Activation Materials for Fusion Reactors*, ASTM STP 1047, eds. R. L. Klueh, D. S. Gelles, M. Okada, and N. H. Packan, ASTM, Philadelphia, 113-129 (1990) .
- [20] H. Kayano et al., *J. Nucl. Mater.*, 179-181 (1991) 671.
- [21] R. L. Klueh and P. J. Maziasz, *Met. Trans.* 20A (1989) 373.
- [22] M. Tamura, H. Hayakawa, M. Tanimura , A. Hishinuma, and T. Kondo, *J. Nucl. Mater.*, 155-157 (1988) 620.

- [23] M. Yamanouchi, M. Tamura, H. Hayakawa , A. Hishinuma, and T. Kondo, J. Nucl. Mater., 191-194 (1992) 822.
- [24] F. Abe, T. Noda, H. Araki, and S. Nakazawa, J. Nucl. Mater., 179-181 (1991) 663.
- [25] A. Kohyama, Y. Kohno, K. Asakura, and H. Kayano, J. Nucl. Mater., 212-215 (1994) 684.
- [26] K. Ehrlich, S. Kelzenberg, H. D. Röhrig, L. Schäfer, and M. Schirra, J. Nucl. Mater., 212-215 (1994) 678.
- [27] K. Ehrlich, S. Kelzenberg, H. D. Röhrig, L. Schäfer, and M. Schirra, J. Nucl. Mater., 212-215 (1994) 678.
- [28] B. van der Schaaf, D. S. Gelles, S. Jitsukawa, A. Kimura, R. L. Klueh, A. Moslang, and G. R. Odette, J. Nucl. Mater., 283-287 (2000) 52.
- [29] S.J. Zinkle, J.T. Busby, Mater. Today 12 (2009) 12.
- [30] S.J. Zinkle, Phys. Plasmas 12 (2005) 058101.
- [31] N.M. Ghoniem, R.W. Conn, in: Fusion Reactor Design and Tech., II, IAEA-TC-392/62, International Atomic Energy Agency, Vienna (1983) 389.
- [32] R. L. Klueh, J. J. Kai, and D. J. Alexander, J. Nucl. Mater. 225 (1995) 175.
- [33] D. S. Gelles and L. E. Thomas, Ferritic Alloys for Use in Nuclear Energy Technologies, eds. J. W. Davis and D. J. Michel, Met. Soc., AIME, Warrendale, Pa. (1984) 559.
- [34] E. A. Little and L. P. Stoter, Effects of Irradiation on Materials: Eleventh Conference, ASTM STP 782, eds. H. R. Brager and J. S. Perrin, American Society for Testing and Materials, Philadelphia (1982) 207.
- [35] J. D. Hunn, M. B. Lewis, E. H. Lee, Second International Topical Meeting on Nuclear Applications of Accelerator Technology, Gatlinburg, Tenn., American Nuclear Society, 375-381, September 1998.
- [36] P. Marmy and B. M. Oliver, J. Nucl. Mater. 318, (2003) 132.
- [37] Y. Dai, Y. Foucher, M. R. James, and B. M. Oliver, J. Nucl. Mater. 318, (2003) 167.
- [38] C. A. Wert, Phys. Rev., 79 (1950) 601.
- [39] C. Zener, "Imperfections in Nearly Perfect Crystals", edited by W. Shockley, J. H. Hollomon, R. Maurer and F. Seitz, J. Wiley and Sons, New York (1952) 289.
- [40] T. Kurosawa, "Theory of physical property (about the solid)", Shokabo, Tokyo (1970) 198, in Japanese.
- [41] J. L. Bocquet, G. Brebec and Y. Limoge, "Diffusion in metals and alloys (Ch.7 in Physical Metallurgy, edited by R. W. Cahn and P. Hassen)" , Elsevier Science Publishers, New York, (1983) p.535.

- [42] A. D. Brailsford and R. Bullough, J. Nucl. Mater., 69/70 (1978) 434.
- [43] R. Bullough and M. H. Wood, J. Nucl. Mater., 90 (1980) 1.
- [44] A. Horsewell and B. N. Singh, ASTM STP, 955 (1988) 220.
- [45] B. B. Glasgow, A. Si-Ahmed, W. G. Wolfer and F. A. Ganer, J. Nucl. Mater., 103/104 (1981) 981.
- [46] R. E. Stoller and G. R. Odette, J. Nucl. Mater., 131 (1985) 118.
- [47] 1993 Annual Book of ASTM Standards, Vol. 12.02 (1993) 171.
- [48] K. Shiraishi, T. Kinoshita, H. Yamaoka and A. Kohyama, "Irradiation Effects in Materials (edited by Materials Science Society of Japan)", (Shokabo, Tokyo, 1994) p.18, in Japanese.
- [49] G. H. Kinchin and R. S. Pease, Rep. Prog. Phys., 18 (1955) 1.
- [50] P. Sigmund, Appl. Phys. Lett., 14 (1969) 144.
- [51] G. R. Odette and D. R. Doiron, Nucl. Technol., 29 (1976) 346.
- [52] A. Seeger, "On the Theory of Radiation Damage and Radiation Hardening", Proc. 2nd U. N. Int. Conf. on the Peaceful Uses of Atomic Energy, vol. 6 United Nations, Geneva (1958) 250.
- [53] W. Jäger, J. Microsc. Spectrosc. Electron., 6 (1981) 437.
- [54] M. Kiritani, *"Nature of Point Defects and Their Interactions Revealed by Electron Microscope Observation of Their Clusters"* (Point Defects and Defect Interactions in Metals, edited by J. Takamura, M. Doyama and M. Kiritani)", Univ. of Tokyo Press., Tokyo (1982) 59
- [55] R. Wagner, "Field Ion Microscopy (Crystals Growth Properties and Applications, edited by H. C. Freyhardt)", Springer, Berlin (1982).
- [56] D. N. Seidman, Surf. Sci., 70 (1978) 532.
- [57] R. G. Berggren, W. E. Brundage, W. W. Davis, N. E. Hinkle and J. C. Zukas, Proc. of the USAEC Conf. on the Status of Rad. Eff. Research on Struc. Mater., USAEC Report TID-7588 U. S. Atomic Energy Comm., Chicago (1959) 205.
- [58] J. O. Stiegler and J. R. Weir, Jr. , "Ductility" American Society of Metals, Metals Park, OH (1967) pp. 311-342.
- [59] C. Cawthorne and E. J. Fulton, Nature, 216 (1967) 575.
- [60] S. F. Pugh, M. H. Loretto, D. I. R. Norris (Editors), "Voids Formed by Irradiation of Reactor Materials", Brit. Nucl. Energy. Soc., Reading (1971).
- [61] J. W. Corbett and L. C. Ianniello (Editors), "Radiation-Induced Voids in Metals", U. S. Atomic Energy Comm., Albany (1971).
- [62] Z. Yao, M. Hernandez-Mayoral, M.L. Jenkis, M.A. Kirk, Philos. Mag. 88 (2008) 2851.
- [63] G.W. Greenwood, A.J.E. Foreman and D.E. Rimmer, J. Nucl. Mater. 4 (1959) 305.

- [64] C. Cawthorne and E.J. Fulton, *Nature* 216 (1967) 575.
- [65] B. van Guerard, D. Grasse and J. Peisl, *Phys. Rev. Lett.* (1980) 44262.
- [66] T. Diaz de la Rubia and M.W. Guinan, *Phys. Rev. Lett.* (1991) 662766.
- [67] A.J.E. Foreman, W.J. Phythian and C.A. English, *Phil. Mag. A* (1992) 66671.
- [68] A.J.E. Foreman, UK Atomic Energy Authority Harwell Report No. AERE-R-7135 (1972).
- [69] J.H. Evans, *Nature* 229 (1971) 403.
- [70] K. Krishan, *Phil. Mag. A* (1982) 45401.
- [71] H. Trinkaus, B.N. Singh and A.J.E. Foreman, *J. Nucl. Mater.* 199 (1992) 1.
- [72] B.N. Singh, *Radiat. Eff. Defects Solids* 148 (1999) 383.
- [73] S.I. Golubov, B.N. Singh and H. Trinkaus, *Phil. Mag.* (2001) 812533.
- [74] R. Bullough, B.L. Eyre and K. Krishan, *Proc. R. Soc. Lond. A* 346 (1975) 81.
- [75] H. Matsui, D.S. Gelles, and Y. Kohno, in *Effects of Radiation on Materials*, 15th International Symposium, ASTM STP 1125 (1992) 928.
- [76] F.A. Garner, D.S. Gelles, H. Takahashi, S. Ohnuki, H. Kinoshita and B.A. Loomis, *J. Nucl. Mater.* 191-194 (1992) 948.
- [77] F.A. Garner, M.B. Toloczko, B.H. Sencer, *J. Nucl. Mater.* 276 (2000) 123.
- [78] D.S. Gelles, *J. Nucl. Mater.* 148 (1987) 136.
- [79] D.S. Gelles, R.L. Meinecke, in *Alloy Development for Irradiation Performance Semiannual Progress Report*, DOE/ER-045/11 (1984) 103.
- [80] M.B. Toloczko, F.A. Garner, C.R. Eiholzer, *J. Nucl. Mater.* 212-215 (1994) 604.
- [81] M.B. Toloczko, F.A. Garner, *J. Nucl. Mater.* 233-237 (1996) 289.

Chapter 2 Experiments

2.1 Irradiation experiments

2.1.1 Specimen preparation

F82H sheets were prepared by the Japan Atomic Energy Agency (JAEA) and model alloys of F82H prepared by plasma jet melting were used in this study. The solute atom ratio of each model alloy was similar to that of practical F82H steels. High-purity Fe (99.999%) specimens (C:11 ppm, O:77 ppm, S, P, Si, N<1 ppm) were also prepared for reference. The specimen compositions are shown in Table 2-1.

Table 2-1 Symbols and composition of specimens.

Symbols	Composition (wt. %)
A	Fe
B	Fe-8Cr
C	Fe-8Cr-2W
D	Fe-8Cr-2W-0.2V-0.04Ta
E	Fe-8Cr-2W-0.1C
F	Fe-8Cr-2W-0.2V-0.04Ta-0.1C
G(F82H)	Fe-8Cr-2W-0.2V-0.04Ta-0.5Mn-0.2Si-0.1C

Two groups of specimens were prepared for experiments. For different kinds of irradiation, the specimens were first cold rolled to a thickness of 0.1 mm and punched out into 3 mm-diameter discs. For Mössbauer spectroscopy, specimens were rolled to the best to a thickness of 0.05 mm $\times$ 5mm $\times$ 12mm (With intervening annealed at 1313 K for 0.5 h to eliminate cold hardening to make the desirable thickness). After thinning, Fe was annealed at 973 K for 2 h in a hydrogen atmosphere. The other specimens were annealed in high vacuum at 1313 K for 0.5 h and then tempered at 1013 K for 2 h followed by air cooling.

2.1.2 Electron irradiation

Electron irradiations were conducted by using an electron linear accelerator (LINAC) in Kyoto University Research Reactor Institute. Fig.2-1 shows the LINAC. The electron beam is generated by a thermionic gun and accelerated to 46 MeV in two accelerator tubes by L-band (1.3 GHz) microwave. The pulse width is variable from 2 ns to 4 μ s. A low energy beam around 10 MeV and a single-bunched beam are also available. The research region covers a wide field

of nuclear data acquisition with the neutron time-of-flight method and a lead slowing-down spectrometer, isotope production by the (γ, n) (γ, p) reaction, low-temperature electron irradiation, a photon activation analysis, and a spectroscopy with coherent THz radiation. In this study, two kinds of electron irradiation at different temperatures were conducted. One was at 77 K with liquid nitrogen as cryogen. Fig.2-2 shows schematic drawing of electron irradiation at this temperature. The other was at 673 K by using a vacuum capsule with electric heater.

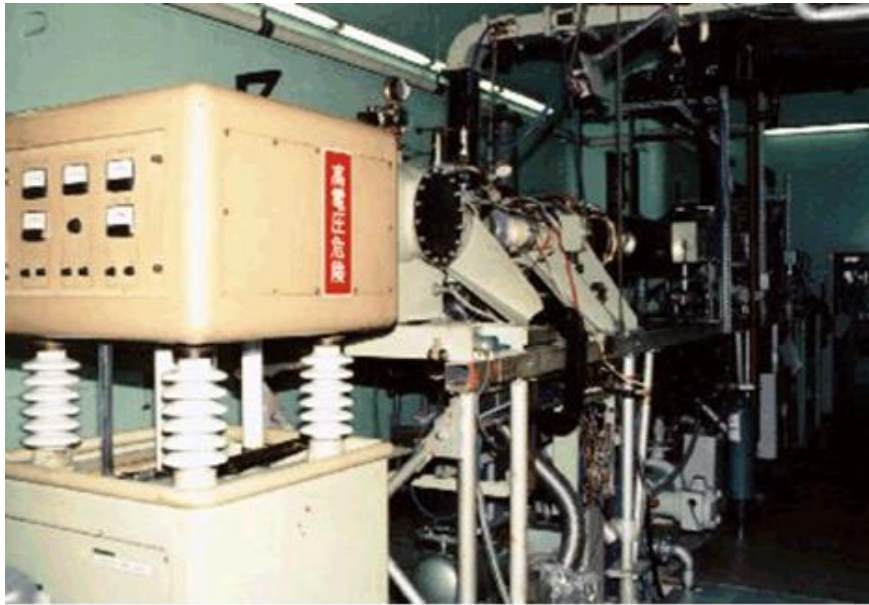


Fig.2-1 Electron linear accelerator in Kyoto University Research Reactor Institute (Accelerator part).

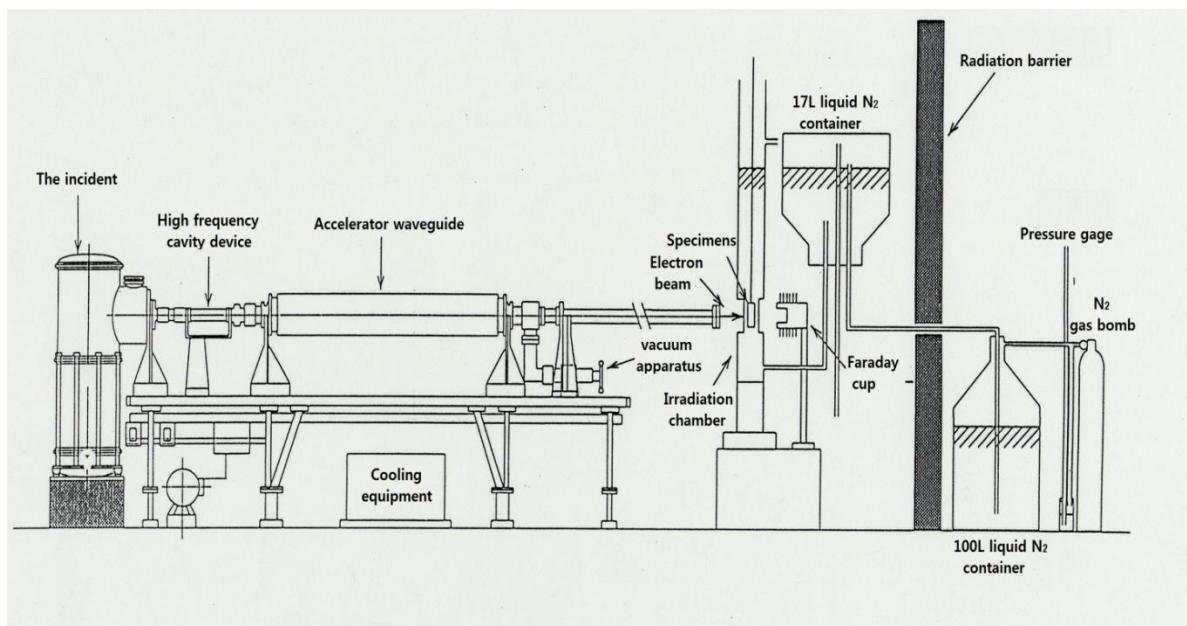


Fig.2-2 Schematic drawing of electron irradiation at temperature of liquid nitrogen by using LINAC.



Fig.2-3 Target of electron irradiation at liquid nitrogen temperature.

2.1.3 Neutron irradiation

Neutron irradiation experiments with nuclear reactors are the most important way of testing the resistance of nuclear materials for irradiation damage. In this study, two research reactors were used for the irradiation experiments. One was the Kyoto University Reactor (KUR) (Fig.2-4) which is light water reactors. The other was Belgian nuclear research center located in Mol, Belgium (SCK•CEN-BR2).

• *Kyoto University Research Reactor*



Fig.2-4 Kyoto University Research Reactor.

The irradiation facility, the Materials Controlled Irradiation Facility, which has improved control capabilities of irradiation conditions, was installed in the KUR during fiscal year 1996–2000. The KUR is a light water moderated 5MW research reactor using 93% enriched uranium fuel. The core is housed at the bottom of an aluminum tank 2m in diameter and 7m in depth. Fig.2-5 shows a schematic vertical cut drawing of the reactor pool and the Materials Controlled Irradiation Facility.

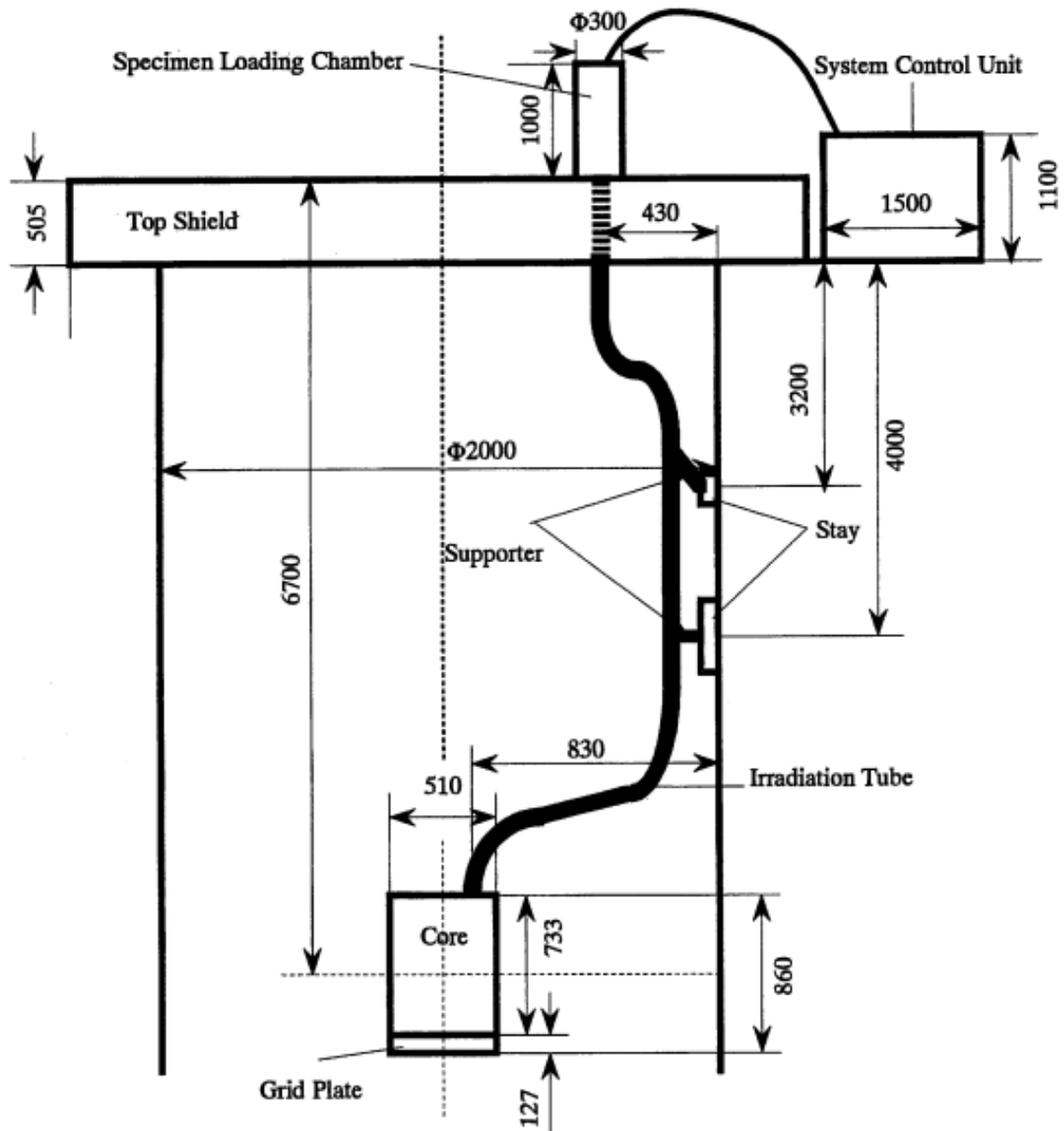


Fig.2-5 Schematic vertical cut drawing of the reactor pool and the Materials Controlled Irradiation Facility in the KURR [1].



Fig.2-6 Specimen loading chamber of Materials Controlled Irradiation Facility on the top of KURR.

It contains three parts, i.e., the specimen loading chamber (Fig.2-6), the irradiation tube and the system control unit. The specimen loading chamber is located at the top shield of the reactor pool. It is shielded by lead 5 cm in thickness. The irradiation tube runs from the specimen loading chamber to the core. It is a pipe 8 m in length, 8 cm in diameter and 1cm in thickness, made of an aluminum alloy, A5052. At the bottom of the tube near the core center, where an irradiation capsule is placed, the inner diameter is 4 cm and the wall thickness is 2cm. It is possible to insert into positions “a-7”, “a-8” or “a-9” in the core. An example of the core configuration where the tube is in “a-8” is shown in Fig.2-7.

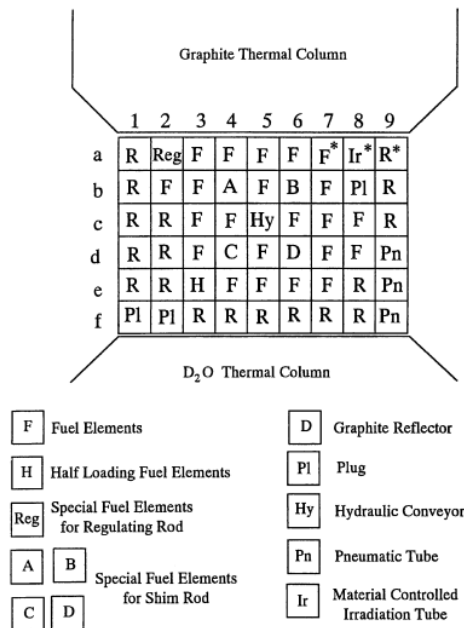


Fig.2-7 An example of the KUR core configuration, where the irradiation tube is in “a-8”. “*” shows possible positions of the materials controlled irradiation tube [1].

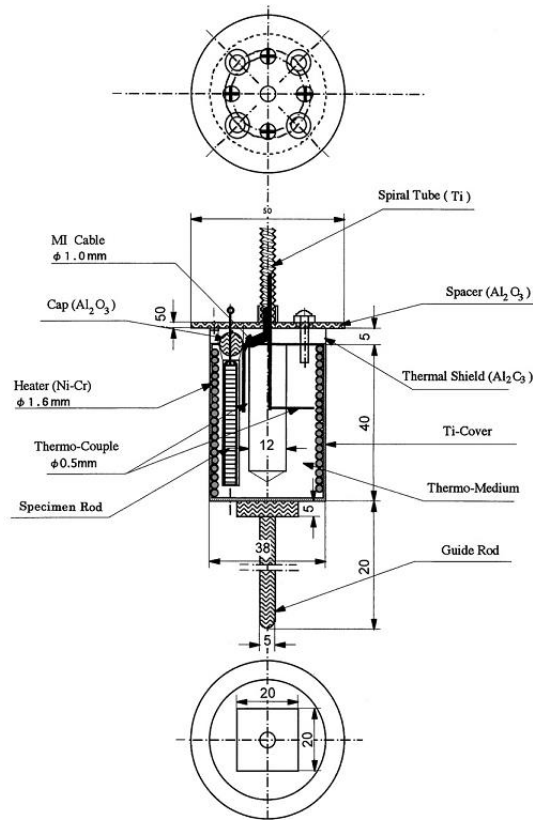


Fig.2-8 An example of an irradiation capsule inserted in the irradiation tube [1].

The irradiation capsule is conveyed in the tube. An example of an irradiation capsule is shown in Fig.2-8 and Fig.2-9. It is equipped with an electric heater and two thermo-couples. Four specimen rods, 5 mm in diameter and 5 cm in length, can be charged. The mineral insulated (MI) cable for the supply of electric current and thermo-couples are stored in a flexible spiral tube made of titanium. The irradiation capsule is rolled down using the flexible tube to the core position of the irradiation tube and irradiated. After irradiation the capsule is pulled up and stored in the specimen loading chamber. The chamber consists of two parts. One is the base part fixed to the top shield. The other is the removal part. The removal part is lifted by a crane and moved to the materials treatment station on the floor of the reactor room. The specimen rods (Fig.2-9 (b)) which contain several pieces of specimens are taken out of the capsule automatically using a robot and new specimen rods are charged. Then the chamber is lifted again and moved to the top shield. The system control unit measures and controls the irradiation conditions. The neutron-temperature history is controlled using the electric heater in the irradiation capsule and changing helium pressure in the irradiation tube. The neutron spectrum is varied by changing the position of irradiation and further by changing the combination of fuel and reflector elements. The irradiation dose is controlled by withdrawing or inserting the irradiation capsule during the normal operation of the KUR. Therefore there is no effect of transient low-intensity neutron irradiation at the beginning and end of the reactor

operation.

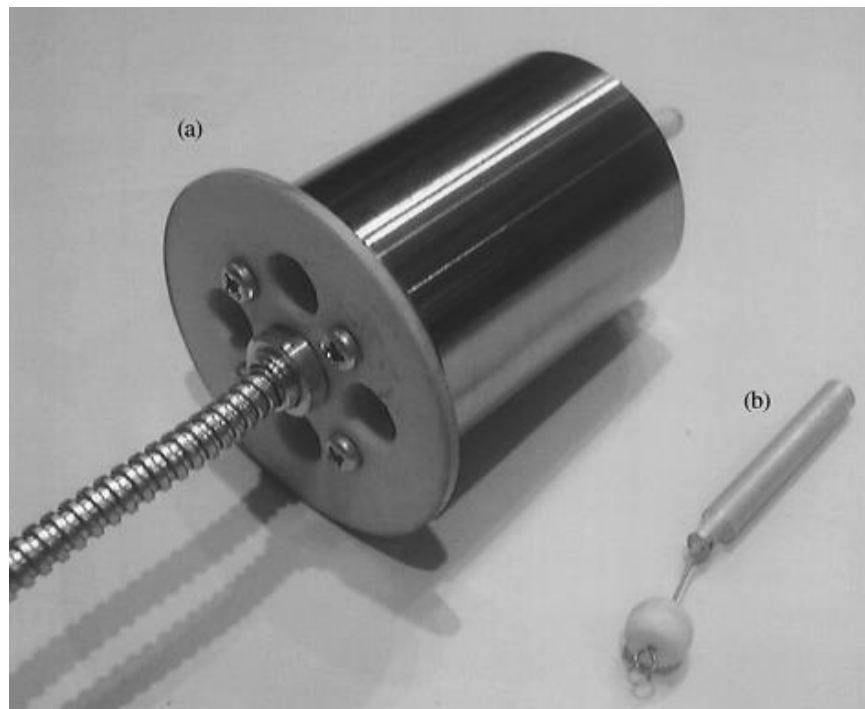


Fig.2-9 A photograph of an irradiation capsule (a) and a specimen rod (b) [1].

• *BR2 Reactor*

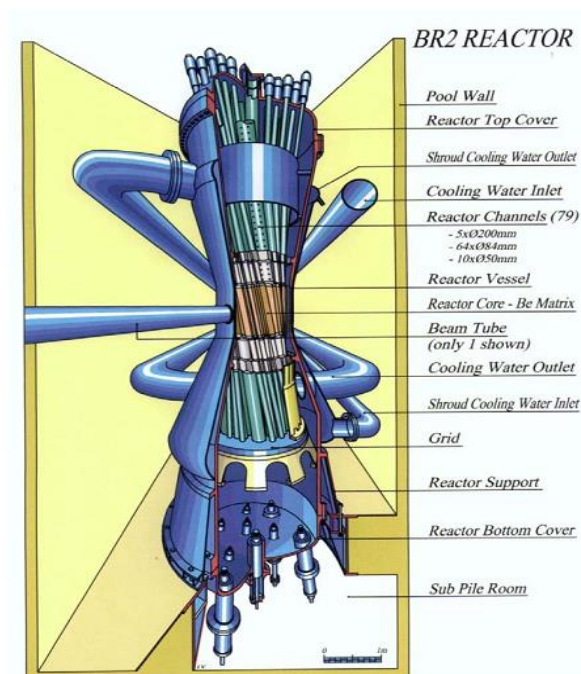


Fig.2-10 Schematic graph of BR2 Reactor.

BR2 Reactor (Fig.2-10) is a tank-in-pool type reactor. The reactor core is constituted by a Be matrix. This matrix is placed in an Al pressure vessel in the shape of a hyperboloid of

revolution. The vessel is located in a pool of demineralized water. The reactor is H₂O cooled, Be and H₂O moderated, can be operated at > 100 MWth.

2.1.4 Ion irradiation

The neutron irradiation experiment at required conditions, particularly high dose irradiation, is not easy even in today's facilities. In this case, alternative experiments are usually used for accelerative irradiation tests, such as electron irradiation with a high-voltage electron microscope and ion irradiation with an ion accelerator. Above all things, ion irradiation is a very effective alternative with the following advantages.

- (i) The damage rate is much higher than that for neutron irradiation.
- (ii) There is a capability to cause cascade damage.
- (iii) The control of experimental conditions as expectation is relatively easy (temperature, dose rate).

In this study, 6 MV Fe ion irradiation was conducted using a 2.0 MV tandem Pelletron accelerator at Quantum Science and Engineering Center, Kyoto University at 593 K. Fig.2-11 shows the schematic diagram of the whole device.

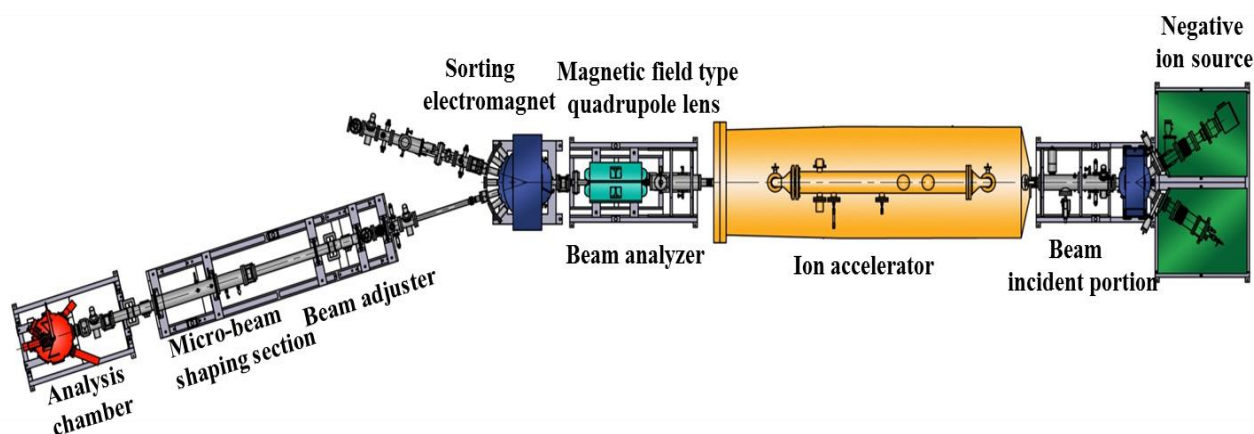


Fig.2-11 Tandem Pelletron accelerator at Quantum Science and Engineering Center, Kyoto University.

For negative ion source SNICS II Ion Sources system (Fig.2-12) is used in this device. Source of Negative Ions by Cs “Sputtering” happened from solid materials. Cs ions come from hot “ionizer” surface are accelerated to the cathode. Cathode contains element (s) for beams. In principle, Cs vapor comes from the Cs oven into an enclosed area between the cooled cathode and the heated ionizing surface. Some of the Cs condenses on the front of the cathode and some of the Cs is ionized by the hot surface. The ionized cesium accelerates towards the cathode, sputtering particles from the cathode through the condensed cesium layer. Some materials will preferentially sputter negative ions. Other materials will preferentially sputter neutral or

positive particles which pick up electrons as they pass through the condensed cesium layer, producing negative ions.

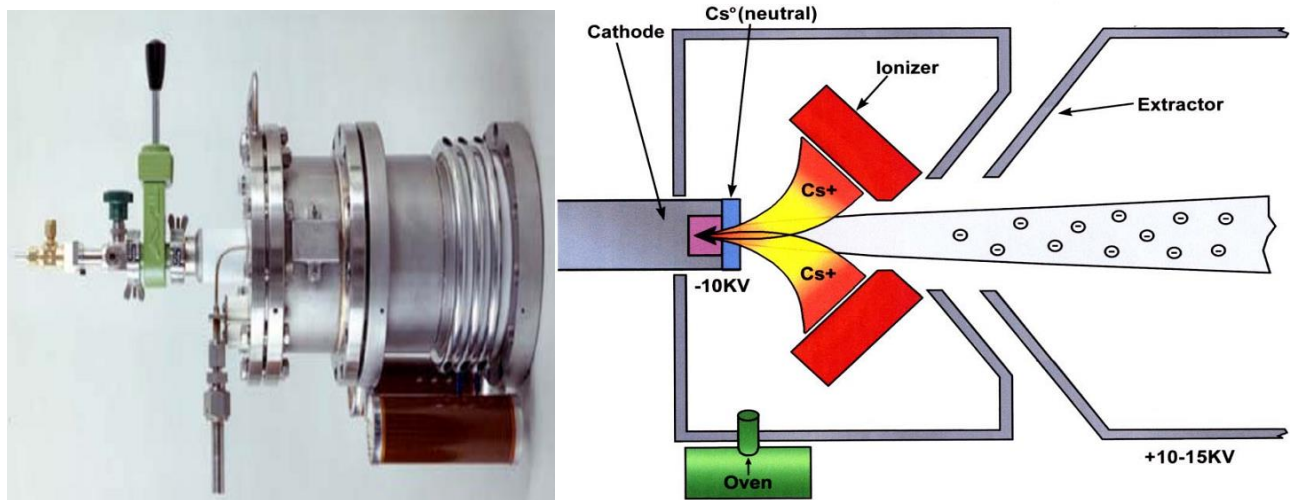


Fig.2-12 SNICS II Ion Sources.

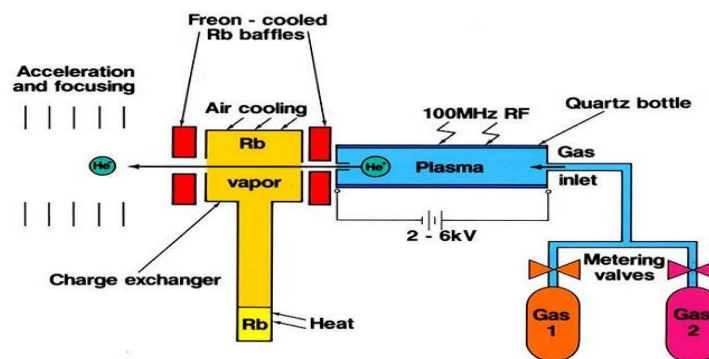


Fig.2-13 RF Charge Exchange Source.

For the RF Charge Exchange Source (see Fig.2-13), there are two main components in this device. The first one is the radio frequency positive ion source. He gas is bled into a quartz discharge bottle through a metering valve to maintain a pressure of 10-50 millitorr. An RF oscillator induces a plasma in the bottle which is intensified by the solenoid magnet.

2.2 Transmission electron microscopy

2.2.1 Principle of transmission electron microscopy

After the first-ever observation of dislocations in metals, transmission electron microscopy (TEM) became the most fundamental and important experimental technique in the research of

physical metallurgy [2-4]. Within recent times, the resolution limit for direct imaging of structural details has reached below 0.1 nm. Although it is still not easy to observe the motion of point defects at an atomic level, TEM observations are essential for studying and developing microstructural behaviors in materials even today. In this study, TEM observations were performed using a 200 keV electron microscope, a JEM 2010.

An electron microscope consists of an electron gun and an assembly of electron lenses. Fig.2- 14 and Fig.2- 15 show the formation of the microscopic image and the diffraction image in the electron microscope, respectively. After being focused onto the specimen in a parallel beam by magnetic condenser lenses, the beam is transmitted through the thin foil and diffracted in a number of directions by the crystal. Each diffracted beam focuses in a focus plane of the objective lens. A diffraction image is formed by the interference of several beams in the focus plane of the objective lens. The resulting image may be suitably magnified and projected onto a projection screen. The final magnification is varied by regulating the currents of either the intermediate or projector lenses. Lattice images can be observed if a row of systematic beams (reflected at the lattice planes) is used for imaging, while a structure image is formed using many beams present in a low-indexed Laue zone. At the objective lens an aperture is inserted not to allow all Bragg reflections to pass. When the aperture is centered to pass on the main transmitted beam, a bright-field (BF) image is obtained. On the other hand, a dark-field (DF) image is obtained by tilting the electron gun so that the aperture is on one of the diffracted beams.

The nature of the observed image is actually determined by the precise diffraction conditions. The Burgers vector of the dislocation can be determined by varying the diffraction conditions. The condition for no contrast is commonly written as $\mathbf{g} \cdot \mathbf{b} = 0$, where $\mathbf{g}$ is the reciprocal lattice vector of the reflecting planes and $\mathbf{b}$ is the Burgers vector.

The observation method associated with the sort of lattice defect is usually determined by the deviation from the reciprocal lattice point, which is given by the distance between $\mathbf{g}$ and the vector of the nearest reciprocal lattice point. For instance, typical investigations for defects in bcc metals involve tilting the specimens to obtain [110] crystal direction and $\mathbf{g} = 110$ to photograph the various defects. Strong diffraction conditions are employed to image the dislocation structure with $s > 0$, while voids are normally imaged in absorption contrast with $s \gg 0$ in focus. In addition, tiny defects, such as "black-dot" loops, are observed using DF images usefully.

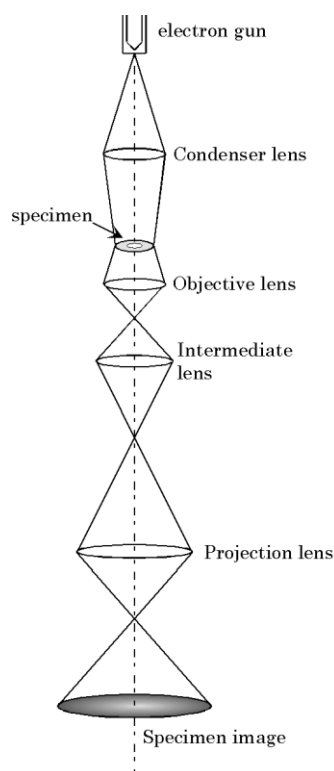


Fig.2- 14 Ray paths in the electron microscope under microscopy conditions.

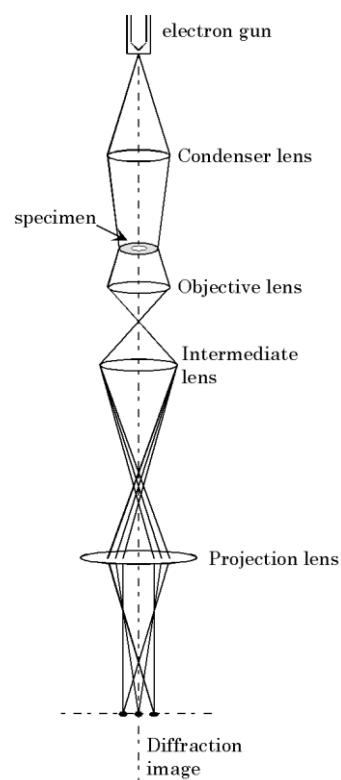


Fig.2- 15 Ray paths in the electron microscope under diffraction conditions.

2.2.2 Preparing TEM foils

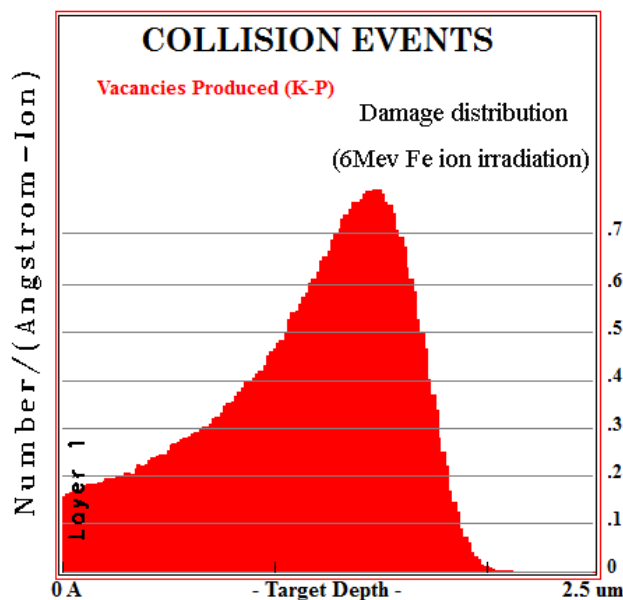
Foils used for TEM are typically about several dozen nm in thickness. Materials with a high atomic number absorb electrons effectively and must be prepared in thinner foils. There are several ways to polish specimens in order to prepare TEM foils, such as electro-polishing, chemical polishing, mechanical polishing, etc. In this study, Both chemical and electro-polishing technique were employed to obtain TEM specimens.

The thinning of neutron-irradiated specimens is relatively easy except for the difficulty in treating radioactive waste fluid because specimens have uniform damage. Specimens were rapidly thinned with the jet electro-polishing technique [4] by using a Tenupol (Struers Inc.) at first. After jet electro-polishing, specimens were electro-polished again with low voltage for finishing in this study. The final state of a foil surface is very important because a slightly dirty surface or a thin layer of amorphous material can greatly reduce the transparency of the polished specimen. The chemical compositions of electrolytes used for each electro-polishing technique are listed in Table 2-2.

Table 2-2 Chemical compositions of electrolytes to be used for each electropolishing technique.

Specimen	Polishing	Voltage	Composition
Fe, Fe-Cr alloys	Jet	50~60V	CH ₃ COOH:950ml, HClO ₄ : 50ml (90%:10%)
Fe	Finishing	~10V	HPO ₃ :84%, H ₂ O:16%, K ₂ Cr ₂ O ₇ :100g/l [5]
Fe-Cr alloys	Finishing	2~5V	H ₂ SO ₄ :60ml, H ₂ O:50ml, HPO ₃ :80ml (31.6%:26.3%:42.1%)
Fe-Cr alloys	Finishing	~10V	HClO ₄ , CH ₃ OH (5%:95%)

The thinning of ion-irradiated specimens needs polishing to the depth of peak damage. Fig.2-16 shows the damage distribution calculated with SRIM code [6] with Kinchin-Pease model for Fe irradiated with 6 MeV Fe ions. The damage peak in this case can be determined to be 1500 nm, approximately. The method of thinning of ion-irradiated specimens is a focused ion beam technique by using a Quanta 3D 200FEL. The specimen processing is shown in Fig.2-17, The polishing thickness was about 1000nm and the depth was about 4000 nm to see both the irradiated and non-irradiated area of the specimens The band area can be also observed. Finally, the specimens were electro-polished with electrolyte (5%HClO₄+ 95%CH₃OH) for 0.01s to move the damage coursed during thinning polishing from surface.

**Fig.2-16** Damage distribution calculated with SRIM code [6] (Kinchin-Pease model) for Fe irradiated with 6 MeV Fe ions.

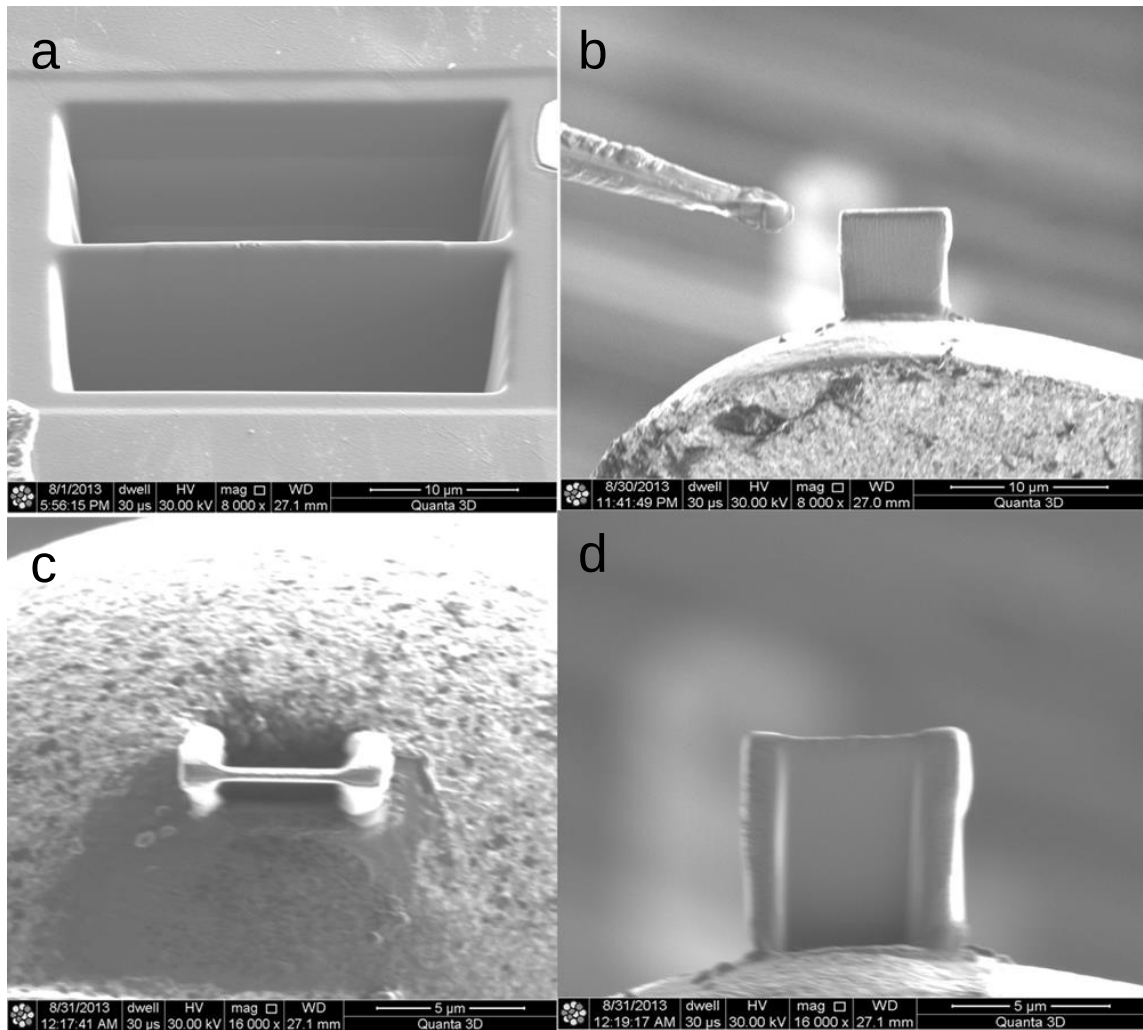


Fig.2-17 Specimens processing using focused ion beam. a : after grooving, b : after putting specimen on a mesh by a needle , c and d : specimen on the grid.

2.3 Positron annihilation lifetime spectroscopy

2.3.1 History of positron annihilation spectroscopy

The positron is an antielectron. It has the same rest mass, the same magnitude of charge and the same magnetic moment as an electron, but its charge is opposite. Because the positron is unstable in the real world, it is annihilated just after encountering an electron and converted into two γ -rays of about 511 keV with energy conservation, or three γ -rays. Positron annihilation spectroscopy (PALS) is an experimental technique utilizing this feature of positrons to investigate lifetimes and momentum distribution of electrons around trapping-sites for positrons, such as vacancy-type defects, or vacant sites around precipitates.

The first measurement of the annihilation γ -rays in solids was performed by DeBenedetti with the emergence of the scintillation counter in 1949 [7]. In the same year, DuMond *et al.* revealed that the Doppler shift effect from the momentum of the annihilated electron gives an energy difference between two annihilation γ -rays [8]. The angular correlation between the directions of the emitted annihilation γ -rays was found in 1955 [9,10]. The first measurement

of the positron annihilation lifetime was performed for gases in 1952 [11,12] and solids in 1953 [13]. The study of lattice defects using PALS was begun gradually after 1967. Several significant works for the application of positron annihilation to the study of lattice defects were published in and just after 1967, for example the increasing of annihilation lifetimes of positrons in deformed Al [14] and the trapping model of positrons by vacancy-type defects in solids [15,16]. The wide application of the positron annihilation technique to the detection of lattice defects was organized by several researchers in the beginning of the '70s [17-20] and experiments for determining vacancy formation energies in metals by positron annihilation were started around the same time. In 1972, the standard analysis program for positron annihilation lifetimes, POSITRONFIT EXTENDED, was exhibited by Kirkegaard and Eldrup [21] and this program is still used to analyze annihilation-lifetime spectra. In order to use this program, however, the time resolution of the measurement system must be known in advance. Therefore, an improved program, RESOLUTION, was later produced by the same group [22], which involved the automatic calculation of time resolution of systems. From the '80s, innovative experimental techniques were developed, such as the two-dimensional angular correlation of annihilation radiation (2D-ACAR) and the slow positron radiation beam. The improvement of devices and their precision promoted the popularization of PALS in the field of solid-state physics. Following the initial development for experimental techniques, the theory underlying positron annihilation had been developed from simple models describing the positron-solid interaction to "first-principles" predicting the annihilation characteristics for different environments and conditions. This study proceeded on a parallel with the development of electronic structure calculations. It goes without saying that the progress in computational techniques was a great help for the study. Puska and Nieminen published a general method for calculating positron annihilation lifetimes and the results for many elemental metals and semiconductors [23,24]. Now, the correlation between experimental results and calculations is good and the theory is of assistance to examine the behavior of vacancy-type defects from experimental results.

2.3.2 Principle of positron annihilation

Fig.2-18 shows the principle of application of positron-electron pair annihilations to detect point defects and their clusters in solids. When high energy positrons generated from the β^+ decay of a radioactive source, such as ^{22}Na , are injected into metal crystals, they are rapidly thermalized by electron-hole excitations and interactions with phonons to be in a low energy condition within about 1 ps. Thermalized positrons diffuse through the lattice, migrate into a depth of 10~100 μm and are finally annihilated by electrons. Positrons are influenced by repulsive forces by positively charged nuclei in the metal crystal during diffusion.

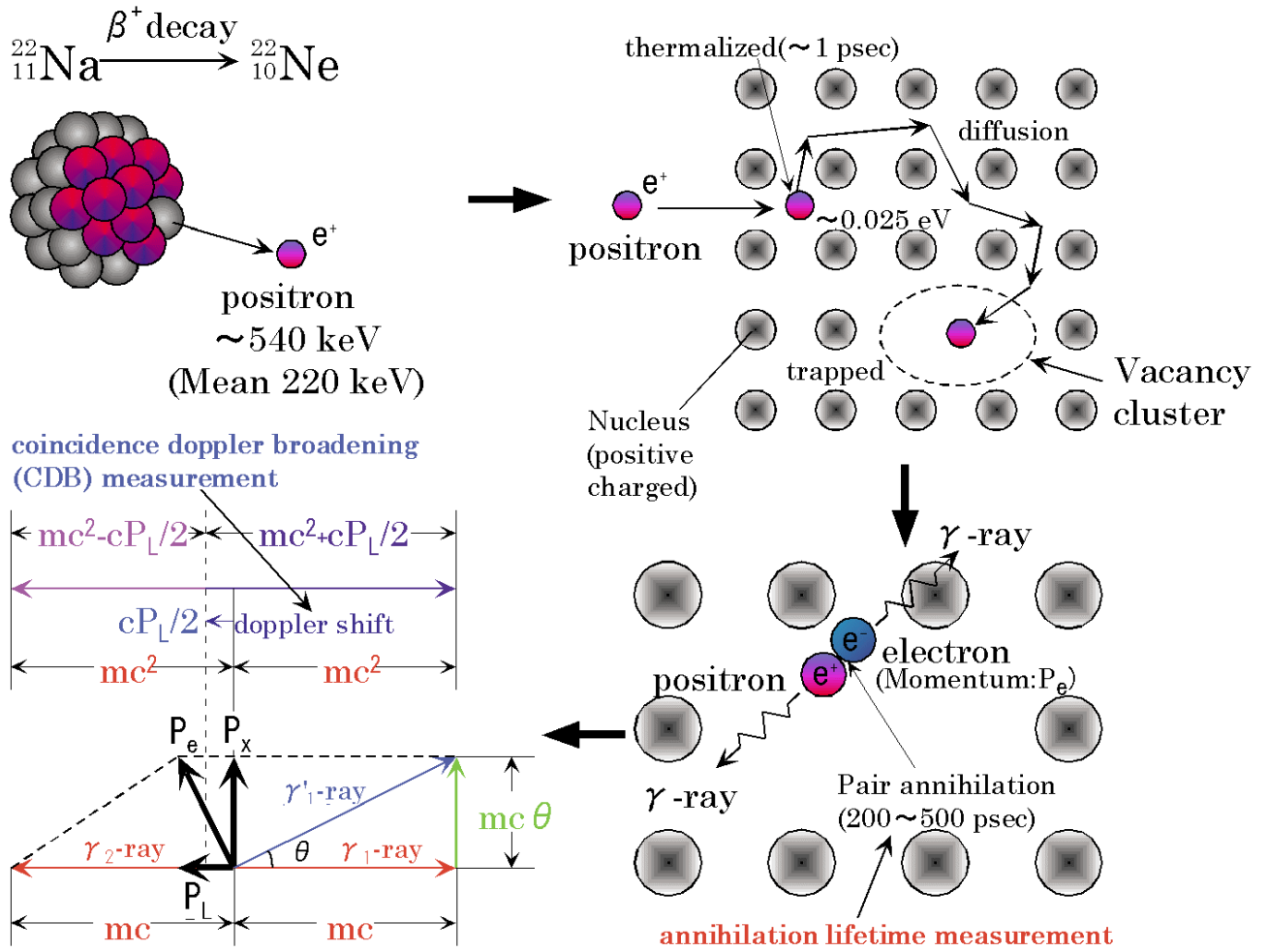


Fig.2-18 The model for the principle of application of positron-electron pair annihilations to detect point defects and their clusters in solids.

If there are open spaces in the lattice, such as vacancies and their clusters, positrons will be trapped in a bound state by such defects because there is no positive charge and the local electron density is significantly reduced due to the missing core electrons. This increases the lifetime of trapped positrons by 20~80% as compared with that of free positrons in a perfect lattice. The lifetime is increased in relation to the sort of defect and the size of vacancy-type defects. The positron annihilation lifetime measurement detects open-volume defects by the use of this feature of positrons. The lifetime obtained from experiments is usually decomposed into a long and a short component in cases where the measured specimen can be considered to contain vacancy-type defects. It is generally thought for positron annihilation lifetime measurements that a long lifetime reflects the positron annihilation after trapping by vacancy-type defects and a short lifetime reflects that by electrons in matrix or trapping sites not to give a large enhancement of the lifetime. The enhancement for the positron lifetime is not only caused by vacancies and vacancy clusters but also by dislocations, jogs on dislocations,

SFTs, etc [25-28]. The lifetime of vacancy-type defects is, however, larger than that of other defects and the long lifetime mainly involves the effect of vacancy trapping as shown in Fig.2-19. It is generally thought that the positron can seek vacancies and their clusters whose concentration in the lattice is higher than about 10^{-6} per atom. If the spectra from experiments cannot be decomposed into two components, there exist few vacancy-type defects whose concentration is less than 10^{-6} per atom or dislocations.

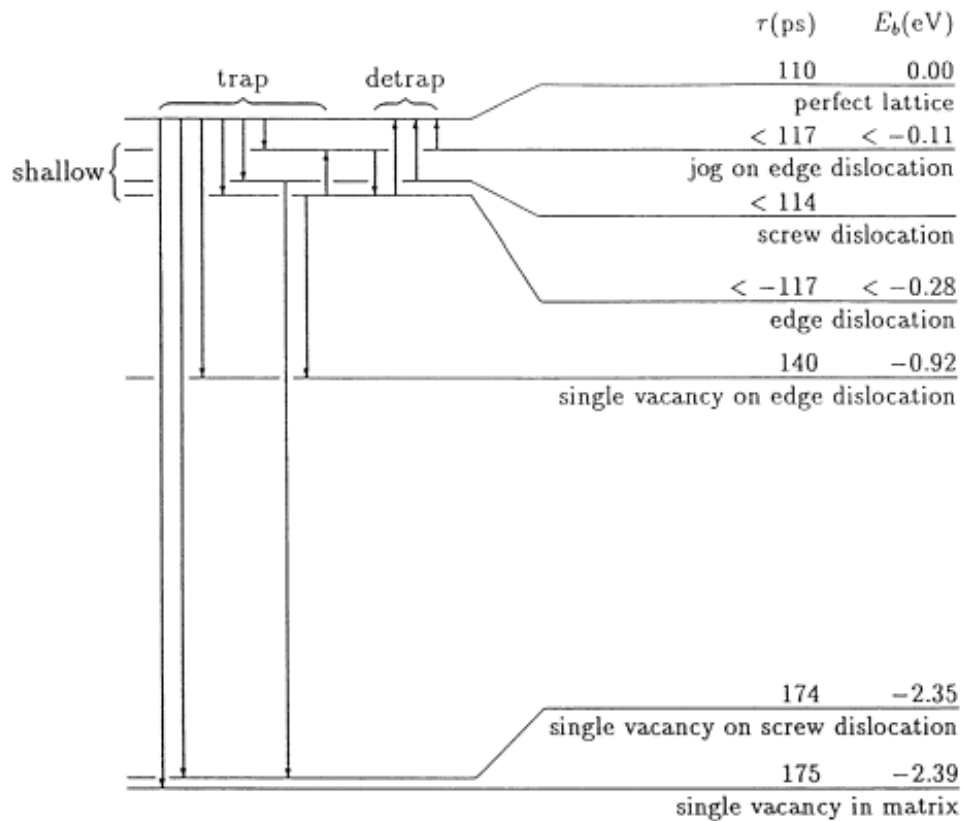


Fig.2-19 Level scheme drawing for positron lifetimes (τ) and binding energy levels (E_b) at each defect in Fe [27].

2.3.3 Positron annihilation lifetime (PAL) measurement

Fig.2-20 shows the system for positron annihilation lifetime (PAL) measurements used in this study. Typical radioactive sources for positrons are ^{22}Na , ^{58}Co , ^{64}Cu , etc [29]. ^{22}Na is the most commonly used source for experiments because of the following advantages.

- (i) This source emits 1.28 MeV γ -ray before β^+ decay, which is used as a start signal of lifetime measurements.
- (ii) The half decay period is 2.6 years which is relatively longer than other sources (^{58}Co : 71.3 days, ^{64}Cu : 12.8 hours).
- (iii) The emission rate of positrons is about 90%.

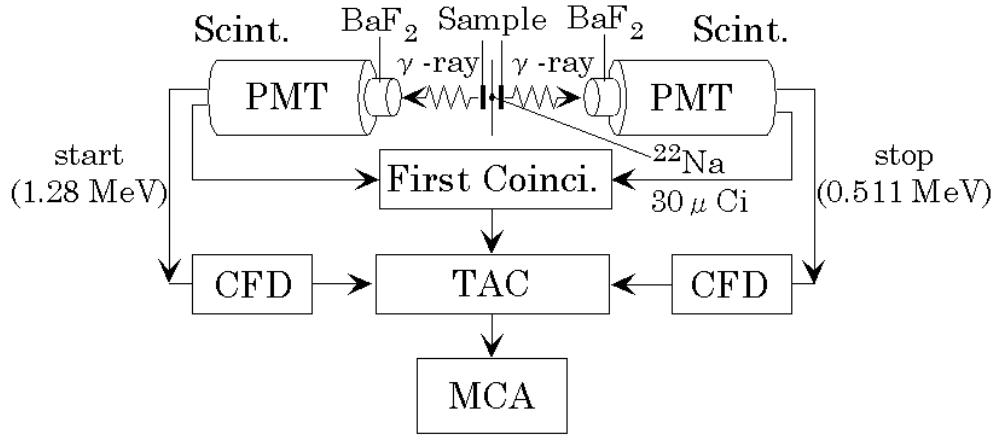


Fig.2-20 Diagram of the fast-fast system for the positron annihilation lifetime measurement consisting of a ^{22}Na radiation source, two BaF_2 scintillators, two photomultiplier tubes (PMT) and other modules.

In this study, the ^{22}Na source of about $30 \mu\text{Ci}$ (1.1 MBq) was used for lifetime and the radioactivity of the source for lifetime measurements. BaF_2 was used as the scintillator for detecting γ -rays because this scintillator emits fluorescent light with a short decay time, and the coincidence count rate with these scintillators is five times larger than with other conventional organic scintillators [30]. Now, BaF_2 is the most common scintillator for detecting γ -rays. The system in Fig. 2-11 is called a fast-fast system. It is simpler and has a higher count rate than the fast-slow system. The fast-slow system incorporates a fast channel for timing and a slower channel for energy selection and coincidence, while the fast-fast system has only a fast channel for timing and coincidence [31,32]. Energy selections and coincidence decisions are done at the constant fraction discriminators (CFD) and the time resolution and counting rate of the system are mainly governed by regulation of this module. The time-to-amplitude converter (TAC) generates an output pulse in proportion to the period between the input of a start signal and a stop signal. The multi-channel analyzer (MCA) converts the logic pulse from the TAC into the time spectrum between start γ -rays (1.28 MeV) and stop (annihilation) γ -rays (511 keV). The time resolution of the system in this study was about 220 ps in full width at half maximum (FWHM) and the lifetimes were obtained by analyzing the lifetime spectra using the RESOLUTION program [22].

- The lifetime spectrum function with the trapping model

The lifetime spectrum can be obtained using the trapping model of positrons by trapping sites. The rate of free positrons in the lattice $n_f(t)$ and the rate of trapped positrons $n_t(t)$ are written as follows.

$$\frac{dn_f(t)}{dt} = -\lambda_f n_f(t) - \kappa n_f(t), \quad \dots(2.1)$$

and

$$\frac{dn_t(t)}{dt} = -\lambda_t n_t(t) + \kappa n_f(t), \quad \dots(2.2)$$

where λ_f is the annihilation rate of free positrons, λ_t is the annihilation of trapped positrons and κ is the trapping rate of positrons by trapping sites, such as vacancy-type defects. κ is given as,

$$\kappa = \nu \cdot C_d, \quad \dots(2.3),$$

where ν is the coefficient of trapping and C_d is the density of defects. The equation (2.1) will be solved by the initial condition of $n_f(0) = n_{f0}$,

$$n_f(t) = n_{f0} \cdot \exp\{-(\lambda_f + \kappa)t\}. \quad \dots(2.4)$$

Substituting $n_f(t)$ of equation (2.4) into equation (2.2) gives the next equation,

$$\frac{dn_t(t)}{dt} + \lambda_t n_t(t) = \kappa n_{f0} \cdot \exp\{-(\lambda_f + \kappa)t\}. \quad \dots(2.5)$$

Then, $n_t(t) = F(t)\exp(-\lambda_t t)$ can be substituted into equation (2.5), where $F(t)$ is the given function.

$$F'(t)\exp(-\lambda_t t) - \lambda_t F(t)\exp(-\lambda_t t) + \lambda_t F(t)\exp(-\lambda_t t) = \kappa n_{f0} \exp\{-(\lambda_f + \kappa)t\},$$

$$F'(t) = \kappa n_{f0} \exp\{-(\lambda_f + \kappa)t\} \times \exp(-\lambda_t t) = \kappa n_{f0} \exp\{(\lambda_t - (\lambda_f + \kappa))t\},$$

$$F(t) = \frac{\kappa n_{f0}}{\lambda_t - (\lambda_f + \kappa)} \exp\{(\lambda_t - (\lambda_f + \kappa))t\} + C_2, \quad \dots(2.6)$$

where C_2 is the given constant. Since the initial density of positrons trapped by defects is 0 ($n_t(0)=0$), the equation for $F(t)$ is given as follows.

$$F(0) = \frac{\kappa n_{f0}}{\lambda_t - (\lambda_f + \kappa)} + C_2 = 0,$$

$$C_2 = -\frac{\kappa n_{f0}}{\lambda_t - (\lambda_f + \kappa)},$$

$$F(t) = \frac{\kappa n_{f0}}{\lambda_t - (\lambda_f + \kappa)} [\exp\{(\lambda_t - (\lambda_f + \kappa))t\} - 1]. \quad \dots(2.7)$$

Therefore, $n_t(t)$ is given as,

$$n_t(t) = \frac{\kappa n_{f0}}{\lambda_t - (\lambda_f + \kappa)} \{\exp(-(\lambda_f + \kappa)t) - \exp(-\lambda_t t)\}. \quad \dots(2.8)$$

From equations (2.4) and (2.8), the rate of free positrons in the lattice $n_f(t)$ and the rate of trapped positrons $n_t(t)$ are obtained. When the constants are defined as follows,

$$\begin{aligned}\tau_1 &= \frac{1}{\lambda_f + \kappa}, \\ \tau_2 &= \frac{1}{\lambda_t}, \\ I_1 &= \frac{n_{fo}(\lambda_f - \lambda_t)}{\lambda_t - (\lambda_f + \kappa)}, \\ I_2 &= \frac{n_{fo}\kappa}{\lambda_t - (\lambda_f + \kappa)},\end{aligned}$$

the lifetime spectrum function $T(t)$ is determined by the above equations,

$$T(t) = \lambda_f n_f(t) + \lambda_t n_t(t) = \frac{I_1}{\tau_1} \exp\left(-\frac{t}{\tau_1}\right) + \frac{I_2}{\tau_2} \exp\left(-\frac{t}{\tau_2}\right). \quad \cdots(2.9)$$

The definition of each constant is as follows.

τ_1 $\cdots$ The lifetime of positrons annihilated in the lattice, I_1 $\cdots$ The relative intensity of τ_1
 τ_2 $\cdots$ The lifetime of positrons annihilated in the defects, I_2 $\cdots$ The relative intensity of τ_2

The relation between I_1 and I_2 is

$$I_1 + I_2 = 1. \quad \cdots(2.10)$$

When a real experiment is performed, an ideal time spectrum of $T(t)$ determined by equation (2.9) is scarcely obtained due to the time resolution of the measuring device. The time resolution function $G(t)$ is generally given by the Gauss function with the standard deviation $\sigma/2^{0.5}$,

$$G(t) = \frac{1}{\sigma\sqrt{\pi}} \cdot \exp\left(-\frac{t^2}{\sigma^2}\right). \quad \cdots(2.11)$$

The time resolution is defined as full width at half maximum (FWHM) of this Gauss function.

$$\text{FWHM} = 2\sigma\sqrt{\ln 2}. \quad \cdots(2.12)$$

The time resolution of normal measuring devices for counting γ -rays is about 200 $\sim$ 300 ps. A real time spectrum $T_r(t)$ is obtained by summing of the folding integration between $G(t)$ and $T(t)$ and the background spectrum B .

$$T_r(t) = \int_{-\infty}^{\infty} G(t-t')T(t')dt' + B. \quad \cdots(2.13)$$

A comparison between the real and the ideal lifetime spectrum normalized by dividing peak counts into each count for pure Fe is shown in Fig.2-21, where the point "time=0" is defined at the point of peak count and the background spectrum is fixed as 0.00016 to calculate the ideal spectrum. It shows that the count ratio of each time in the real spectrum is larger than that in the ideal spectrum for a limitation of the time resolution of the measuring device.

The analysis for the real spectrum resulted in a time resolution of about 220 ps. In the real spectrum, the point "time=0" shifts slightly to a lower side of the time spectrum due to the time resolution and the fitting analysis program, such as RESOLUTION, also calculates the point "time=0" by fitting a measured spectrum with the Gauss resolution function.

In addition, the real time spectrum usually obtains the other lifetime components of positrons annihilated in a radiation source or a protective polyimide film on a radiation source [33]. For real experiments, an analysis for the spectrum of pure Fe was performed at first and lifetimes and their intensities of the other components were found, which are called the source components. In order to calculate long and short lifetimes of a measured specimen, lifetimes of a radiation source and a protective polyimide foil are usually fixed. The decomposition of a measured spectrum into long and short lifetimes is called two-component analysis. In this study, the lifetime of the ^{22}Na source was about 350 ps (intensity: about 10%) and that of the used foil was about 1000~1500 ps (intensity: about 1%), and these values agreed with general results [33]. Fig.2-22 shows a comparison of the obtained spectrum between pure Fe and neutron irradiated Fe-0.15 wt. % Cu. As can be seen from this figure, the spectrum of neutron irradiated Fe-0.15 wt. % Cu shifts to a higher side of the time spectrum and it can be decomposed into long and short lifetimes with fixed source components. The long lifetime of 412 ps (intensity: 17%) and the short lifetime of 128 ps (intensity: 83%) were obtained from an analysis for this spectrum. This long lifetime corresponds to micro-voids of 50 vacancies whose size is about 1nm.

A mean lifetime between long and short lifetimes is also obtained by the analysis for the spectrum generally, which is called one-component analysis. In the case of the one-component analysis, lifetimes of a radiation source and a protective polyimide foil are also fixed. The mean lifetime roughly corresponds to the amount of total residual defects and the value of the mean lifetime is much more confidential than the long and short lifetimes because of the much lower statistical error [34]. Actually, in the case of our experiments, the statistical error for the mean lifetime was always less than 0.5 ps and was one tenth or hundredth of that of the long lifetime. In Table 2-3, the lifetimes of bulk and vacancy clusters in some metals are listed.

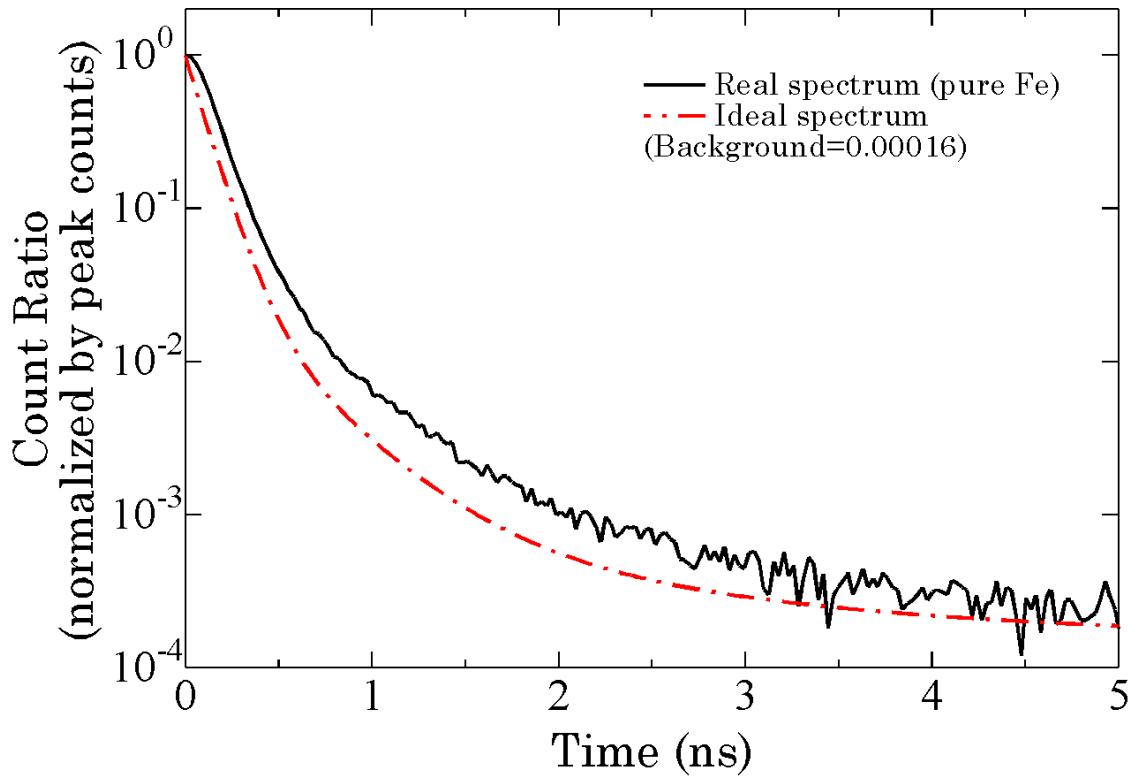


Fig.2-21 Comparison between the real and the ideal lifetime spectrum of Fe normalized by dividing peak counts into each count.

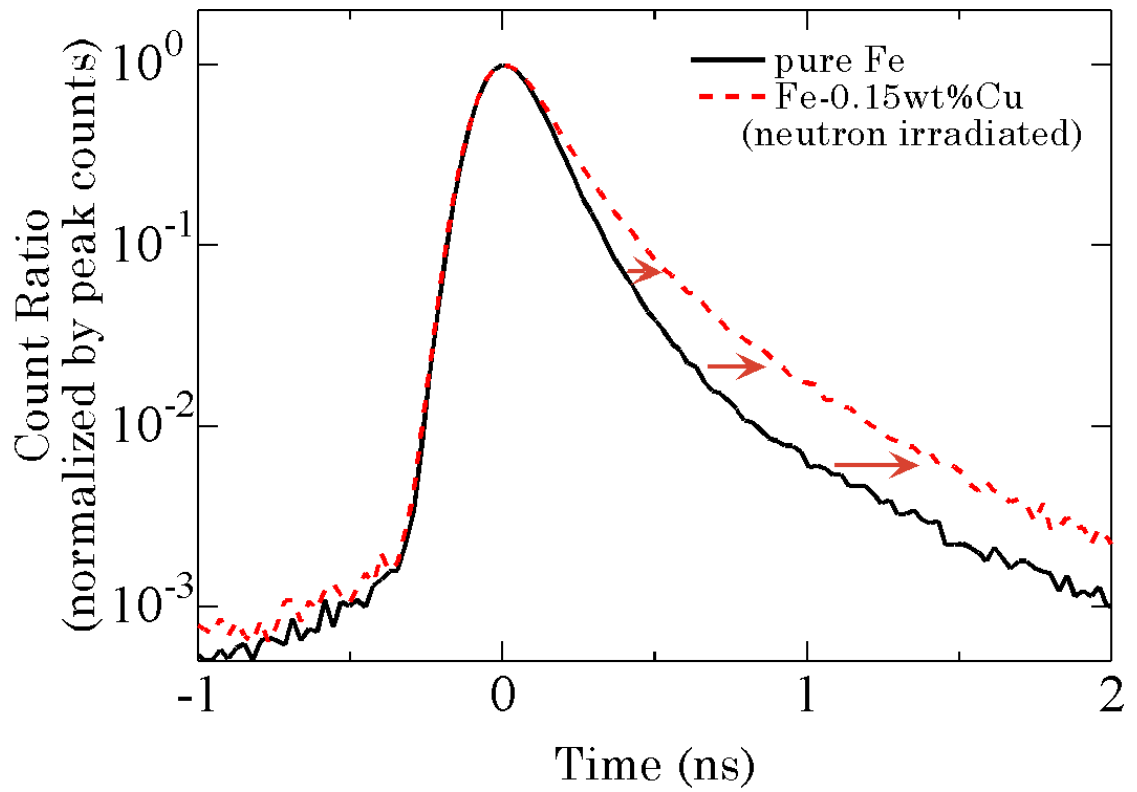


Fig.2-22 Comparison of the obtained spectrum between pure Fe and neutron irradiated Fe-0.15 wt. % Cu.

Table 2-3 Calculated results for lifetimes of bulk specimens, vacancies and vacancy clusters in typical transition metals [23].

Metal	Bulk lifetime(ps)		Number of vacancies	Lifetime(ps)		Number of vacancies	Lifetime (ps)	
				Fe	Mo		Al	Ni
Al	166		1	190	213	1	253	184
V	120		2	197	224	2	273	203
Cr	120		3	232	262	4	329	263
Fe	110		4	262	293	6	351	288
Ni	110		6	304	334	13	422	376
Cu	122		9	294	321			
Nb	120		10	334	363			
Mo	120		15	386	410			

2.4 Mössbauer spectroscopy

2.4.1 Principle of Mössbauer spectroscopy

Mössbauer spectroscopy (MS) is based on recoilless emission and resonant absorption of γ -radiation by atomic nuclei. In MS, the γ -ray emitted from a radioactive nucleus is modulated by inducing Doppler velocity to the source, and the γ rays of discrete energies are resonantly absorbed by absorber nuclei.

Nuclei are exposed to electric and magnetic fields created by the electrons of the Mössbauer atom itself and by other atoms in the neighborhood. These fields generally interact with the electric charge distribution and the magnetic dipole moment of the Mössbauer nucleus and perturb its nuclear energy states. The perturbation, called nuclear hyperfine interaction, is such that it shifts the nuclear energy levels, as is the case in the electric monopole interaction (e_0), or such that it splits degenerate states, as afforded by the electric quadrupole interaction (e_1) and the magnetic dipole interaction (m_1). Only these three kinds of interaction must be considered in practical MS.

A Mössbauer spectrum, in general, reflects the nature and the strength of the hyperfine interactions. The e_0 interaction alters the position of the resonance lines on the energy scale in units of the Doppler velocity and gives rise to the so-called isomer shift (chemical shift) δ , whereas the e_2 and the m_1 interactions induce splitting of the resonance lines according to the allowed transitions from the ground to the excited state. Most valuable information regarding the chemical and physical characteristics of the sample under study can be extracted from these hyperfine interactions.

• Isomer Shift

If there is a difference in the chemical environments of the source and the absorber the resonance absorption will not occur because of mismatch in energies. In Fig.2-23(a) resonance absorption occurs when the emitter ^{57}Co and the absorber ^{57}Fe are in the same matrix, say of metallic palladium. But resonance does not occur (Fig.2-23 (b)) when ^{57}Fe is in a different matrix, say of a mineral, viz. olivine, pyroxene, amphibole, iron ore etc. The difference in energies $E_t' - E_t$ is called chemical shift or isomer shift, denoted by IS or δ .

Essentially IS arises out of the difference in s-electron density at the nuclei of radioactive source and the absorbing Fe nuclei in the sample or absorber. IS represents the electric monopole interaction involving the positive nuclear charge and the electric field of surrounding electrons. This interaction causes a shift of the nuclear energy levels with respect to the bare nucleus. It is, therefore, sensitive to the charge density distribution caused by the electronic environment around the nucleus. IS is affected by oxidation state, coordination number, ligand-type coordinated to Fe cations, spin state of Fe, and may be augmented by a second-order Doppler shift, which is temperature dependent. IS depends heavily on a calibration standard, the calibration standards normally used are α -Fe foil, stainless steel, α - Fe_2O_3 etc., in which the mid-point of the individual spectrum is measured for the zero velocity position. The values for IS, relative to α -Fe, of various standards in different matrices are reported by Mössbauer Effect Data Center (Getteys and Stevens, 1981) and in mm/sec as: stainless steel, -0.09; Cr, -0.154; Pd, +0.177; Rh, +0.106; Cu, -0.225.

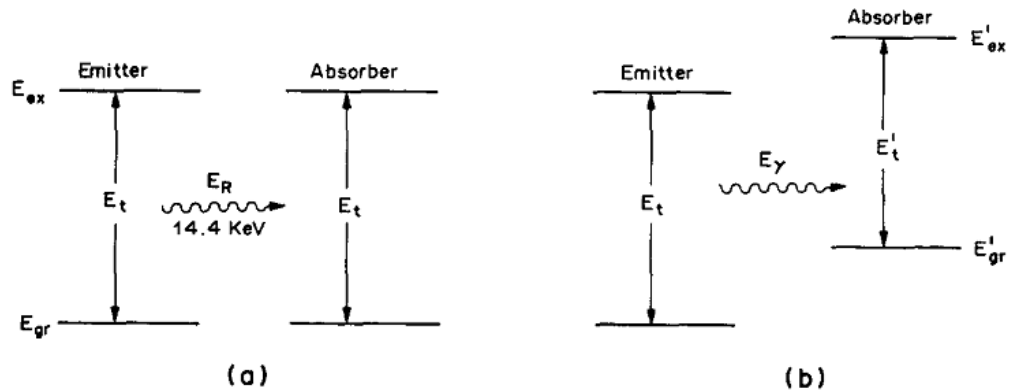


Fig.2-23 (a) Resonance absorption when emitter and absorber in identical matrix and (b) no absorption in non-ideal matrix.

In detail, the electric monopole interaction between a nucleus (with mean squareradius R^2) and its environment is a product of the nuclear charge distribution ZeR^2 and the electronic charge density $e|\psi(0)|^2$ at the nucleus, $\delta E = \text{const} \cdot R^2 e |\psi(0)|^2$. However, nuclei of the same mass and charge but different nuclear states (isomers) have different charge distributions ($ZeR^2 g \neq ZeR^2 e$), because the nuclear volume and the mean square radius depend on the state of nuclear

excitation ($R^2g \neq R^2e$). Therefore, the energies of a Mössbauer nucleus in the ground state (g) and in the excited state (e) are shifted by different amounts $(\delta E)_e$ and $(\delta E)_g$ relative to those of a bare nucleus. It was recognized very early that this effect, which is schematically shown in Fig. 2-24, is responsible for the occurrence of the Mössbauer IS [35].

Recently, a new physically interesting approach has been suggested in which the isomer shift is treated as a derivative of the total electronic energy with respect to the radius of a finite nucleus [36].

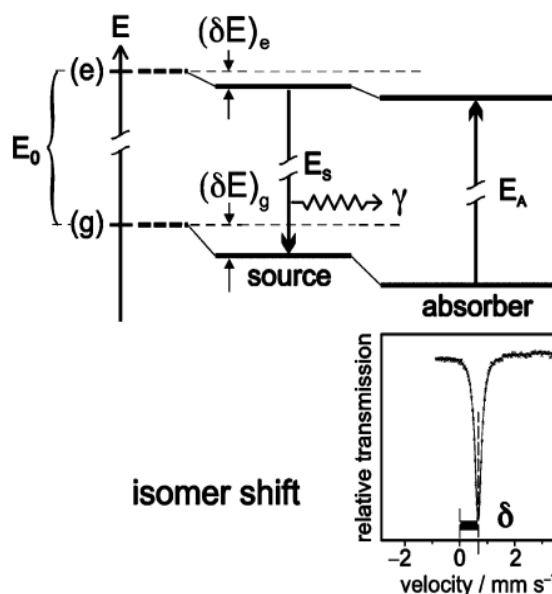


Fig.2-24 Schematic mechanism of Mössbauer isomer shift [37].

The electric monopole interaction between the nuclear charge and the electron density at the nucleus shifts the energy of the nuclear states and gives the Mössbauer IS.

• *Quadrupole splitting*

While discussing the IS parameter, it has been assumed that the nucleus is spherically symmetrical. This is true for nuclear states with spin quantum number $I = \frac{1}{2}$, such as the ground state of ^{57}Fe . But if the spin quantum number is 1 or greater ($I \geq 1$) the nuclei will have a quadrupole moment, eQ , which may interact with the surrounding electric field gradients (EFG). The excited state of ^{57}Fe ($I = 3/2$) has a quadrupole moment. In the presence of a non-spherically symmetrical electrical field the excited state having non-spherical (elliptical) charge distribution assumes different orientations in relation to the field, and the energy levels split. This is called quadrupole splitting (QS), the magnitude of which is equal to $\frac{1}{2}e^2qQ$, where e is the electron charge, q is the gradient of the electrostatic field at the nucleus, and Q is the nuclear quadrupole moment. Transition to these splitted levels from the ground state gives a two-line pattern. The velocity

difference between the lines is a measure of the QS. In axially symmetric fields (linear, square planar etc.) there are $I + \frac{1}{2}$ different levels for half integral spins ($3/2, 5/2, 7/2$ etc.) and $I + 1$ different levels for integral spins ($I = 1, 2, 3$, etc.). In a spherically symmetric field, the excited state will occur when there is a field gradient at the nucleus caused by asymmetric s -electron distribution in a compound. QS also depends on Fe valence, spin state and relative site ordering.

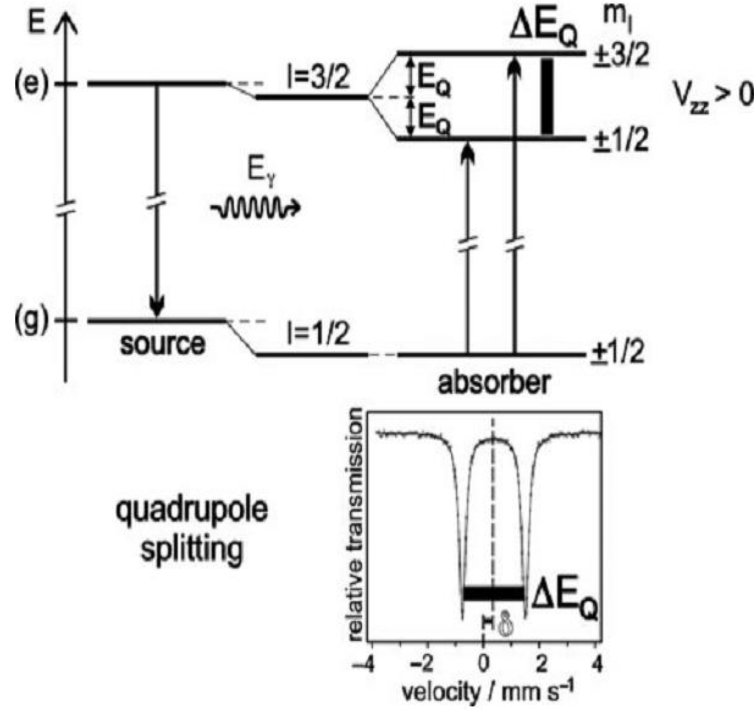


Fig.2-25 Schematic mechanism of Mössbauer quadrupole splitting [37].

Quadrupole splitting of the excited state of ^{57}Fe with $I = 3/2$ and the resulting Mössbauer spectrum. Quadrupole interaction splits the spin quartet into two degenerate sublevels $|I, \pm m_I\rangle$ with energy separation $\Delta E_Q = 2E_Q$. The ground state with $I = 1/2$ remains unsplit. The nuclear states are additionally shifted by electric monopole interaction giving rise to the isomer shift δ .

• Hyperfine magnetic splitting

A nucleus in a state with spin quantum number $I > 0$ will interact with a magnetic field by means of its magnetic dipole moment $\vec{\mu}$. This magnetic dipole interaction or nuclear Zeeman effect may be described by the Hamiltonian

$$H_m = -\vec{\mu} \cdot \vec{B} = -g_N \mu_N \vec{I} \cdot \vec{B} \quad \dots (2.14)$$

where the field $\vec{B}$ represents the magnetic induction, g_N is the nuclear Landé factor, and $\mu_N = e\hbar/2M_p c$ is the nuclear magneton (M_p : proton mass). Diagonalization Hamilton matrix yields

the eigenvalues of E_M :

$$E_M(m_I) = -\mu_B m_I / I = -g_N \mu_N B m_I \quad \dots (2.15)$$

The nuclear Zeeman effect splits the nuclear state with spin quantum number I into $2I + 1$ equally spaced and nondegenerate substates $|I, \pm m_I\rangle$, which are characterized by the sign and the magnitude of the nuclear magnetic spin quantum number m_I . Fig.2-26 shows schematically the effect of magnetic dipole interaction for ^{57}Fe , where the excited state with $I = 3/2$ is split into its four magnetic substates and the ground state with $I = 1/2$ into the two substates. The allowed γ transitions between the sublevels of the excited state and those of the ground state are found following the selection rules for magnetic dipole transitions: $\Delta I = 1$, $\Delta m = 0, \pm 1$. The six allowed transitions for ^{57}Fe are shown in Fig.2-26. In a Mössbauer experiment with a single-line source, one would usually observe a resonance sextet, the centroid of which may be shifted from zero velocity by electric monopole interaction (isomer shift). The relative line intensities taken from left to right exhibit a 3:2:1:1:2:3 pattern for an isotropic distribution of the magnetic field with respect to the γ -ray propagation. The line intensities are determined by the squares of the relevant Clebsch–Gordan coefficients. When the hyperfine field $\vec{B}$ at the nucleus is perpendicular to the γ -direction, the intensity ratio is 3:4:1:1:4:3, whereas for $\vec{B}$ parallel to the γ -direction, the ratio is 3:0:1:1:0:3. Thus, the relative intensities of the $\Delta m = 0$ transitions (lines “2” and “4”) are indicative of the field orientation. The magnetic hyperfine splitting allows the determination of the effective magnetic field acting on the nucleus, which may be a superposition of an applied field $\vec{B}_{\text{ext}}$ and an internal field $\vec{B}_{\text{int}}$ arising from a magnetic moment of the valence electrons. The various sources contributing to the internal field are:

- 1) The isotropic Fermi contact field B^C , which arises from a net spin-up or spin-down s-electron density at the nucleus as a consequence of spin polarization of s-electrons by unpaired valence electrons [38];
- 2) An anisotropic contribution $\vec{B}^L$ from the orbital motion of valence electrons with the quantum number L for the total orbital moment;
- 3) An anisotropic spin-dipolar contribution $\vec{B}^d$ arising from nonspherical distribution of the electronic spin density.

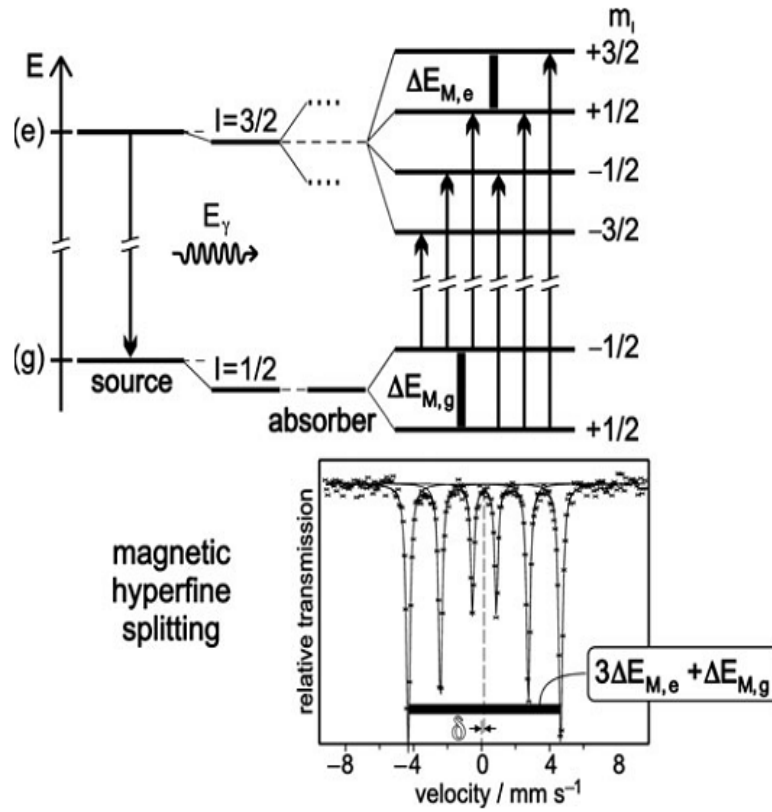


Fig.2-26 Schematic mechanism of Mössbauer magnetic hyperfine splitting[37].

Figure 2-27 shows magnetic dipole splitting (nuclear Zeeman effect) in ^{57}Fe and resultant Mössbauer spectrum (schematic). The mean energy of the nuclear states is shifted by the electric monopole interaction which gives rise to the isomer shift δ . $\Delta E_{M,g} = g_g \mu_N B$ and $\Delta E_{M,e} = g_e \mu_N B$ refer to the Zeeman energies of the ground and the excited states, respectively. The splitting of the $I = 3/2$ state into two dotted lines in the middle panel indicates the effect of quadrupole splitting discussed earlier.

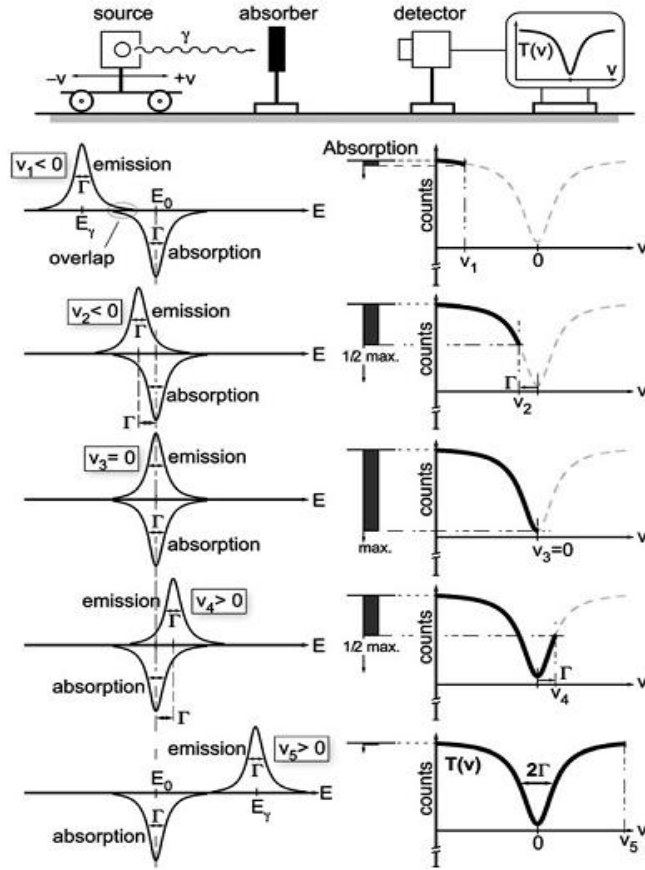


Fig.2-27 Schematic illustration of a Mössbauer transmission experiment in five steps. The “Absorption” bars indicate the strength of recoilless nuclear resonant absorption as determined by the “overlap” of emission and absorption lines when the emission line is shifted by Doppler modulation (velocities $v_1, \dots, v_5$). The transmission spectrum $T(v)$ is usually normalized to the transmission $T(\infty)$ observed for $v \rightarrow \infty$ by dividing $T(v)/T(\infty)$.

2.4.2 Experimental

A Mössbauer equipment basically consists of a source (^{57}Co), a drive mechanism for producing a Doppler velocity, a γ -ray detector with amplifying and sorting attachment followed by a data sorting device viz. a multi-channel analyzer. The Mössbauer spectrum is a record of the transmission rate of the resonant γ -rate as a function of Doppler velocity between the source and the absorber. In this regard it is akin to infrared spectroscopy. In two ways the γ -ray transmission as a function of Doppler velocity can be measured. By mounting the source on a mechanical constant-velocity drive, the total number of counts can be registered in a fixed time at constant velocity, and subsequently remeasured at different velocities. In the other method, the whole velocity range is scanned cyclically so that the whole spectrum is accumulated simultaneously. This is most commonly used.

In an actual Mössbauer transmission experiment, the radioactive source is periodically moved with controlled velocities, $+v$ toward and $-v$ away from the absorber. The motion modulates the energy of the γ -photons arriving at the absorber because of the Doppler effect: E

$\gamma = E_0 (1 + v/c)$. Alternatively, the specimens are moved with the source remaining fixed. The transmitted γ -rays are detected with a γ -counter and recorded as a function of the Doppler velocity, which yields the Mössbauer spectrum, $T(v)$. The amount of resonant nuclear γ -absorption is determined by the overlap of the shifted emission line and the absorption line, such that greater overlap yields less transmission; maximum resonance occurs at complete overlap of emission and absorption lines. Fig.2-28 is the photo of the Mössbauer measurement equipment. MS was conducted at room temperature.

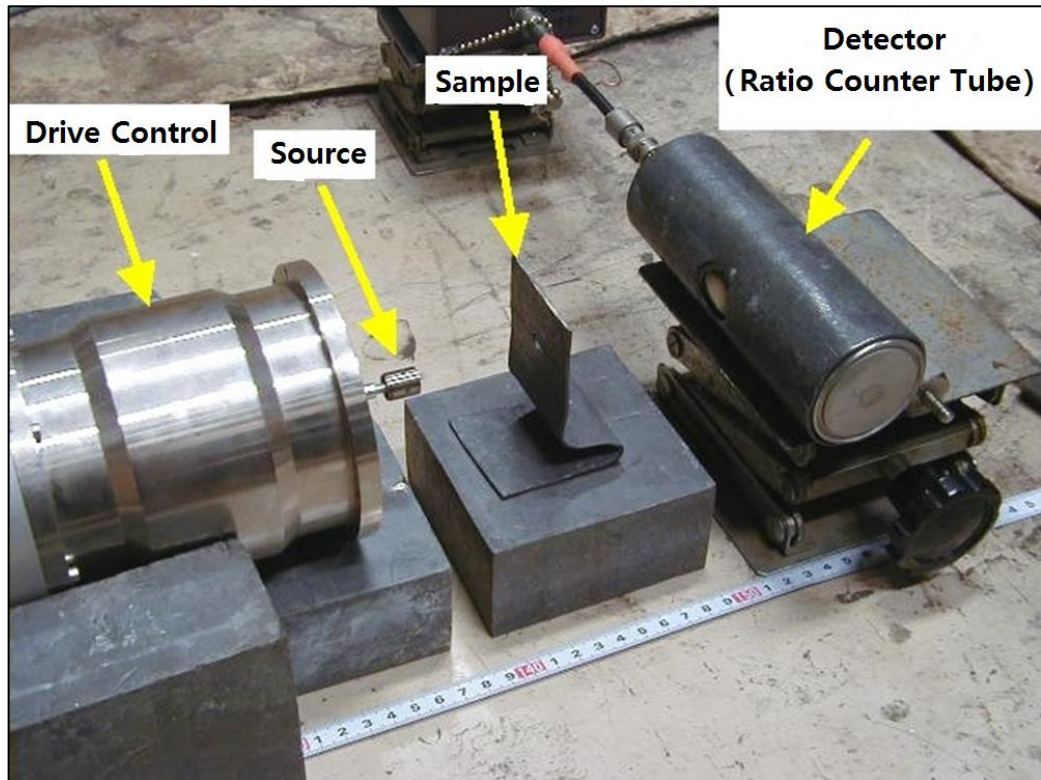


Fig.2-28 Photograph of the Mössbauer measurement equipment.

Reference (Chapter 2)

- [1] T. Yoshiie, Y. Hayashi, S. Yanagita, Q. Xu, Y. Satoh, H. Tsujimoto, T. Kozuka, K. Kamae, K. Mishima, S. Shiroya, K. Kobayashi, M. Utsuro, Y. Fujita Nucl. Instrum. Methods Phys. Res., Sect. A 498 (2003) 522.
- [2] P. B. Hirsch, A. Howie, R. B. Nicholson, D. W. Pashley and M. J. Whelan, "Electron Microscopy of Thin Crystals", Krieger Publ. Co., Malabar, Florida (1965).
- [3] M. Rühle and M. Wilkens, "Transmission Electron Microscopy (Ch.11 in Physical Metallurgy, edited by R. W. Cahn and P. Hassen)", Elsevier Science Publishers, New York (1983) 1033.
- [4] H. G. F. Wilsdorf, Rev. Sci. Instrum., 29 (1958) 323
- [5] S. Yanagita, "The study of damage-rate dependence in defect structures in Fe-Cu alloys irradiated by neutrons", Doctoral dissertation of Kyoto University (1999) in Japanese
- [6] James Ziegler - SRIM & TRIM <http://www.srim.org/>
- [7] S. DeBenedetti, C. L. Cowan and W. R. Konneker, Phys. Rev., 76 (1949) 440(L).
- [8] J. W. M. DuMond, D. A. Lind and B. B. Watson, Phys. Rev., 75 (1949) 1226.
- [9] A. T. Stewart, Phys. Rev., 99 (1955) 594.
- [10] G. Lang, S. DeBenedetti and R. Smoluchowski, Phys. Rev., 99 (1955) 596(L).
- [11] S. DeBenedetti and H. J. Riching, Phys. Rev., 85 (1952) 377.
- [12] M. Deutsch and S. C. Brown, Phys. Rev., 85 (1952) 1049.
- [13] R. E. Bell and R. L. Graham, Phys. Rev., 90 (1953) 644.
- [14] B. T. A. Mckee, H. M. B. Bird and I. K. MacKenzie, Bull. Am. Phys. Soc., 12 (1967) 687.
- [15] D. C. Connors and R. N. West, Phys. Lett., 30A (1969) 24.
- [16] B. Bergersen and M. J. Stott, Solid. State. Comm., 7 (1969) 1203.
- [17] A. Seeger, J. Phys. F: Metal Phys., 3 (1973) 248.
- [18] P. Hautojärvi, A. Tamminen and P. Jauho, Phys. Rev. Lett., 24 (1970) 459.
- [19] J. Baram and M. Rosen, Phys. Stat. Sol. (a), 16 (1973) 263.
- [20] Ch. Dauwe, D. Segers, L. Dorikens-Vanpraet and M.. Dorikens, Phys. Stat. Sol. (a), 17 (1973) 443.
- [21] P. Kirkegaard and M. Eldrup, Comp. Phys. Commun., 3 (1972) 240; 7 (1974) 401.
- [22] P. Kirkegaard, M. Eldrup, O. E. Morgensen and N. Pedersen, Comp. Phys. Commun., 23 (1981) 307.
- [23] M. J. Puska and R. M. Nieminen, J. Phys. F: Met. Phys., 13 (1983) 333.
- [24] M. J. Puska and R. M. Nieminen, Rev. Mod. Phys., 66 (1994) 841.
- [25] Y. Kamimura, T. Tsutsumi and E. Kuramoto, Phys. Rev. B, 52 (1995) 879.
- [26] E. Kuramoto, H. Abe, M. Takenaka, F. Hori, Y. Kamimura, M. Kimura and K. Ueno, J. Nucl. Mater., 239 (1996) 54

- [27] E. Kuramoto, K. Ohsawa, T. Tsutsumi and M. Koyanagi, *J. Nucl. Mater.*, 271/272 (1999) 26
- [28] E. Kuramoto, T. Tsutsumi, K. Ueno, M. Ohmura and Y. Kamimura, *Comp. Mater. Sci.*, 14 (1999) 28.
- [29] M. Doyama, "Studies of Point Defects by Positrons and Positive Muons (Point Defects and Defect Interactions in Metals, edited by J. Takamura, M. Doyama and M. Kiritani)", Univ. of Tokyo Press., Tokyo (1982) 3.
- [30] W. Bauer, J. Major, W. Weiler, K. Maier and H. E. Schaefer, "Positron Annihilation, edited by P. C. Jain, R. M. Singru and K. P. Gopinathan", World Scientific Publ. Co., Singapore (1985) 804.
- [31] W. H. Hardy II and K. G. Lynn, *IEEE Trans. Nucl. Sci.*, NS-23 (1976) 229.
- [32] M. O. Bedwell and T. J. Paulus, *IEEE Trans. Nucl. Sci.*, NS-26 (1979) 422.
- [33] F. Hori, "The study for the microstructural behavior of irradiation induced Cu precipitates in Fe-Cu alloys by the use of positron annihilation lifetime measurements", Doctoral dissertation of Kyushu University (1994) in Japanese.
- [34] A. Vehanen, P. Hautojärvi, J. Johansson and J. Yli-Kauppila, *Phys. Rev. B*, 25 (1982) 762.
- [35] Kistner, O.C., Sunyar, A.W.: *Phys. Rev. Lett.* 4 (1960) 229.
- [36] Filatov, M.: *J. Chem. Phys.* 127 (2007) 084101
- [37] Philipp Gutlich, Eckhard Billl, Alfred X. Trautwein, *Mössbauer Spectroscopy and Transition Metal Chemistry Fundamentals and Applications*, springer, (2010)
- [38] Freeman, A.J., Watson, R.E.: *Phys. Rev. B* 131 (1963) 2566.

Chapter 3 Defect evolution by isolate point defects in F82H steel and its model alloys

3.1 Role of point defects on the void swelling resistance

As mentioned in previous sections, ferritic/martensitic steels are known mostly owing to their resistance to avoid swelling. The lower swelling observed in bcc steels relative to fcc steels is shown to be primarily a consequence of much longer transient regimes prior to the onset of steady-state swelling. The development of universal swelling rate is preceded by a transient regime whose duration is dominated first by the initial alloy composition, and second by the subsequent irradiation-induced micro-chemical evolution of the alloy matrix.

Recent studies [1] of resistivity recovery have clarified the effects of Cr concentration on the evolution of irradiation-induced defects in Fe–Cr alloys upon annealing after low-temperature electron irradiation. However, unlike for Fe–Cr alloys, irradiation damage of commercial steels is also affected by the interaction between irradiation-induced defects and solute additives. The physical basis of the swelling resistance of these materials is not yet well understood. Changes in the microstructure of the alloys and steels during their exploitation are governed by the kinetics of defects produced by irradiation. Therefore, reliable determination and clear understanding of properties of the irradiation-induced defects are the first step in solving the above problem. This work was aimed at qualitatively investigating the role of point defects during the microstructural evolution of Fe–Cr model alloys. Attention was focused on the basic properties of point defects especially for vacancy and their clusters introduced.

In the present work, isolate point defects were deliberately introduced to a serial of designed F82H model alloys to systematically analyze the synergistic effects of additive solute atoms on defect evolution. The goal of the work was a positron lifetime spectroscopic investigation of model alloys of F82H-type ferritic/martensitic steels before and after irradiation. Isochronal annealing of low-temperature irradiated alloys was also performed to clarify the characteristics of point defect evolution.

3.2 Electron irradiation

All of the prepared specimens for irradiation (see Section 2.1) were bombarded with 30 MeV electrons to a fluence of about 10^{18} electron/cm² using the LIANC in the Research Reactor Institute, Kyoto University. Under these conditions, mainly Frenkel pairs are introduced, which is desirable for the study of the basic interactions between vacancies and solute atoms. Two kinds of electron irradiation at different temperatures were conducted. One was at 77 K to

a dose of 1.2×10^{-3} dpa with displacement threshold energy of 40 eV. The other was at 673 K to a higher dose of 3.5×10^{-2} dpa. The as-irradiated specimens were employed to perform positron annihilation measurements at room temperature. Each of the 77 K electron irradiated specimens was isochronally annealed for 1 h from 300 K to the corresponding temperature. Positron annihilation measurements were conducted after each step.

3.2.1 Microstructure of specimens before irradiation

• X ray diffraction

As mentioned above, the composition of F82H steel is mainly Fe-8Cr-2W-0.2V-0.04Ta-0.5Mn-0.2Si-0.1C, for this class of steels, the major precipitate is the Cr-rich $M_{23}C_6$ carbide at temperatures corresponding to conventional tempering conditions (i.e. 973–1073K) [2]. At the same time, by air cooling, a typical martensite with a sub-grain structure and dislocations can be formed in these tempered steels [3]. X-ray diffraction were carried out on specimens containing C by using Cu $K\alpha$ ($\lambda = 0.15405$ nm) radiation. Fig.3-1–Fig.3-3 show the X-ray diffraction spectrum of (Fe-8Cr-2W-0.1C, Fe-8Cr-2W-0.2V-0.04Ta-0.1C and F82H) before irradiation respectively.

According to the Bragg equation and the surface space expression of the cubic crystal system, an equation can be obtained.

$$\sin^2\theta = \frac{\lambda^2}{4a^2}(H^2 + K^2 + L^2) \quad \dots(3.1)$$

By removing the constant term, a series can be written as:

$$\sin^2\theta_1 : \sin^2\theta_2 : \dots = (H_1^2 + K_1^2 + L_1^2) : (H_2^2 + K_2^2 + L_2^2) : \dots \quad \dots(3.2)$$

The subscript 1, 2 ... of $\sin^2\theta$ in equation represent order of experimental data of the diffraction peak numbered from left to right. The H , K and L are integers; the sum of the squares of these integers must be also an integer. By extinction condition of crystal structure, in bcc, a diffraction plane with an odd number for $H + K + L$ does not appear, therefore, the ratio of the sequence should be turned to:

$$\begin{aligned} \sin^2\theta_1 : \sin^2\theta_2 : \dots &= 1:2:3:4:5:6:7:8:\dots \\ &= 2:4:6:8:10:12:14:\dots \end{aligned} \quad \dots(3.3)$$

The corresponding diffraction plane indexes are (110)、(200)、(211)、(220)、(310)、(222)、(321) respectively in bcc.

From the spectrum, we can see except for α -Fe (with lattice indexes with (110), (200), (211)), martensite with α' phase are formed in the specimens. Moreover, carbides as $M_{23}C_6$ (diffraction pattern of approximately 1.06 nm) and M_7C_3 are formed.

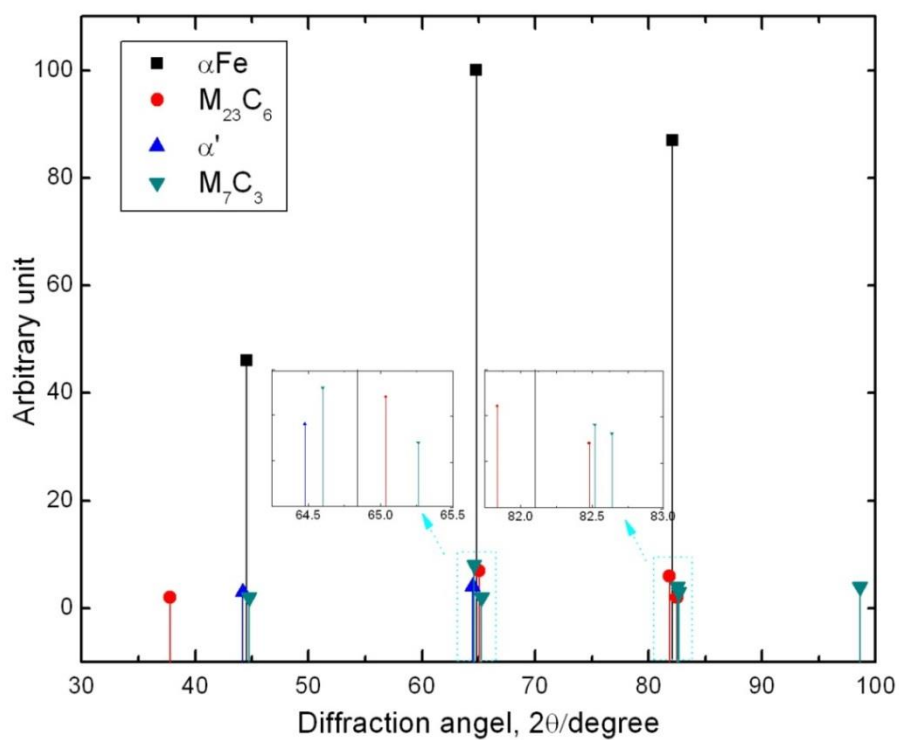


Fig.3-1 X-ray diffraction spectrum of Fe-8Cr-2W-0.1C before electron irradiation.

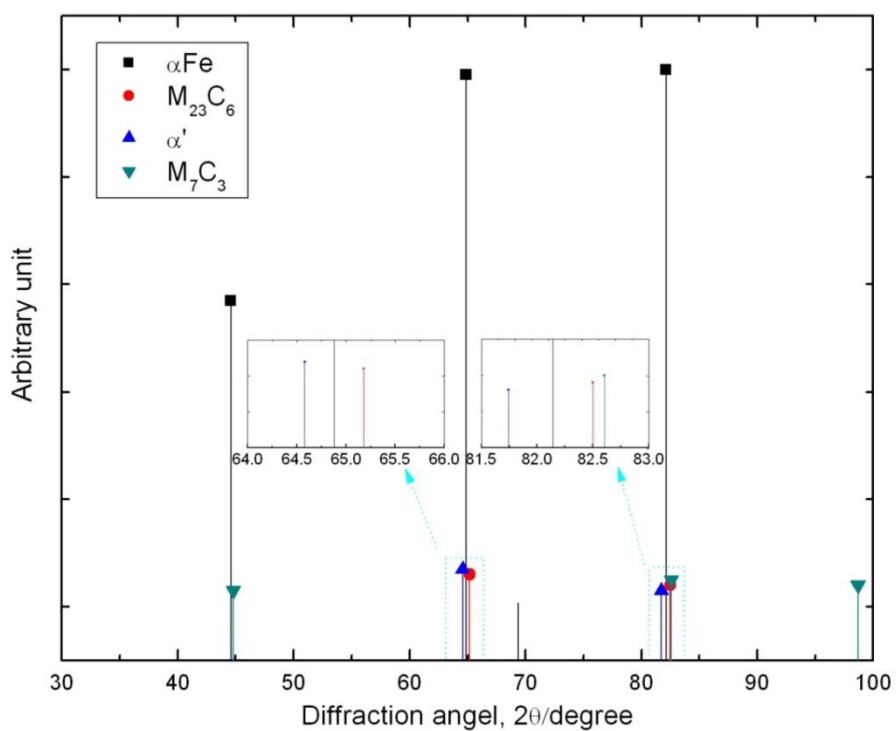


Fig.3-2 X-ray diffraction spectrum of Fe-8Cr-2W-0.2V-0.04Ta-0.1C before electron irradiation.

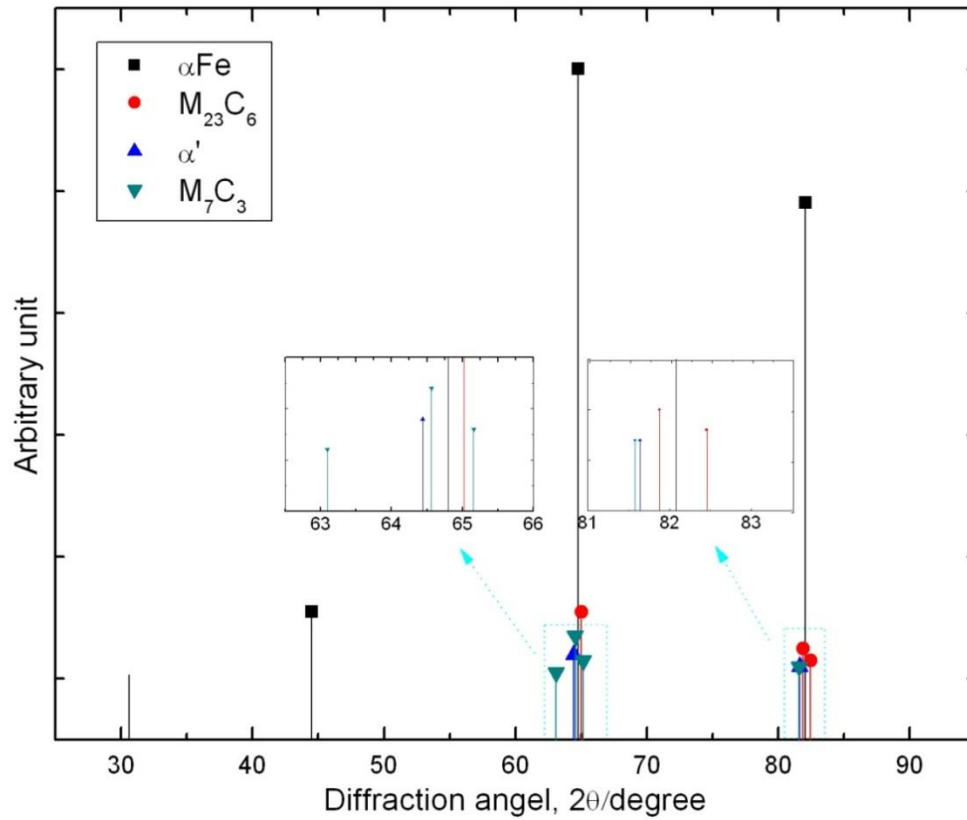


Fig.3-3 X-ray diffraction spectrum of F82H before electron irradiation.

• *TEM observation*

Transmission electron micro-spectroscopy was also conducted to the specimens before irradiation. Fig.3-4 shows TEM micrographs and diffraction patterns of precipitates in Fe-Cr-based steels. From the micrographs we can see big carbides with a size of about 100nm formed. This also corresponds to the size of $M_{23}C_6$.

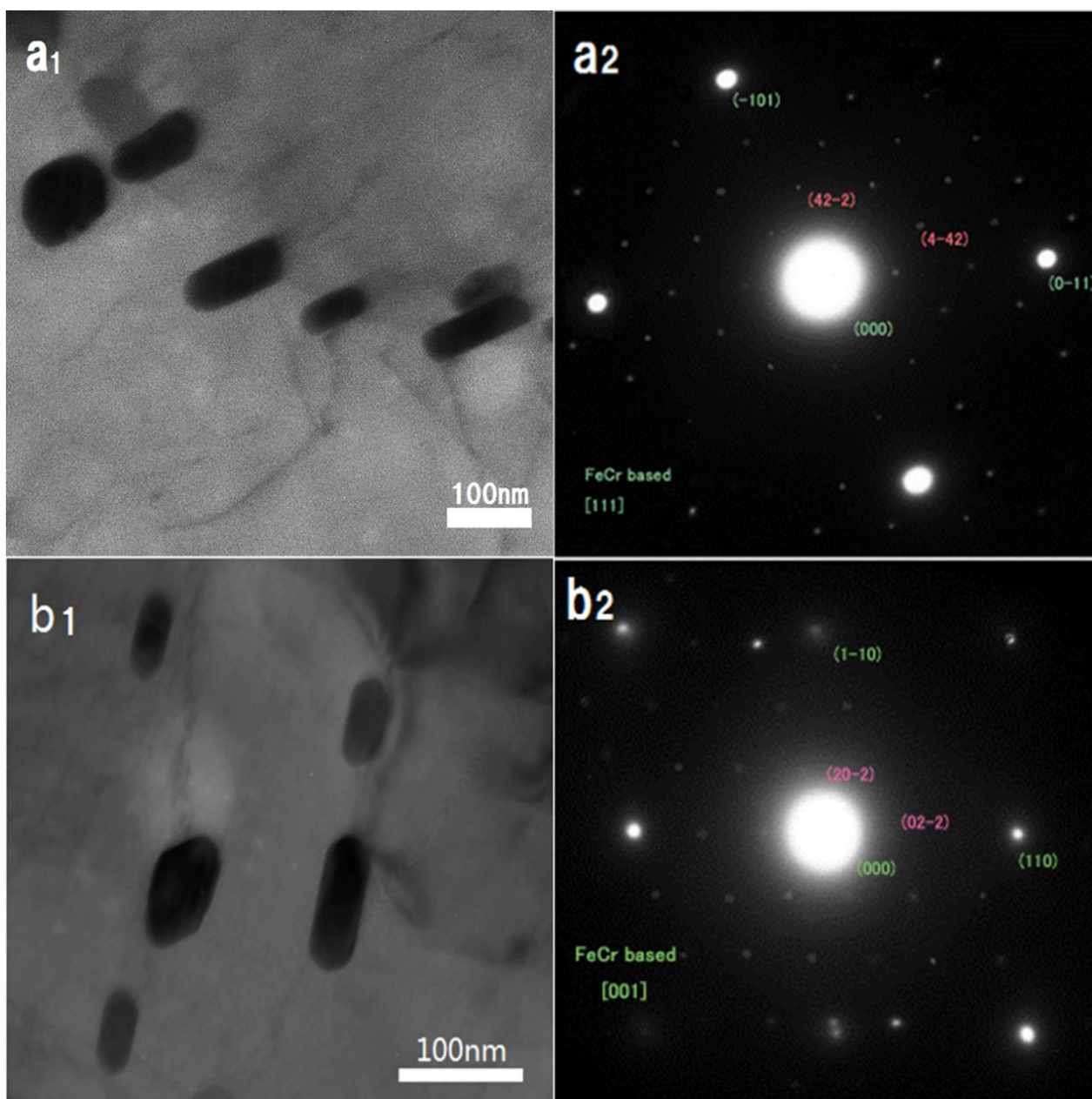


Fig.3-4 TEM micrographs and diffraction patterns of $M_{23}C_6$ in Fe-Cr based steels (a: “Fe-8Cr-2W-0.2V-0.04Ta-0.1C” and b: “F82H”).

Fig.3-5 shows the positron annihilation lifetimes obtained for the model alloys and Fe before electron irradiation. The positron lifetime spectra consisted of one lifetime component of about 107 ps for the Fe-Cr based alloys not containing C (“B”, “C”, and “D”). This experimental result is similar to that of well-annealed Fe [4], indicating that the defect concentrations in these specimens before irradiation are less than the lower limit (10^{-6}) of detection by positron annihilation. For specimens containing C, the long lifetime component τ_2 was about 131–134 ps. This component, with intensity (I_2) of about 82–88%, was dominant. As considered the results of X ray diffraction and Transmission spectroscopy results, the obtained lifetime of about 131–134 ps for alloys containing C before irradiation can be explained by pre-existing precipitates, as positrons are trapped at the precipitate-matrix interface.

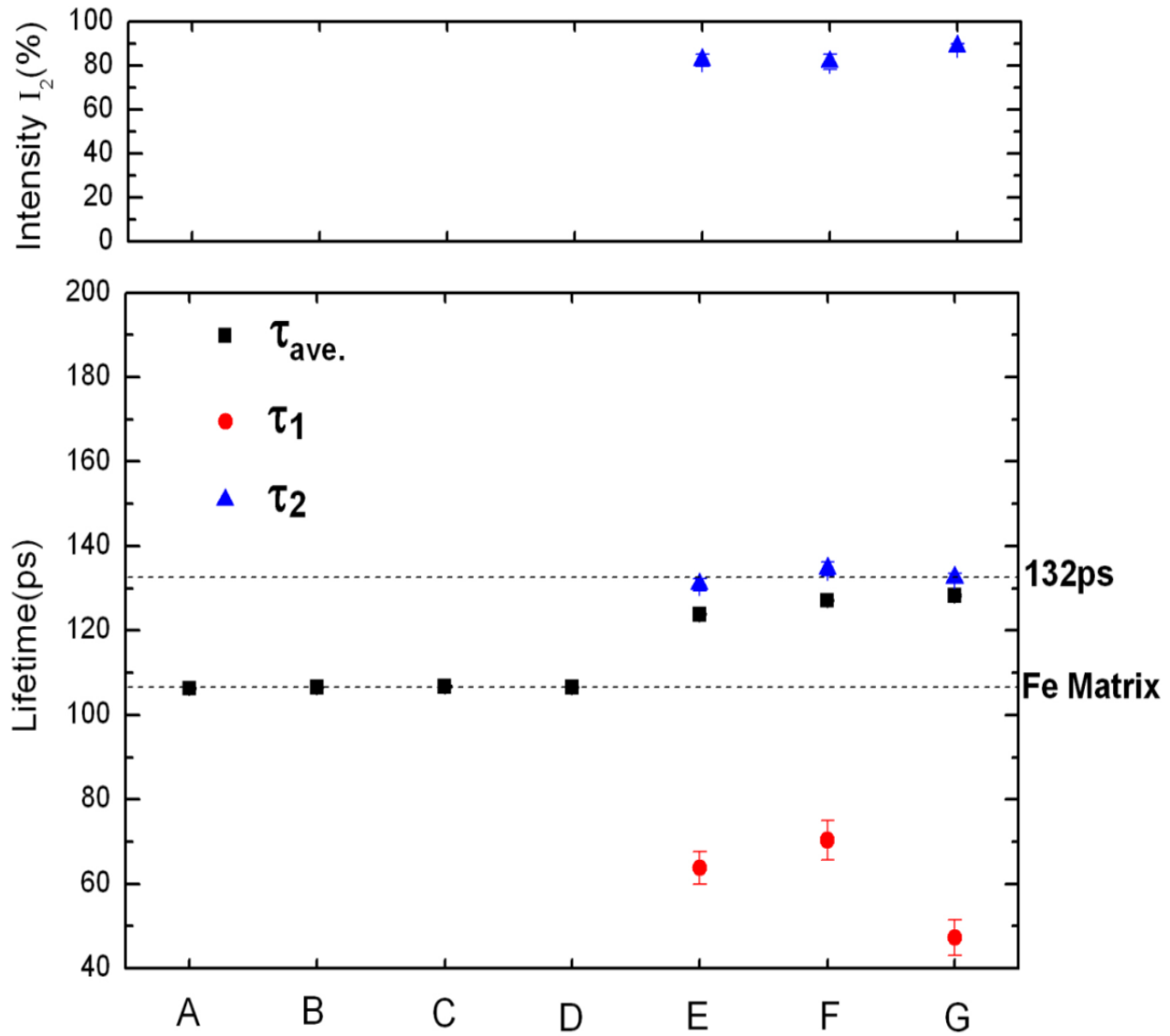


Fig.3-5 Positron lifetimes for specimens before electron irradiation.

3.2.2 Microstructure of specimens after irradiation

• Electron irradiation at 77 K

Fig.3-6 shows the results of positron lifetime measurements at room temperature of the model alloys and Fe irradiated by 30 MeV electrons at 77 K. The calculated positron lifetimes for some vacancy clusters {monovacancy (V_1), divacancy (V_2), quadravacancy (V_4)} in Fe [4] are indicated by horizontal dashed lines. In this spectrum, the long lifetime can be clearly divided into three groups. For Fe after irradiation, a long lifetime component (τ_2) of 256 ps corresponding to V_4 was observed. The lower intensity (I_2) than those of the model alloys indicates that some of the vacancies induced by the electron irradiation recover as the sample returns to room temperature. This is consistent with the fact that vacancies in Fe are mobile below room temperature, but some of the vacancies survive as clusters.

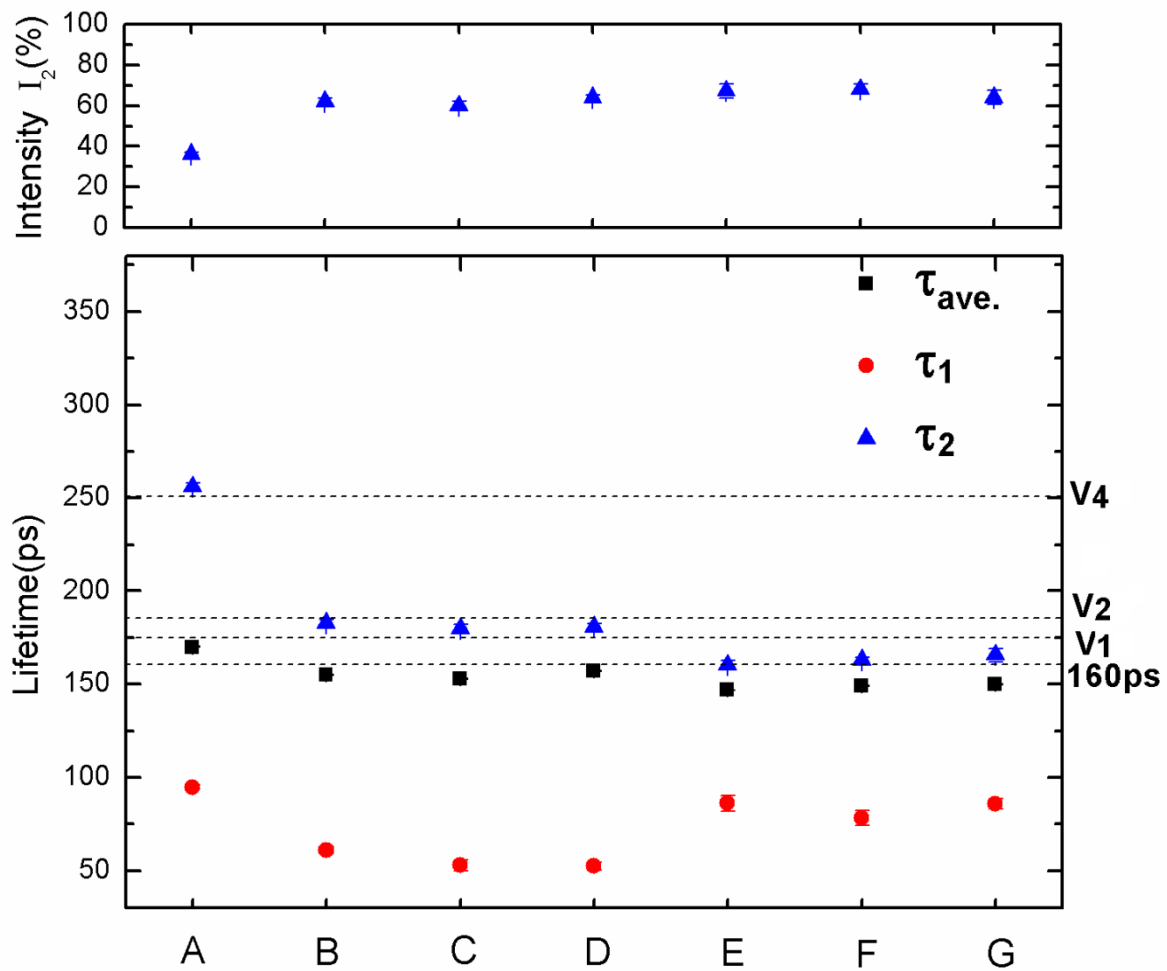


Fig.3-6 Positron lifetimes for specimens after electron irradiation at 77 K to a dose of 1.4×10^{-3} dpa.

For specimens including Cr but not C, a long lifetime τ_2 (~ 183) between that of monovacancies (175ps) and divacancies (187ps) appeared. Other metal element effects were not

as clear, considering their similar long lifetimes and similar intensities. Another interesting result was that for all specimens containing C, a reduced long lifetime of about 160ps which is shorter than that of a monovacancy appeared. Based on these results, the addition of Cr and C strongly affects the evolution of irradiation-induced vacancy clusters. In this case, our results suggest that the effect can be divided into two parts. One is a Cr effect, and the other is an effect of C and/or Cr along with other elements. Note that, the mean lifetime of specimen decreases from “A” to “G”.

• *Electron irradiation at 673 K*

The properties of defects and their interactions with solute atoms at intermediate temperatures of 0.3–0.6 TM (where TM is the melting temperature) are typically of concern for volumetric swelling [5]. Electron irradiation at 673 K was conducted to a dose of 3.5×10^{-2} dpa.

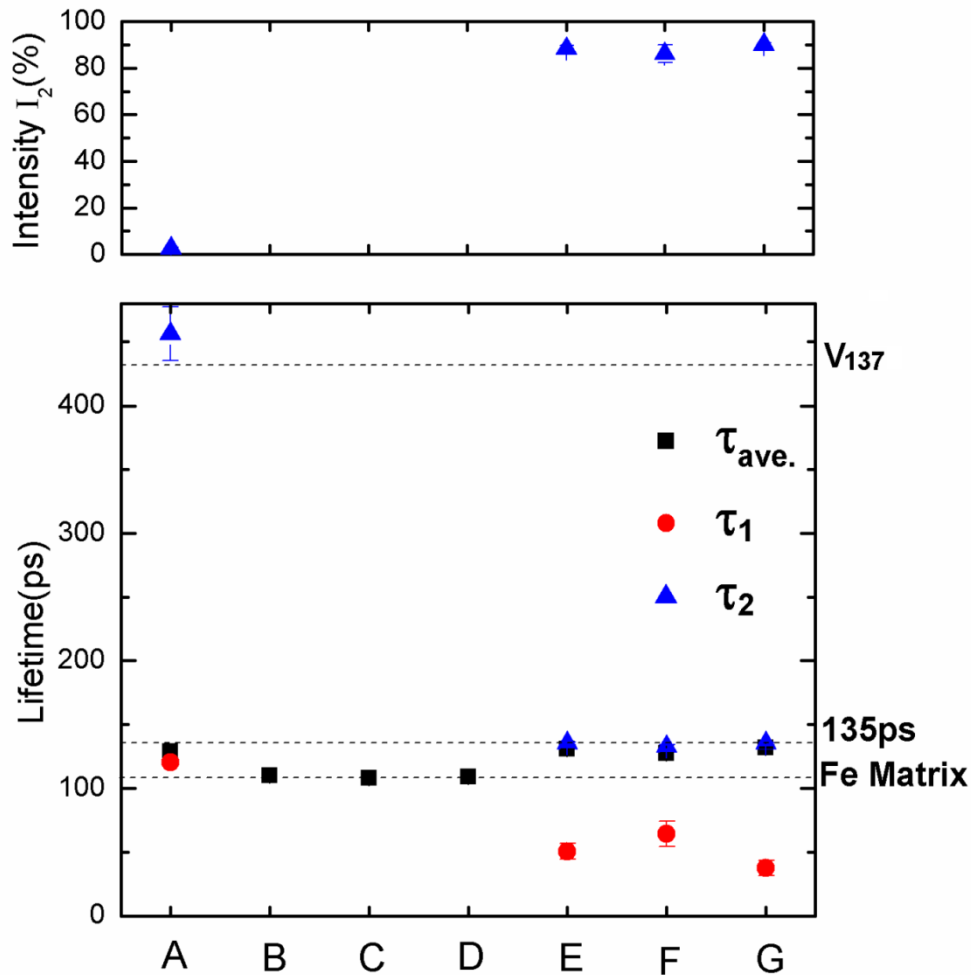


Fig.3-7 Positron lifetimes for specimens after electron irradiation at 673 K to a dose of 3.5×10^{-2} dpa.

Fig.3-7 shows the positron lifetime results of specimens after irradiation. In the case of Fe,

large voids with an average size of 137 vacancy clusters were formed, based on calculations [6]. The relative intensity (I_2) of only a few percent indicated that most of the vacancies induced by electron irradiation recover during the irradiation. For the other alloys, long lifetimes very similar to those of well-annealed alloys were detected, indicating that no vacancy-type clusters were formed. This clearly demonstrates the void swelling resistance of the model Fe-Cr based alloys.

• *Isochronal annealing behavior*

The isochronal annealing behavior of the positron lifetime in Fe and in the model alloys is shown in Fig.3-8 - Fig.3-10. Fig.3-8 shows the isochronal annealing behavior of the mean lifetime in all specimens. Fe recovered at a higher rate (higher slope) than other alloys. This is probably because more vacancy-type defects remain in the Fe specimens after irradiation. The specimens were well recovered until 573 K. For specimens “B”, “C”, and “D”, the recovery process was divided into two stages. The first stage occurred at 300-473 K, as is commonly seen for Fe, and the other occurs at 623-673 K. For specimens containing C (“E”, “F”, and “G”), the recovery was linear until 600 K.

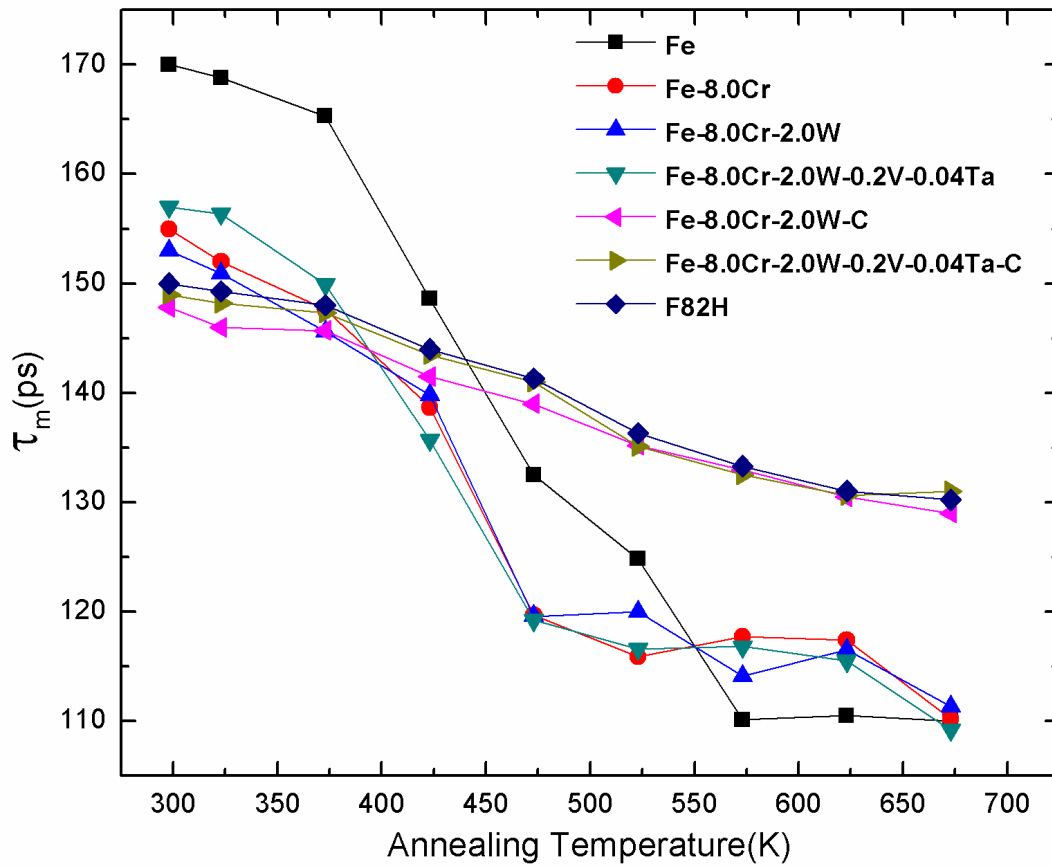


Fig.3-8 Isochronal annealing behavior of the mean positron annihilation lifetime in Fe and the model alloys after electron irradiation at 77 K to a dose of 1.4×10^{-3} dpa

Isochronal annealing behavior of two components positron lifetimes in FeCr alloys not containing carbon is shown in Fig.3-9. For Fe, vacancy clusters gradually grew up to 473 K to a 10 vacancies big size. At the same time, the long lifetime intensity (defect concentration) decreased. Up than 473 K, these vacancy clusters began to dissociate. The specimen was well recovered until 573K. But for other specimens, we did not detect the vacancy clusters. Compared to that of Fe-8Cr, by adding W, the decreasing of long lifetime of about 150ps in Fe-8Cr-2W was postponed to from 473K to 523K. The effects of V and Ta are not so obvious based on the similar recovery behavior in Fe-8Cr-2W and Fe-8Cr-2W-0.2V-0.04Ta.

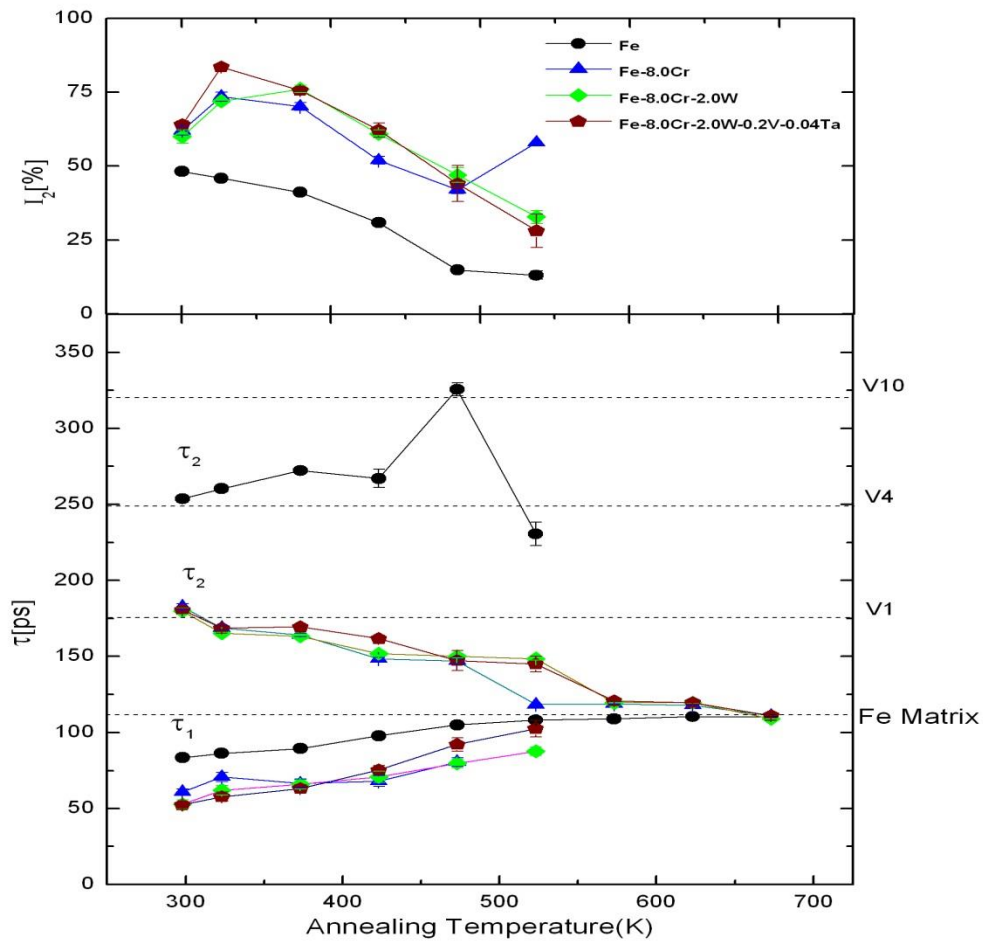


Fig.3-9 Isochronal annealing behavior of the positron mean lifetime in Fe and FeCr based alloys after electron irradiation at 77 K to a dose of 1.4×10^{-3} dpa.

Fig.3-10 shows isochronal annealing behavior of two components positron lifetimes in FeCr alloys including C after electron irradiation at 77 K to a dose of 1.4×10^{-3} dpa. The long lifetime decreased linearly in this group. This indicates that various binding energies exist for the trapping of defects.

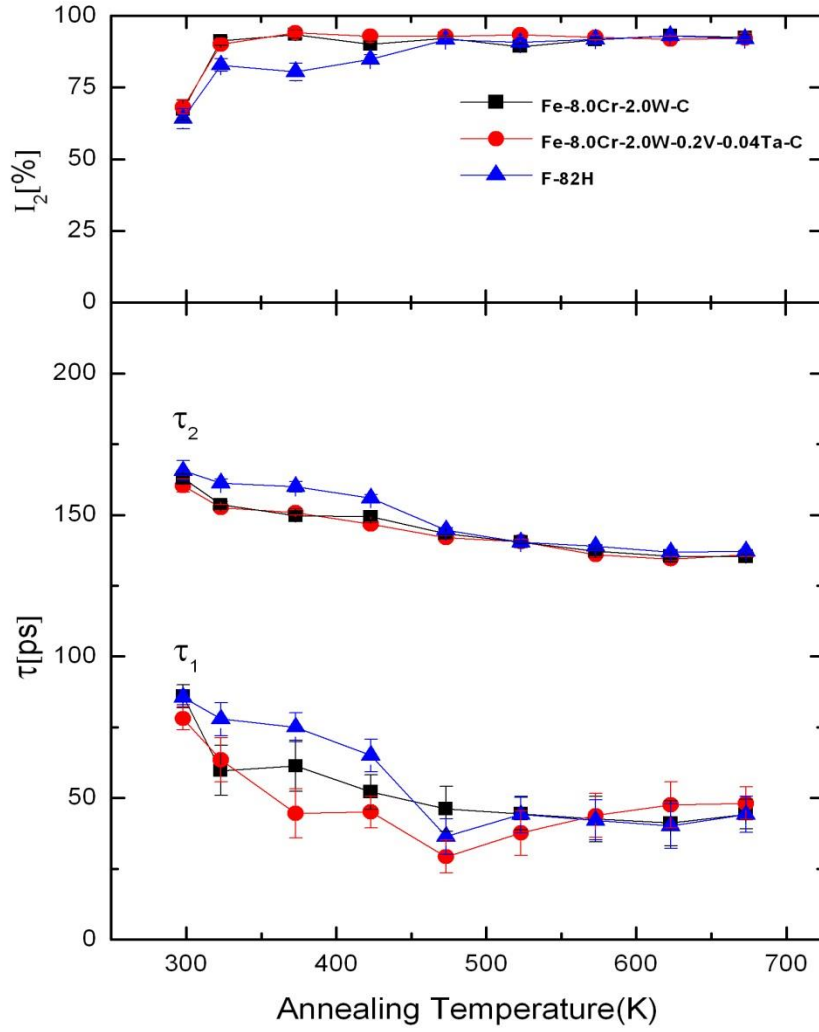


Fig.3-10 Isochronal annealing behavior of two components positron lifetimes in FeCr alloys including C after electron irradiation at 77 K to a dose of 1.4×10^{-3} dpa.

3.2.3 Effects of alloying elements

The results described in 3.2.2 show that C and substitutional atoms have a strong effect on the accumulation and annealing of vacancy-type defects in the present alloys. In this section, the specific features of the interaction between substitutional or interstitial atoms (mainly in the form of carbides) and vacancies in Fe–Cr based alloys are discussed and compared to those in Fe. For minor elements, we will discuss the influence of dislocations in C-containing alloys on defect evolution along with the effects of carbides. Several studies have been conducted on the effects of Cr and temperature on defect accumulation [7,8]. Yoshida *et al.* [7] claimed that in the presence of Cr, dislocation loops nucleate and grow faster at low temperatures. With

increasing temperature, their density decreases while their size increases. Cr also has a strong effect on defect stability. It is known that the addition of Cr to Fe suppresses irradiation-induced swelling, typically by an order of magnitude [9]. This void swelling resistance can be clearly observed in the positron lifetime measurements of 673 K irradiated specimens (Fig.3-7). For better understanding of the reduced swelling rate in Fe–Cr alloys, a mechanism for enhanced recombination of vacancies and interstitials due to Cr in Fe was proposed [10]. In this model, the efficient removal of interstitials from the bulk via fast one-dimensional (1-D) motion of interstitial clusters to sinks is identified as the predominant mechanism leading to the accumulation of excess vacancies in the matrix, thereby producing swelling. Both *ab initio* studies and those based on advanced interatomic potentials have shown that Cr interacts strongly with interstitials [11,12,13], especially in the crowdion configuration. As a consequence, Cr acts as a trap for 1-D migrating interstitial clusters.

Next, we will discuss the long lifetime of about 183 ps in Fe–Cr based alloys not containing C (“B”, “C”, and “D”) after 77 K irradiation (Fig.3-6). Monovacancies in a Fe matrix move at 220 K, which is well below room temperature [14]. A recent study [1] and our research [15] both showed that Cr has little effect on the vacancy migration energy. On the other hand, the trapping of monovacancies by Cr is very weak (binding energy < 0.1 eV [16]), which means that monovacancies bound by Cr cannot survive below 300 K. Therefore, the long lifetime of ~183 ps, which is longer than that of a monovacancy (175 ps [4]) and is very close to that of a divacancy (187 ps) should be assigned to divacancies. The dissociation energy of a divacancy is 0.75 eV (a monovacancy migration energy of 0.55 eV plus a divacancy binding energy of 0.2 eV) in Fe [17]. Divacancies dissociate at about 260 K in Fe, while solute Cr makes divacancies more stable below 300 K in specimens “B”, “C”, and “D”. There is a strong possibility that divacancies are bound to Cr. For example, oversized Cr trap divacancies in the {110} plane. The slightly shorter positron lifetime for divacancies of 183 ps, compared to the usual 187 ps, could be due to distortion introduced by the bounding of Cr.

In the isochronal annealing behavior of specimens “B”, “C”, and “D”, the recovery process can be divided into two phases, at 300–473 K and at 623–673 K. Based on previous study, the trapping of monovacancies by Cr is very weak (binding energy < 0.1 eV [14]). Both experimental and Metropolis Monte Carlo analysis suggested that there was no formation of vacancy–Cr complexes in binary Fe–Cr alloys with Cr contents of 5, 9, and 15 wt.% after electron irradiation of 1×10^{18} e/cm² below 323 K [18]. In this case, we believe that Cr-stabilized vacancy defects should decompose below 323 K.

One study showed that the addition of small amounts of Cr (up to 0.1 at. %) to Fe results in a change in the configuration of interstitial atoms (IAs) by the formation of mixed Fe–Cr dumbbells [19]. A further increase in Cr concentration leads to the capture of these mixed

dumbbells by configurations consisting of several Cr (configuration trapping) [19,20]. As a result, interstitial migration and recombination at stage I temperatures are progressively suppressed with increasing Cr concentration. Therefore, Frenkel pairs (FPs) survive in stage I as discrete entities, including close pairs at Cr concentrations of about 10 at. %. Nikolaev traced features of stage III in the resistivity recovery data of electron-irradiated Fe-Cr alloys (4–10 at. %) [1]. He concluded that the onset temperatures of long-range migration for vacancies and interstitials are very close, and are 205–210 K and 220 K, respectively. The low mobility of interstitials leads to the easy formation of interstitial clusters [21].

First stage of the recovery process at 300–473 K should be ascribed to the dissociation of Cr-stabilized divacancies, the trapping of vacancies at dislocations, and the release of vacancies from dislocations. The positron annihilation lifetime of vacancies trapped by dislocations is between 142 and 165 ps [22]. In the second-stage recovery at 623–673 K, Cr can be an obstacle to fast interstitial cluster motion [12], so the recovery at 623–673 K is due to interstitial clusters released from Cr and subsequent annihilation at sinks. This can be clearly seen in Fig.3-9 by two components analysis. Note that the positron annihilation lifetime is about 117 ps, which is consistent with the calculated value [4]. Therefore, this explanation is reasonable, as is the configuration trapping model.

Based on the enhanced recombination mechanism [10], any obstacle to fast interstitial cluster motion will enhance recombination, and will thereby suppress swelling. Furthermore, the similar intensities and lifetimes in specimens from “B” to “D” indicate that W, V, and Ta have little effect on interstitial cluster mobility. On the other hand, these oversized atoms tend to bind with vacancies. Systematic studies have been performed on the interactions between transition metals and vacancies [16,23]. For V, the binding energy with a vacancy is less than 0.1 eV. For W and Ta, which have relatively large atomic sizes, the binding energy is 0.14 and 0.16 eV respectively. It has been suggested [24] that the trapping of weakly bound vacancies by solutes would lead to enhanced recombination of irradiation-induced defects. In our case, the effects of these elements were not so obvious. There may be two reasons for this. First, these additives have a lower content than Cr. Second and potentially more likely explanation is that the irradiation dose is insufficient to make this effect obvious.

3.2.4 Effects of C

For all specimens, the mean lifetime at 300 K (Fig.3-6) after low-temperature irradiation has a tendency to decrease from specimens “A” to “G”. For alloys not containing C, this can be explained by the configuration trapping model [10]. The addition of C can decrease the vacancy mobility, leading to a reduced recovery after electron irradiation. In this case, a longer mean lifetime should be obtained. The observed shorter mean lifetimes indicate that more recombination sites exist in specimens containing C during irradiation process. The lifetime of

160 ps was not resolved into two or more components. This indicates that the 160 ps should be treated as a whole component. There are three possible origins of the reduction in positron lifetime; interstitial C, dislocations and metal carbides. From empirically established equations [25], the M_s (martensite start temperature) of model steels (“E”, “F”, and “G”) ranged from 573 K to 598 K. At these temperatures, the concentration of interstitial C is rather low. Further consideration of the depletion of C by $M_{23}C_6$ would suggest that C interstitials are present in only limited concentrations in these steels. Even though vacancies and C can form complexes in Fe that are stable up to 500 K [14], the effect of C interstitials can be excluded in this case.

Considering dislocations, Asoka-Kumar *et al.* suggested that the lattice distortion induced by a dislocation can trap vacancies, leading to lifetimes between 142 and 165 ps [22]. In this case, a sharp recovery peak should appear. The observed linearly recovered stage indicates that this dislocation effect can be excluded.

For metal carbides, as mentioned above, $M_{23}C_6$ is the major form. The $M_{23}C_6$ structure Fig.3-11 (cF116) is characterized by 4 symmetrically distinct metal sites with different coordination numbers, and 8-fold coordinated C sites of square antiprism type. Besides the complex structure, voids were often observed at carbides. $M_{23}C_6$ is considered to be a trapping site for vacancies and/or a nucleation site for vacancy clusters. Based on the isochronal annealing results, this reduced long lifetime of 160 ps was assigned to $M_{23}C_6$ type space/vacancy complexes.

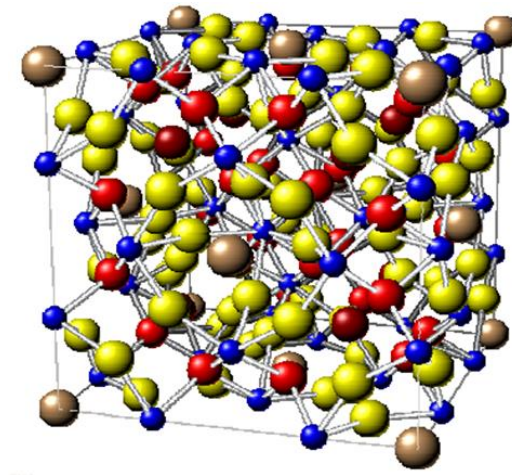


Fig.3-11 Crystal structure of $M_{23}C_6$.

When comparing the isochronal annealing behavior of specimens “E”, “F”, and “G” to the annealing curves of the specimens “B”, “C”, and “D”, the interval 300–473 K can be interpreted in a similar manner. However, the recovery stage at 473–623 K is difficult to interpret. This should be interpreted by vacancy dissociation from the various sites of $M_{23}C_6$ having different binding energies with vacancies due to the complex atomic environments. The existence of large misfit boundaries induced by $M_{23}C_6$ makes it difficult to detect a single stage. The

annihilation of interstitial clusters at 623–673 K is also included, but is not easy to detect, because of the high density of precipitate boundaries. Studies [26] on positron affinity for precipitates in reactor pressure vessel steels show that carbide and nitride precipitates are easy to trap positrons only if they contain metal vacancies, which indicates that the identification of chemical elements of precipitates themselves is rather difficult.

3.3 Conclusion

A series of designed F82H model alloys was examined using positron annihilation spectroscopy after electron irradiation at 77 K or 673 K to a dose of 1.4×10^{-3} and 3.5×10^{-2} dpa, respectively. Additive solute atoms and their synergistic effects on vacancy cluster evolution during an incubation period were systematically analyzed for the first time. The results clearly demonstrated void swelling resistance in Fe-Cr based alloys. Stabilized divacancies were detected at room temperature in Fe-Cr based alloys without C. The trapping of vacancies at interstitial-type dislocation loops is proposed as the mechanism responsible for the observed void swelling resistance in Fe-Cr based alloys at higher temperatures. During the incubation period, elements such as W, V, and Ta had little effect on the evolution of point defect clusters in Fe-Cr based alloys without C. During the recovery stage of Fe-Cr based alloys containing C, the release of vacancies from the complicated $M_{23}C_6$ /matrix interface were detected, indicating that metal carbides have a strong effect on void swelling resistance.

Reference (Chapter 3)

- [1] A.L. Nikolaev, *Philos. Mag.* 87 (2007) 4847.
- [2] J.C. Brachet, L. Gavard, C. Boussidan, C. Lepoittevin, S. Denis, C. Servant, *J. Nucl. Mater.* 258-263 (1998) 1307.
- [3] A. Zeman, L. Debarberis, J. Kočík, V. Slugeň, E. Keilová, *J. Nucl. Mater.* 362 (2007) 259.
- [4] E. Kuramoto, T. Tsutsumi, K. Ueno, M. Ohmura, Y. Kamimura, *Comput. Mater. Sci.* 14 (1999) 28.
- [5] Steven J. Zinkle, Nasr M. Ghoniem, *J. Nucl. Mater.* 417 (2011) 2.
- [6] H. Ohkubo, Z. Tang, Y. Nagai, M. Hasegawa, T. Tawara and M. Kiritani: *Mater. Sci. Eng. A* 350 (2003) 95.
- [7] N. Yoshida, A. Yamaguchi, T. Muroga, Y. Miyamoto, K. Kitajima, *J. Nucl. Mater.* 155–157 (1988) 1232.
- [8] K. Shiba, M. Enoeda, S. Jitsukawa, *J. Nucl. Mater.* 329–333 (2004) 243.
- [9] F.A. Garner, Irradiation Performance of Cladding and Structural Steels in Liquid Metal Reactors, in: *Nuclear Materials and Technology*, Chap. 6, Vol. 10A (1994) 419.
- [10] S.I. Golubov, B.N. Singh, H. Trinkaus, *J. Nucl. Mater.* 276 (2002) 76.
- [11] D. Terentyev, L. Malerba, A.V. Barashev, *Philos Mag Lett.* 85 (2005) 587.
- [12] D. Terentyev, P. Olsson, L. Malerba, A.V. Barashev, *J. Nucl. Mater.* 362 (2007) 167.
- [13] D. Terentyev, L. Malerba, A.V. Barashev, *Philos Mag* 88 (2008) 21.
- [14] A. Vehanen, P. Hautojarvi, J. Johansson, J. Yli-Kauppila, P. Moser, *Phys. Rev. B* 25 (1982) 762.
- [15] K. Sato, Q. Xu, D. Hamaguchi, S.S. Huang, T. Yoshiie et al. *ICPA16.* (2012).
- [16] P. Olsson, T.P. C. Klaver, C. Domain, *Phys. Rev. B* 81 (2010) 054102.
- [17] H.J. Wollenberger: Point defects, in: R.W. Cahn and P. Haasen (Eds.), *Physical Metallurgy*, North-Holland, Amsterdam (1996) pp. 1621.
- [18] J. Kwon, T. Toyama, Y.M. Kim, W. Kim, J.H. Hong *J. Nucl. Mater.* 386–388 (2009) 165.
- [19] F. Maury, P. Lucasson, A. Lucasson, et al., *J. Phys. F: Met. Phys.* 17 (1987) 1143.
- [20] A.L. Nikolaev, *J. Phys.: Condens. Matter* 11 (1999) 8633.
- [21] N. Yoshida and M. Kiritani, *J. Phys. Soc. JPN.* 35 (1973) 1418.
- [22] P. Asoka-Kumar, J.H. Hartley, R.H. Howell, P.A. Sterne, D. Akers, V. Shah, et al. *Acta Mater.* 50 (2002) 1761.
- [23] T. Ohnuma, N. Soneda, M. Iwasawa, *Acta Mater.* 57 (2009) 5947.
- [24] P.R. okamoto, N.Q. Lam, H. Wiedersich, R.A. Johnson, *J. Nucl. Mater.* 69 & 70 (1978) 821.
- [25] F.B. Pickering, *Int. Met. Reviews.* 211 (1976) 227.
- [26] G. Brauer, M.J. Puska, M. Sob, T. Korhonen. *Nucl. Eng. and Des.* 158 (1995) 149.

Chapter 4 Defect evolution by cascade damage in F82H steel

and its model alloy

4.1 Role of dislocations the void swelling resistance in ferritic materials

In ferritic materials there are features specific to the alloy system which is likely to be of special significance in controlling their void swelling response. In particular, in the bcc α -Fe lattice, the interstitial solutes C and N, together with certain interstitial/substitutional element combinations, are associated with highly anisotropic strain fields which render them capable of strong elastic interaction with both point defects and dislocations. It is well established that these interactions influence important aspects of the metallurgical behavior of Fe and ferritic steels. For example, the formation of point defect/interstitial element complexes can control their response to irradiation-hardening [1], while the well-known phenomenon of strain-ageing is attributable to the migration of interstitial solutes to dislocations [2].

Since, as described above, the void-swelling phenomenon depends mechanistically both on the action of dislocations as biased point defect sinks and on the migration kinetics of the point defects, the occurrence of point defect/solute interactions and strong dislocation/solute in ferritic materials might be expected to play a key role in determining their void swelling behavior. In Chapter 3, the defects evolution in F82H steels and its model alloys are presented in detail focusing on the point defect/solute interactions. At the same time, neutron irradiation is the real environment in nuclear power plant. The cascade caused by high energy neutron can make a different microstructural evolution in corresponding materials than those by electron irradiation. Furthermore, as discussed above, strong dislocation/solute in ferritic materials might be expected to play a key role in determining their void swelling behavior. To check this mechanism, in this study, irradiation cascade was induced by neutron irradiation. The defects evolution was compared with those by electron irradiation to further check additive solute atoms and their synergistic effects on vacancy cluster evolution in F82H-type ferritic/martensitic steels. For the defect structure evolution at high irradiation dose in these model alloys, Fe ion irradiation was also conducted in this chapter.

4.2 Neutron irradiation

Neutron irradiation at 573K to a dose of 5×10^{-3} dpa and that at 363 K to a dose of 6×10^{-4} dpa and 1.5×10^{-3} dpa were conducted on prepared specimens (see Section 2.1) in Research Reactor

Institute, Kyoto University. The same specimens were also irradiated in BR-2 of SCK•CEN at 363 K to a dose of 0.2 dpa. Each of the specimens irradiated at 363 K to 1.5×10^{-3} dpa was isochronally annealed for 1 h from 298 K to the corresponding temperature. Positron annihilation measurements were conducted after each step.

4.2.1 Neutron irradiation at 363 K

Positron annihilation lifetime (PAL) results from specimens after neutron irradiation at 363 K are shown in Fig.4-1 – Fig.4-3. For Fe, large voids with an average size of 12 vacancy clusters, 15 vacancy clusters and 27 vacancy clusters were formed by the irradiation dose of 6×10^{-4} dpa, 1.5×10^{-3} dpa and 0.2 dpa, respectively. No dislocation loops were detected in Fe irradiated to the dose of 6×10^{-4} dpa and 1.5×10^{-3} dpa, while in Fe irradiated to 0.2 dpa, short lifetime of about 150ps is obtained. Except for the short lifetime in irradiated Fe, the tendency of the lifetime for all the specimens is exactly the same. For Fe-Cr based alloys without C, the solute atoms have little effect on the size of the voids. This indicates that the solute atoms do not have a significant effect on vacancy mobility at this temperature. However, with the addition of solute atoms, the intensity of long lifetime components in the spectrum decreased for Cr and W containing Fe-Cr alloys more than for Fe, which indicated an increased possibility of vacancy annihilation at sinks or recombination with interstitial type defects. Note that unlike the behavior due to electron irradiation, the solute atoms V, Ta and especially W significantly affect the vacancy cluster evolution with an apparently decreased intensity of the long lifetime components of the spectra and a decreased mean lifetime. No significant differences were observed between the C-containing steels and the Fe-Cr-W based alloys.

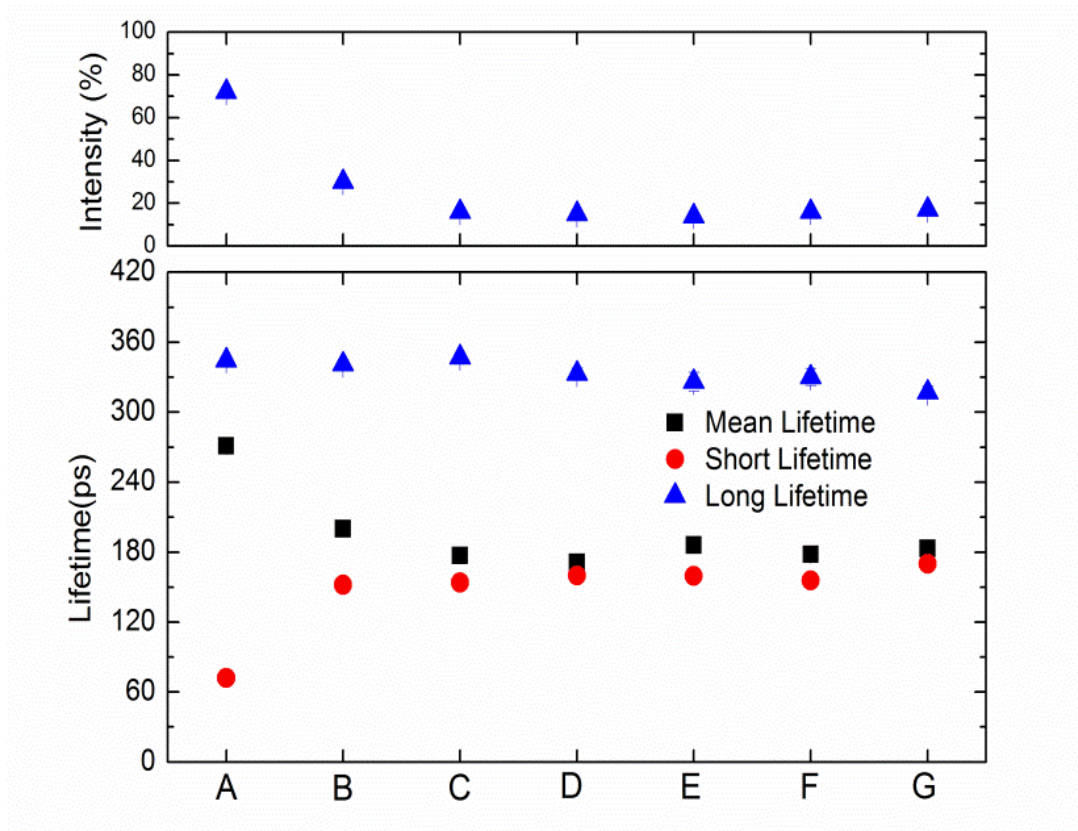


Fig.4-1 PALS of specimens after neutron irradiation in KUR at 363 K to a dose of 6×10^{-4} dpa.

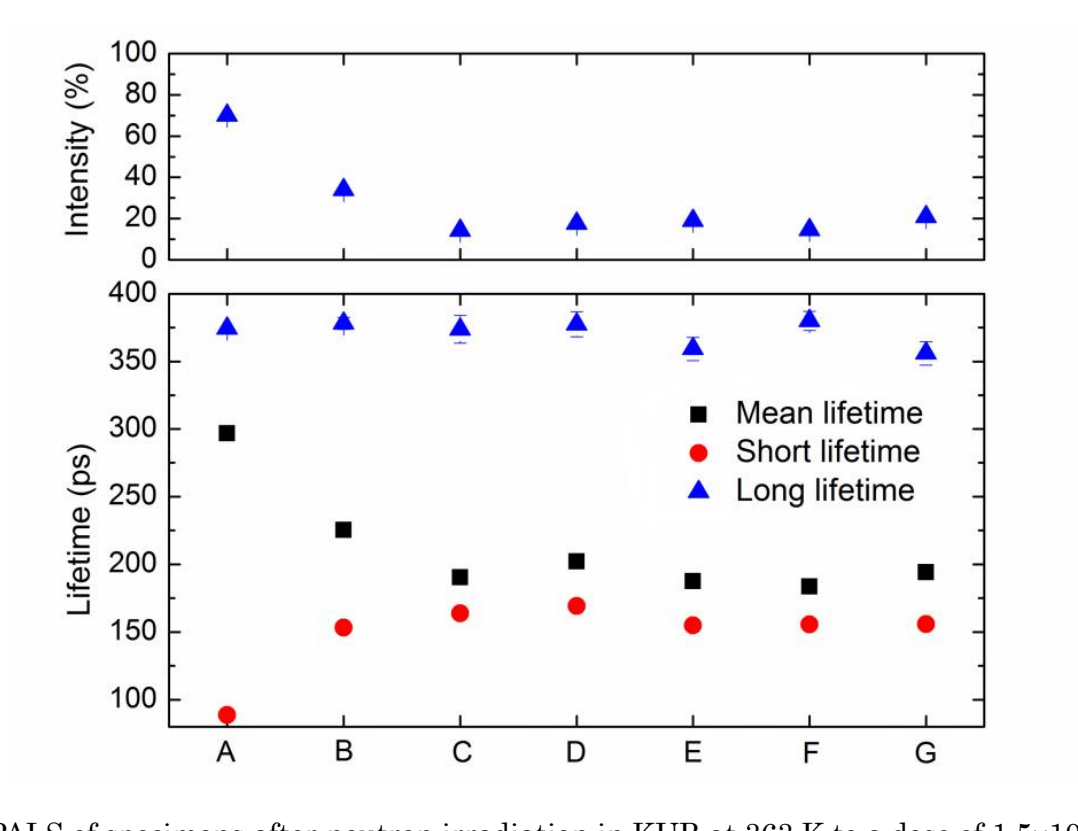


Fig.4-2 PALS of specimens after neutron irradiation in KUR at 363 K to a dose of 1.5×10^{-3} dpa.

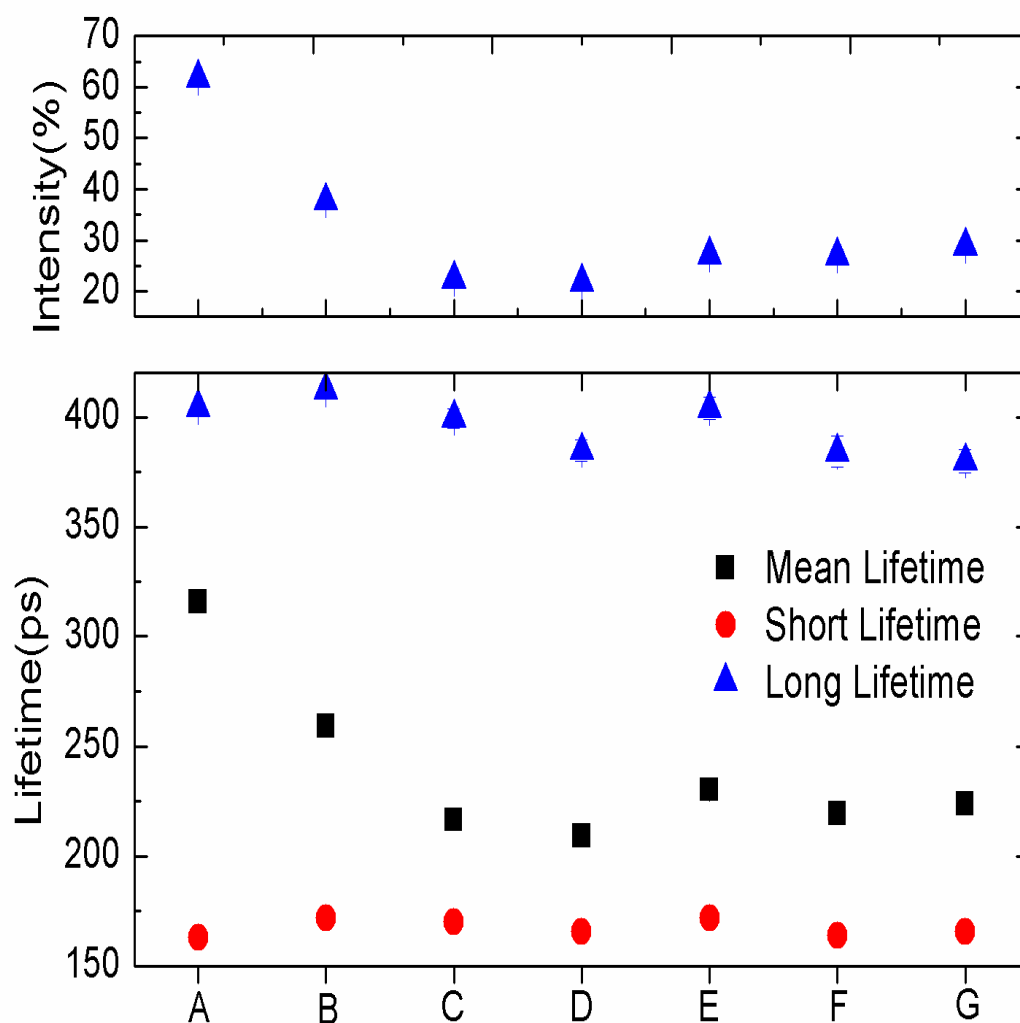


Fig.4-3 PALs of specimens after irradiation in BR2 of SCK•CEN at 363 K to a dose of 0.2 dpa.

4.2.2 Neutron irradiation at 573 K

Fig.4-4 shows the positron lifetime results from specimens after neutron irradiation at 573 K. The long lifetime was clearly divided into three groups, which can also be seen in the two types of electron irradiation. Voids with an average size larger than four vacancy clusters were formed in the Fe. In the Fe-Cr based alloys that lack C, the long lifetimes were approximately 210 ps. Metal element effects, such as the addition of W, V and Ta, can barely be seen in the results. A long lifetime of approximately 140 ps was detected in C-containing steels.

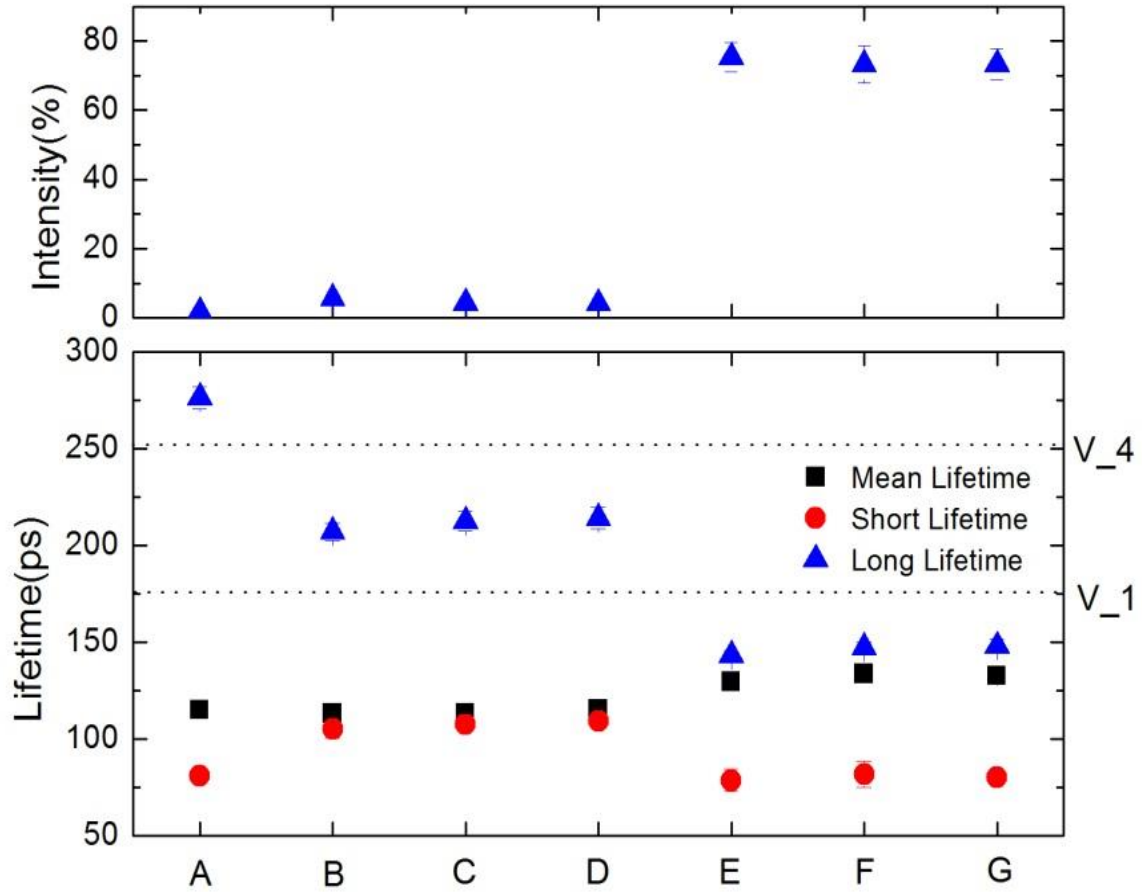


Fig.4-4 PALs of specimens irradiated in KUR at 573 K to a dose of 5×10^{-3} dpa

4.2.3 Defect evolutions in neutron irradiated specimens compared with those in electron irradiated specimens

• *Cr effect*

It is known that the addition of Cr in Fe suppresses irradiation-induced swelling, typically by an order of magnitude [3]. Both in neutron and electron irradiations, similar void swelling resistance behavior in Fe-Cr alloys was obtained. As discussed in Chapter 3 [4], the Cr effect on swelling suppression can be explained by the configuration trapping model [5]. Note that for neutron irradiation performed at 363K, no interstitial-type dislocation loops are detected in Fe because the short lifetime is less than that of the high-purity Fe matrix (110 ps). The interstitial clusters produced by irradiation are removed by fast, one-dimensional (1D) migration [6]. For Fe-Cr, the short lifetime is approximately 152 ps, which corresponds to vacancies at the dislocation sites [7]. This again confirms the validity of the configuration trapping model.

• *W, V and Ta effect*

Regarding solute atom effects, two mechanisms are claimed. One is the solute trapping mechanism, and the other is the dislocation interaction model. In the solute trapping mechanism, solute atoms act as traps, which capture both types of point defects and induce their mutual annihilation. As a consequence, the fraction of point defects available to contribute to the growth of both voids and interstitial dislocation loops decreases [8]. A reduced vacancy super saturation also leads a decrease of void nucleation rate [9]. Thus, in principle, a trapping mechanism can provide a qualitative explanation for the observations of void-swelling suppression induced by minor alloying additions and impurities.

In the dislocation interaction model, the nucleation and growth of voids depends on the continued operation of these dislocations as biased sinks for interstitials. Solutes that are attracted elastically to dislocations will migrate to and form atmospheres around the dislocations by long-range drift interactions. This is essentially the same mechanism that is responsible for strain-aging. In so doing, the solutes in the form of a “condensed” atmosphere close to the dislocation core modify or relax the dislocation strain field [10] and thereby decrease its bias for interstitial capture.

As discussed in section 3, for neutron irradiation at 363K to a dose of 6×10^{-4} dpa, the W, V and Ta solute effects are obvious. Considering the solute trapping mechanism, first, the binding energy between these solutes and vacancies is not high enough (~ 0.15 eV for a mono-vacancy [11]). Second, this mechanism tends to be more effective at low temperatures. However, according to our low-temperature electron irradiation results, the solutes do not show any important effects. In neutron irradiation, cascade damage occurs, which results in the production of interstitial-type dislocation loops. In this case, it is easy to conclude that the effect of these solute atoms has void swelling resistance which can be interpreted by the dislocation interaction model.

On the other hand, for neutron irradiation performed at 573 K, the solute effects do not contribute to the results. The short lifetime of approximately 107 ps in the spectrum indicates that there is no formation of dislocations. Under this neutron irradiation at high temperatures, even though cascade damage occurs, the number of interstitials remaining is insufficient to form interstitial-type dislocation loops that can be detected.

• *Effects of C and/or Cr with other elements*

Different results were obtained from neutron irradiation performed at 363 K and electron irradiation at 363 K and 673 K. For electron irradiation, the effect of metal carbides is very clear, and solute effects can be neglected, whereas for neutron irradiation, the opposite result is

observed. Together with dislocations, solute effects on the void swelling resistance are obvious. In this case, the solute effect may be the dominating factor compared with the $M_{23}C_6$ effect for neutron irradiation. Solute depletion caused by these metal carbides affects the evolution of vacancy clusters. However, we do not see such behavior in specimens “E” and “F”. For specimen “G”, which is composed of F82H, the slightly longer mean lifetime compared to those of specimens “E” and “F” may be caused by other solute atoms.

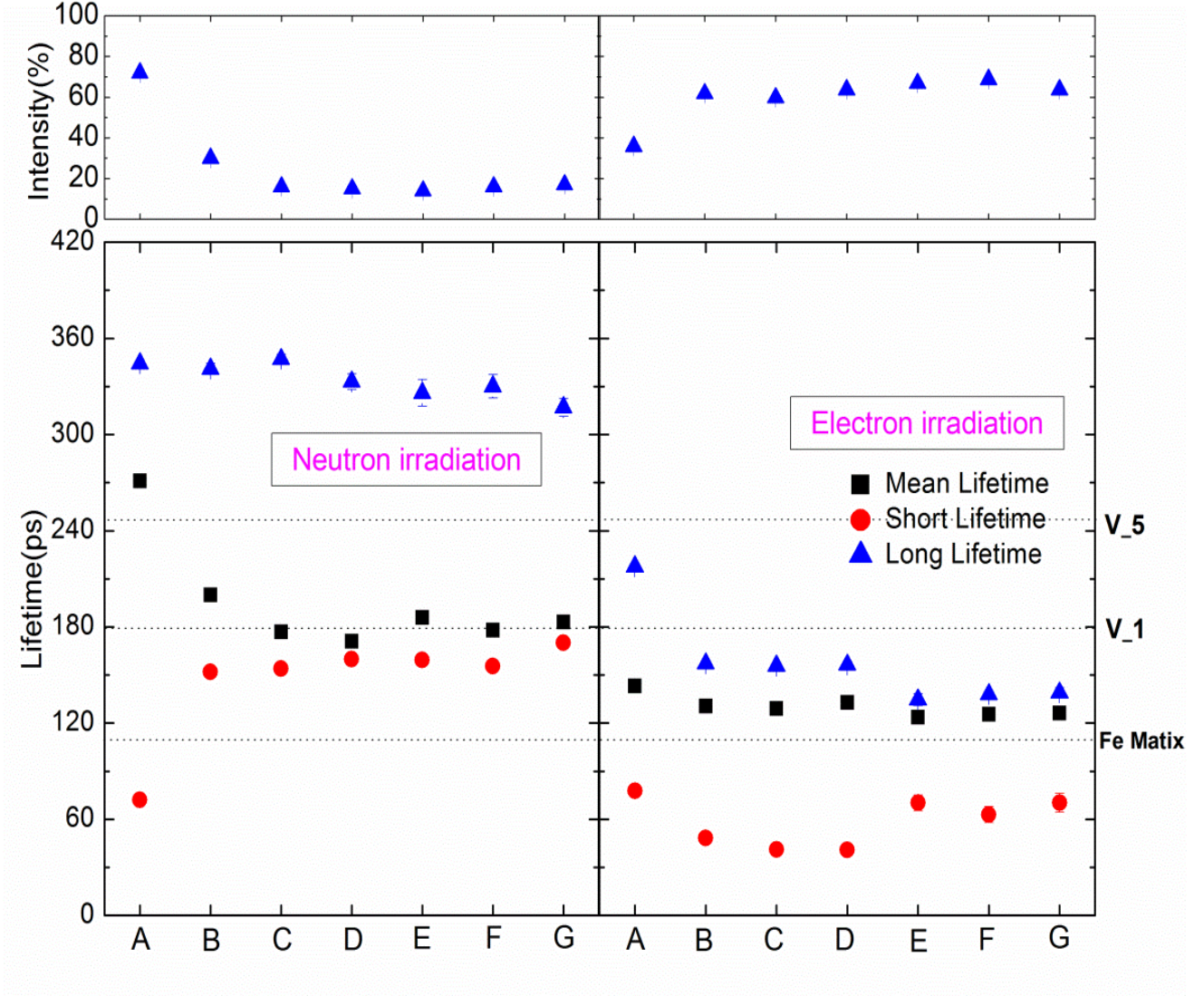


Fig.4-5 Positron annihilation lifetimes for specimens after neutron irradiation at 363 K to a dose of 6×10^{-4} dpa and electron irradiation at 77 K at a dose of 1.4×10^{-3} dpa. Calculated positron lifetimes for V_1, and V_5 (vacancy clusters with average size of corresponding number) in Fe are also shown by horizontal dashed lines.

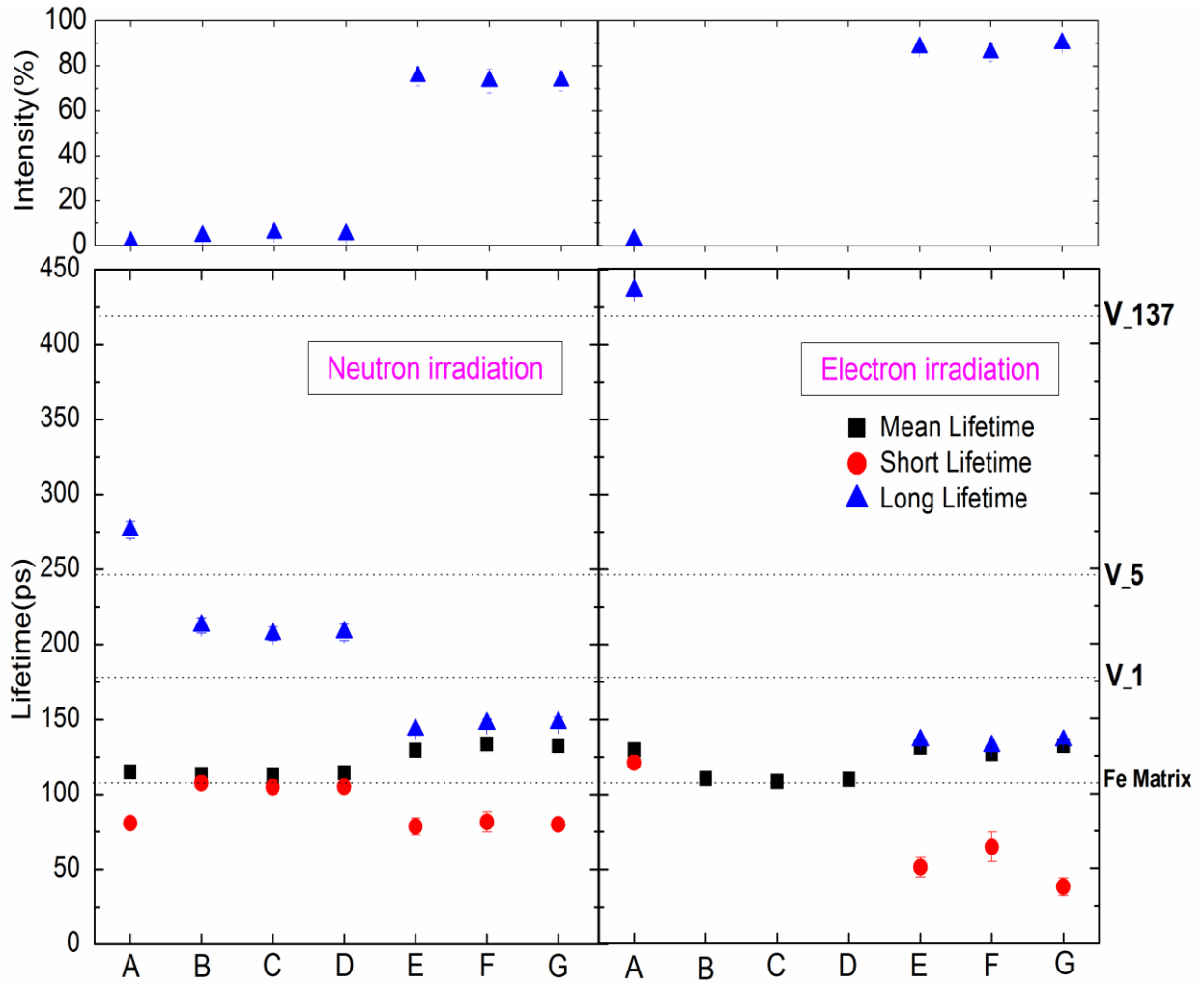


Fig.4-6 Positron annihilation lifetimes for specimens after neutron irradiation at 573 K to a dose of 5×10^{-3} dpa and electron irradiation at 673 K to a dose of 3.5×10^{-2} dpa. Calculated positron lifetimes for V_1, V_5, and V_137 (vacancy clusters with average size of corresponding number) in Fe are also shown by horizontal dashed lines.

4.2.4 Isochronal annealing behavior of defects in specimens irradiated with neutrons at 363 K to 1.5×10^{-3} dpa

• Defects evolution in Fe after isochronal annealing

After neutron irradiation, a long lifetime of about 360ps was obtained by two component analysis (Fig.4-7). This indicates that vacancy clusters with average size of about 15 vacancies were formed [12]. These vacancy clusters were stable until to 423 K. From 423 K, they became unstable. The long lifetime increased while the intensity of long lifetime component decreased. At the same time, the mean lifetime decreased. The decreased mean lifetime indicates the decrease of the total amount of defects in Fe. As the vacancy clusters become unstable, escaped vacancies

move to sinks such as grain boundary and are annihilated; some of them get together to form a larger vacancy clusters. Large vacancy clusters are more stable and can survive to higher temperatures. This processing proceeds until 523 K, and large vacancy clusters with the average size of more than 137 vacancies are formed. From 523 to 623 K, the long lifetime became a constant. The decreasing intensity of long lifetime is explained by decomposition of the large vacancy clusters due to the elevated temperature. Till 623 K, the specimen recovered with a detected single lifetime component of about 107ps.

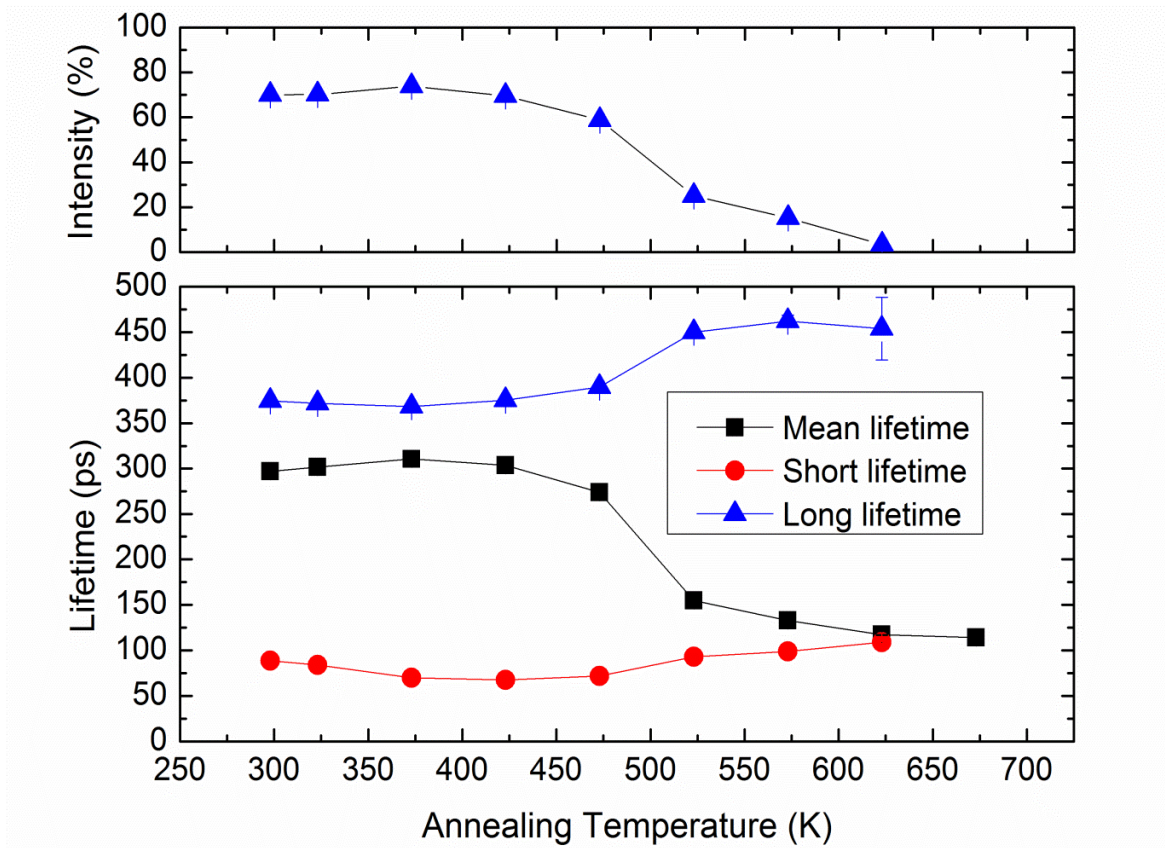


Fig.4-7 Isochronal annealing behavior of the positron lifetime in Fe after neutron irradiation at 363 K to a dose of 1.5×10^{-3} dpa.

• *Cr and W solute atom effects during isochronal annealing*

Fig.4-8 shows isochronal annealing behavior of positron lifetime in Fe, Fe₈Cr and Fe₈Cr₂W. Short lifetimes of about 153ps were detected in Fe₈Cr and Fe₈Cr₂W. From the microstructural point of view, even small percentages (0.1%) of Cr in ultra-pure Fe induces enhanced nucleation of small dislocation loops of interstitial nature in the early stages of irradiation, both neutrons at 673 and 698 K, and electrons in a temperature range of temperatures between 473 and 773 K, with a subsequently higher irradiation-induced hardening [13,14]. This effect becomes even more

pronounced for 2%Cr under neutron irradiation [13] and a significant enhancement of the loop density in electron-irradiated Fe10%Cr at 298 K, as compared to pure Fe, has been also reported [15]. Therefore, these short lifetimes of about 153ps are ascribed to dislocations with vacancies [7]. The defects behavior at elevated temperatures was also different in Fe8Cr and Fe8Cr2W from that in Fe. No increased long lifetimes were detected during the annealing. As mentioned in chapter 3, the trapping of mono vacancies by Cr is very weak; Cr has little direct effect on the evolution of vacancy clusters. Different from the behavior of vacancy clusters in Fe from 423 to 523 K, decreasing long lifetime in this range of Fe8Cr and Fe8Cr2w should due to the release of dislocation loops from Cr, as Cr stabilize dislocation loops. From 423 K, the long lifetimes decreased; note that, the same as that for short lifetime. The decreased short lifetime should be due to releasing of vacancies from dislocation jogs [19]. This provides more annihilation sites or recombination sites for vacancies. This recovery stage proceeds to 523 K. Compared to Fe, this temperature is already too high for a bigger size vacancy cluster formation.

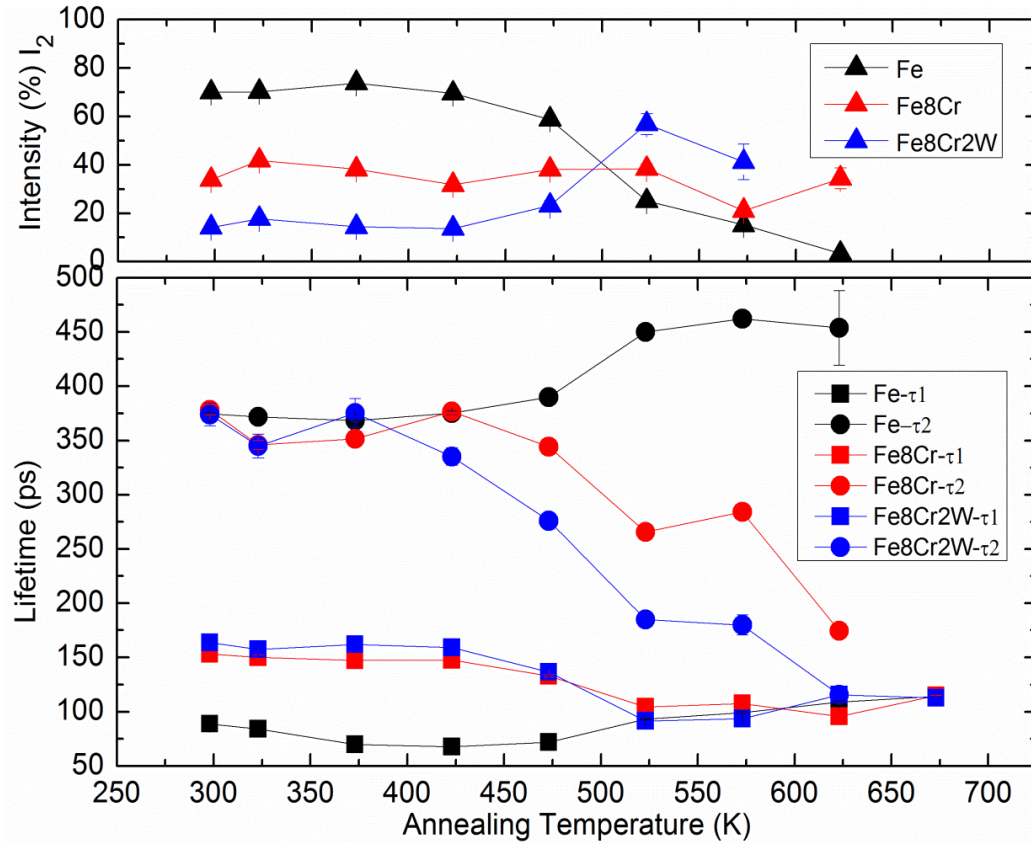


Fig.4-8 Comparison of isochronal annealing behavior in Fe, Fe8Cr and Fe8Cr2W after neutron irradiation at 363 K to a dose of 1.5×10^{-3} dpa (τ_1 : short lifetime, τ_2 : long lifetime).

Fig.4-9 shows isochronal annealing behavior of positron lifetime in Fe, Fe8Cr and F82H. The long lifetime of F82H is not obviously changed until 523 K. From 523 K, the long lifetime decreased quickly. This behavior is much different from those of isochronal annealing behavior of positron lifetime in electron irradiated C containing alloys (see 3.2.2). This is because the different irradiation damage left in the specimens. Though the irradiation dose is similar in these two different irradiations, rather higher defect concentration is detected in neutron irradiated specimens than those of electron irradiated specimens. We can see this clearly in Fig.4-2 and in Fig.3-6. By neutron irradiation, a mean lifetime of about 200ps is detected in F82H, while by electron irradiation, the value is about 150ps. Considering long lifetime, large vacancy clusters with an average size of 15 vacancy clusters were formed in neutron irradiated F82H, while a long lifetime of about 160ps is detected in electron irradiated F82H. In this case, for the isochronal annealing behavior in C containing alloys, the recovery of large misfit boundaries induced by $M_{23}C_6$, compared to the large vacancy clusters formed in these specimens, is negligible small. These large vacancy clusters dissociate at 523K due to their instability at high temperature.

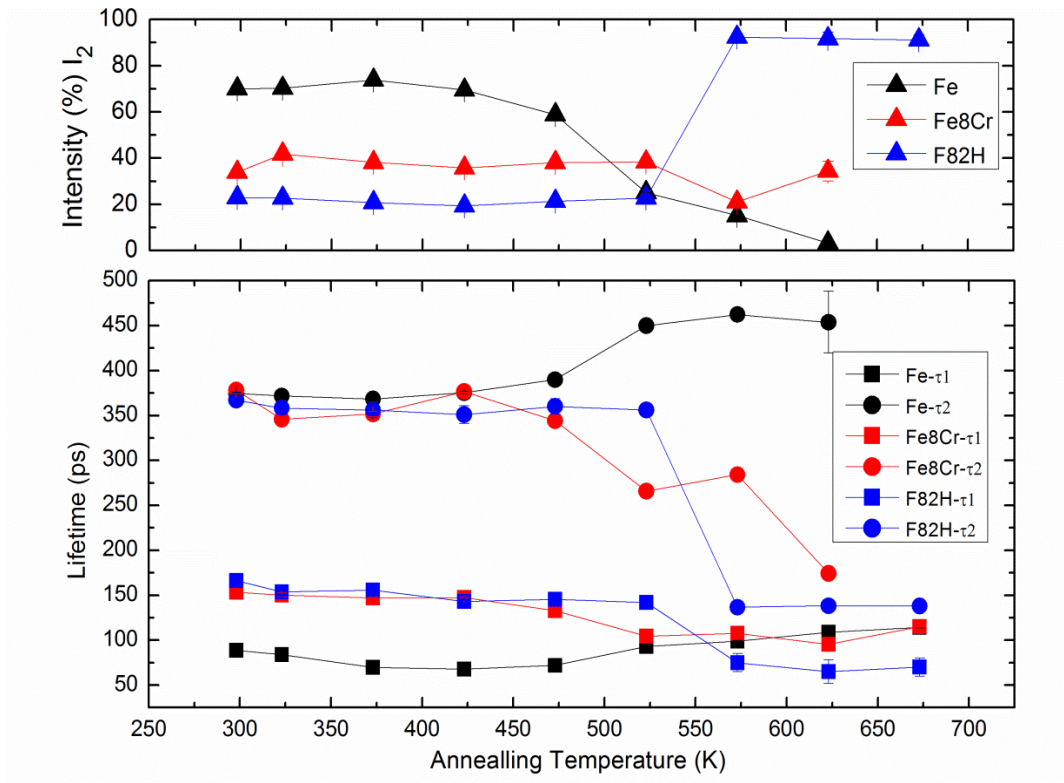


Fig.4-9 Comparison of isochronal annealing behavior in Fe, Fe8Cr and F82H after neutron irradiation at 363 K to a dose of 1.5×10^{-3} dpa (τ_1 : short lifetime, τ_2 : long lifetime).

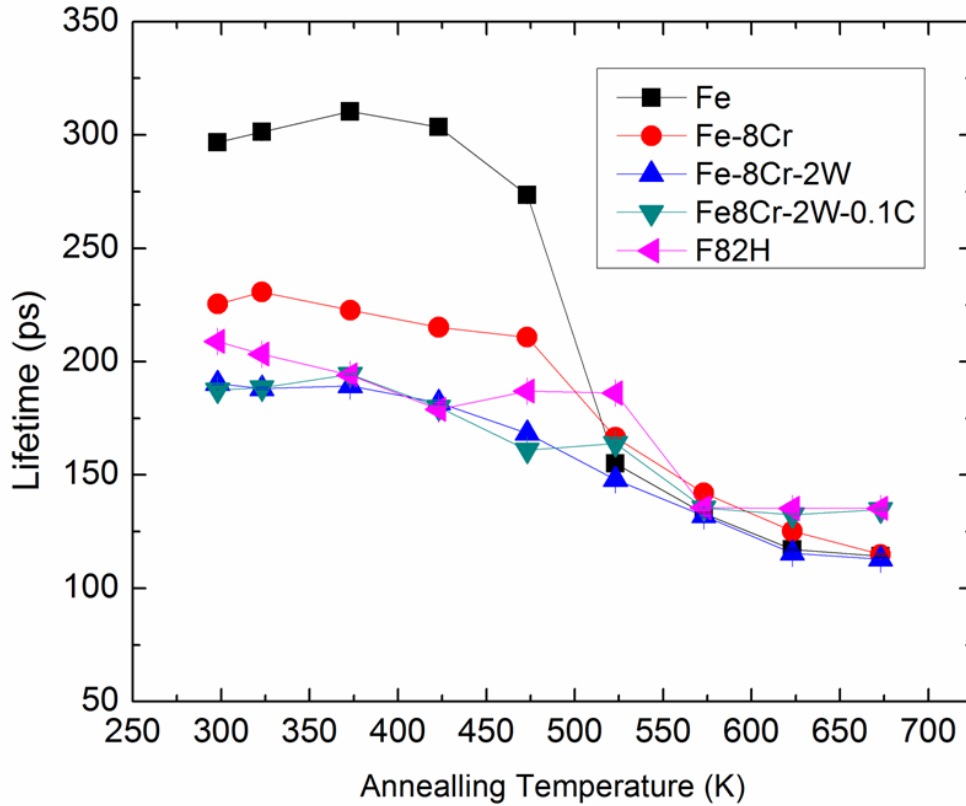


Fig.4-10 Isochronal annealing behavior of positron mean lifetime in specimens irradiated with neutrons at 363 K to 1.5×10^{-3} dpa.

4.3 Fe ion irradiation

6 MeV Fe ion irradiation was conducted using a 2.0 MV tandem Pelletron accelerator at Quantum Science and Engineering Center, Kyoto University at 593 K to a dose of 22 dpa at the peak position.

4.3.1 Positron annihilation lifetime spectroscopy

After 6 MeV Fe ion irradiation at 593 K to a dose of 22 dpa, the increase of positron annihilation lifetimes of all specimens was small compared to those of annealed ones as shown in Fig.4-11. In pure Fe and Fe-Cr based alloys with no C, long lifetimes of about 114 ps were detected. These long lifetimes are exactly the same as that of dislocation loop by calculation [16]. For alloys containing C, both the long life times and the intensities of long lifetimes increased. This result is consistent with neutron irradiated F82H model alloys measured by Mössbauer Spectroscopy as discussed in Chapter 5 [17]. In the study, $M_{23}C_6$ precipitates were clearly detected in

corresponding Mössbauer spectrum. By best fitting the spectrum, the total area of $M_{23}C_6$ was found to increase after neutron irradiation, which indicates that irradiation promotes the growth of $M_{23}C_6$.

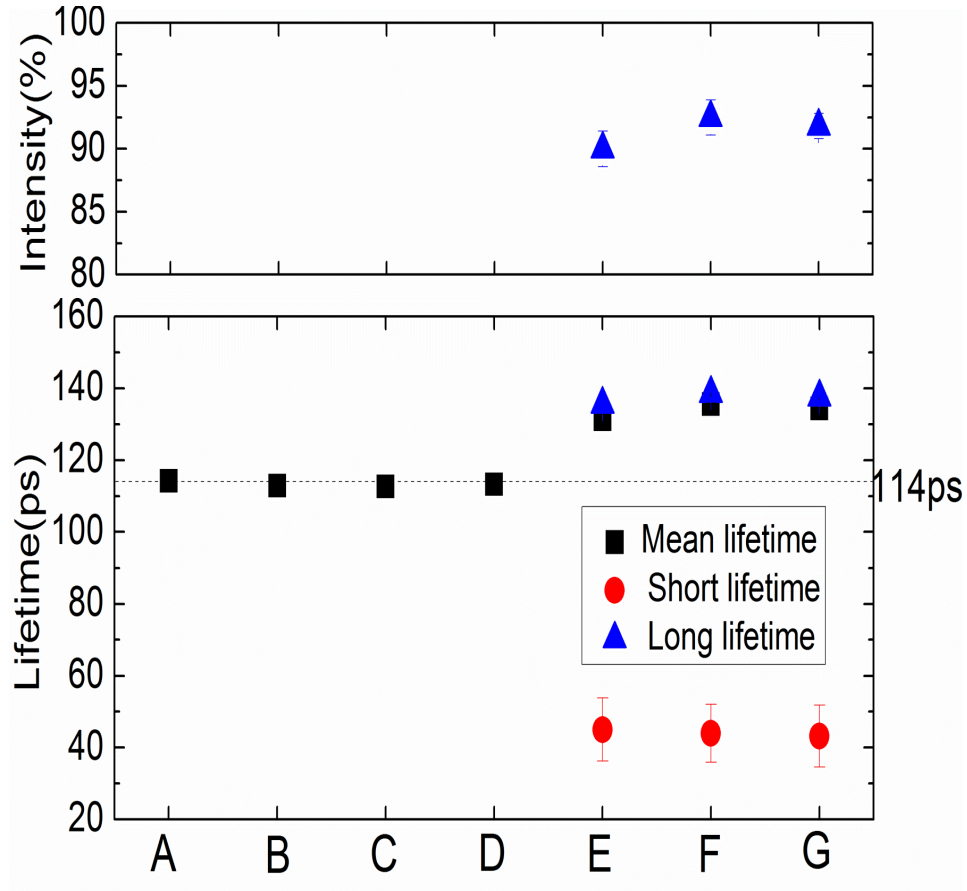


Fig.4-11 Positron annihilation lifetimes and long lifetime intensities after 6MeV Fe ion irradiation at 593 K to 22 dpa.

4.3.2 Cross sectional transmission electron microscopy

Cross sectional transmission electron microscopy (TEM) was performed after the thinning of the Fe ion irradiated specimens by FIB technique described in section 2.2.2. Fig.4-12 shows a photograph of Fe8Cr under TEM observation. Both irradiated area and non-irradiated area of specimens can be investigated by TEM. In all specimens there existed clear band of defects at an area of 1400 nm and 1800 nm from the surface. The band corresponds to the damage peak area of 6 MeV Fe ions, which was a little deeper than damage peak area estimated using SRIM code as shown in Fig.4-15

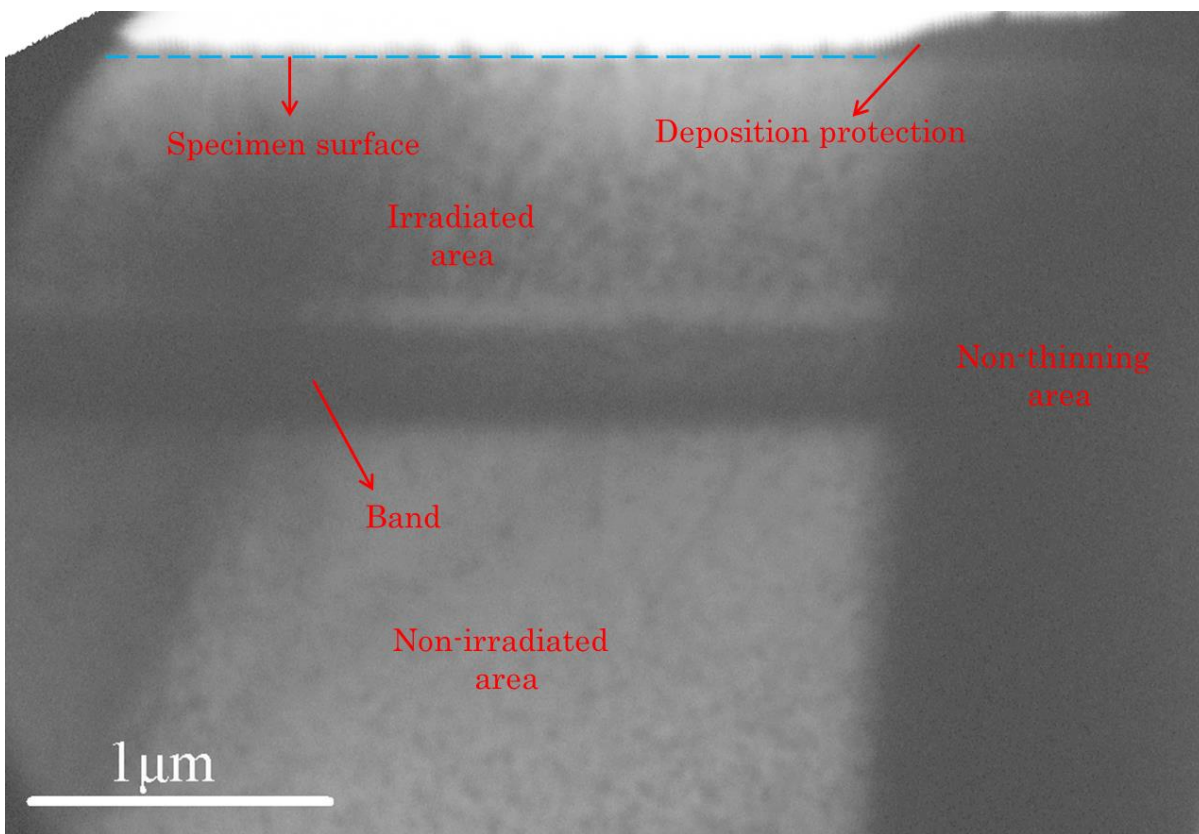


Fig.4-12 Cross sectional transmission electron microscopy of Fe8Cr processed by FIB under TEM observation.

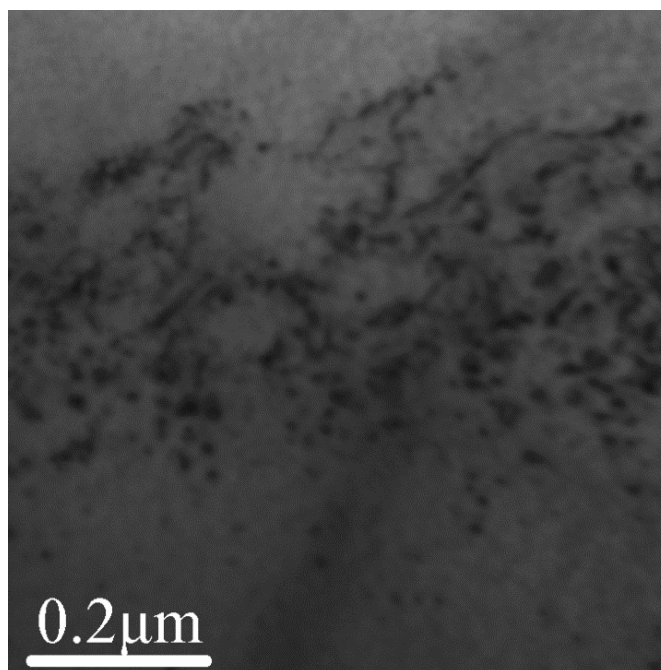


Fig.4-13 Bright-field micrograph for irradiated band area of Fe after 6 MeV Fe ion irradiation at 593K to 22 dpa.



Fig.4-14 Dark-field micrograph for irradiated band area of Fe after 6 MeV Fe ion irradiation at 593 K to 22 dpa.

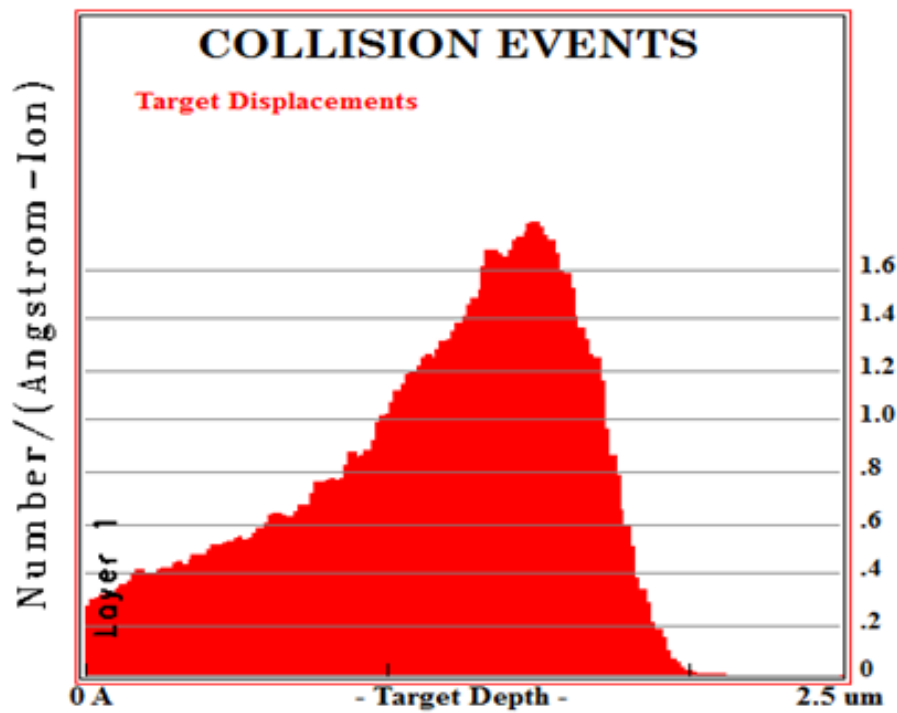


Fig.4-15 Damage distribution of Fe-8Cr by SRIM code.

No voids were observed in these alloys. Fig.4-16 shows the examples of defect structures in Fe (a), Fe-Cr (b) and F82H (c). In Fe, large dislocation loops formed in the damage peak area, while few can be found in other irradiated area between the surface and the layer. In Fe-8Cr and F82H, lots of dislocation loops formed in irradiated area between the surface and the band. Actually, this is an exciting result that the formation of dislocation loops increased by addition of Cr. The dark filed electron micrographs of damage peak area of three specimens are shown in Fig.4-17. In Fe, small loops and large loops which are formed by coalescence of small loops are observed. In Fe-8Cr and F82H, The defect structure at the damage peak part is not clear and high strain fields are observed. It may be caused by a high density of very small loops.

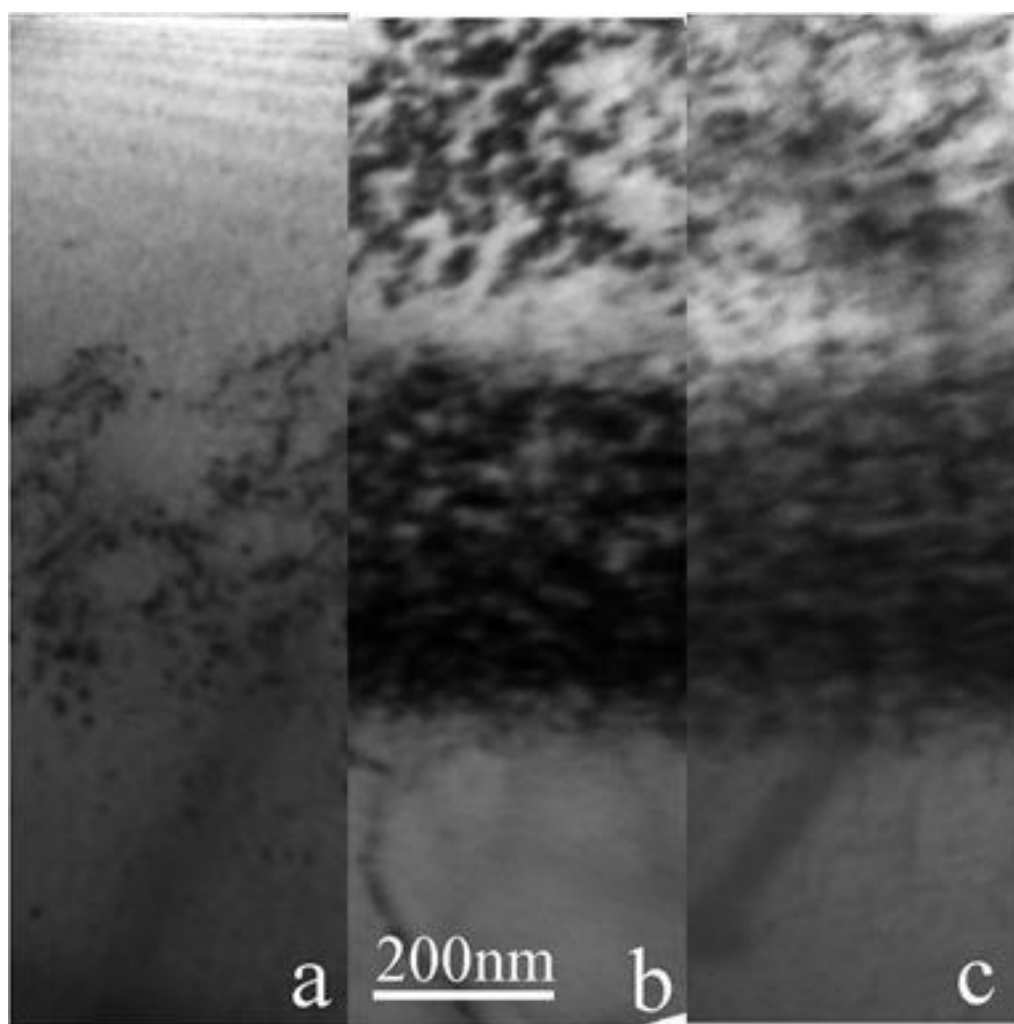


Fig.4-16 Cross sectional transmission electron micrographs after 6 MeV Fe ion irradiation at 593 K to 22 dpa, Fe (a), Fe-8Cr (b), F82H (c).

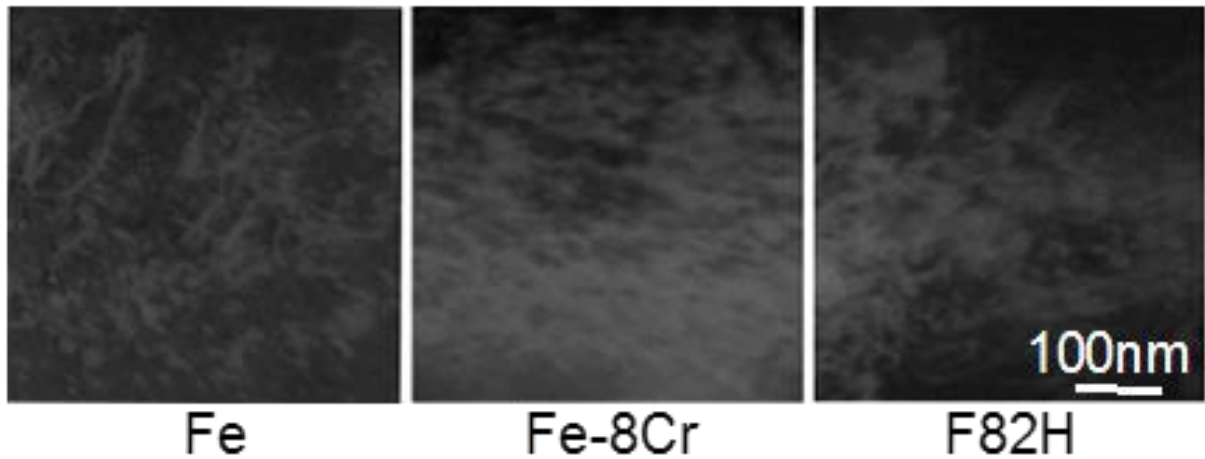


Fig.4-17 Dark filed electron micrographs of 6 MeV Fe ion irradiated Fe, Fe-8Cr and F82H.

The experimental result consistent with a configuration trapping model [5] which is a mechanism proposed on reduced swelling rate in Fe–Cr alloys due to Cr in Fe. In this model, the efficient removal of interstitials from the bulk via fast one-dimensional (1-D) motion of interstitial clusters to sinks is identified as the predominant mechanism leading to the accumulation of excess vacancies in the matrix, thereby producing swelling. Both *ab initio* studies and those based on advanced interatomic potentials have shown that Cr interacts strongly with interstitial clusters [18,19], especially in the crowdion configuration. As a consequence, Cr acts as a trap for 1-D migrating interstitial clusters thereby enhance recombination of vacancies and interstitials.

Terentyev *et al.* [19] performed atomistic simulations to characterize the variation of the free energy of interstitial type dislocation loops in the Fe–15Cr alloy. It was shown that the presence of randomly distributed Cr in Fe leads to the creation of local trapping configurations for small interstitial clusters. The paper also claimed that the mobility of small interstitial clusters is affected more significantly in the low Cr region (up to 10%), where single Cr atoms are generally encountered, while the mobility of large interstitial clusters is affected more strongly in alloys containing more than 10%Cr. In recent experimental work by Klimenkov *et al.* [20], a systematic study of Cr concentration profiles near $1/2 \langle 111 \rangle$ loops has been carried out in Fe-15%Cr after ion implantation. The intensity of Cr along the Burgers vector of the inspected loop was estimated using electron energy loss spectroscopy (EELS) and energy dispersive X-ray analysis (EDX) techniques respectively. The results obtained by both techniques confirmed the increase of Cr concentration near the dislocation loops.

In F82H, the density of dislocation loops is apparently decreased than that in Fe-8Cr. Solute depletion caused by metal carbides can explain the difference. In this way, the solute depletion by metal carbides can be an important way to affect defects evolution.

The existence of vacancy clusters was detected in neutron irradiated in Fe (clusters of 7 vacancies) and Fe-Cr alloys with no C (clusters of 2-3 vacancies) at 573 K to a dose of 5×10^{-3} dpa (damage rate : 3×10^{-9} dpa/s) using Kyoto University Reactor [21]. In the present Fe ion irradiation at 593 K, no void can be detected by positron annihilation lifetime measurements. Corresponding cross sectional transmission electron microscopy supports this result. This should be due to that defect structure evolution by ion irradiation delays compared to neutron irradiation because of high damage rate and relative low temperature [22]. (Present case: 7.6×10^{-3} dpa/s, 593K). Recombination rate of point defects can be enhanced by high damage rate.

4.4 Conclusions

Neutron irradiation-induced vacancy defects in F82H model alloys were studied using positron lifetime measurements. Results showed that Cr has a consistent effect on void swelling resistance compared to electron irradiation. For neutron irradiation performed at 363 K, no interstitial-type dislocation loops are detected in Fe, while for Fe-Cr alloy, the short lifetime of about 152 ps, which corresponds to the vacancies at the dislocation, was detected. The presence of Cr in ultra-pure Fe induces enhanced nucleation of small dislocation loops of interstitial nature in the early stages of irradiation. This supports the configuration trapping model of Cr on void swelling suppression. For solute effects, with isolate point defects induced by electron irradiation, W, V, and Ta have little effect on the evolution of point defect clusters in Fe-Cr based alloys. While with cascade damage induced by neutron irradiation, solute atoms V, Ta and especially W significantly affect the vacancy cluster evolution with an apparently decreased intensity of the long lifetime components of the spectra and a decreased mean lifetime. The results of two types of irradiation support the solute and dislocation interaction model. The effects on metal carbides ($M_{23}C_6$) were investigated using neutron irradiation at 363 K and electron irradiation. For neutron irradiation, the solute effect may be the dominating factor compared to the effects of the $M_{23}C_6$. Solute depletion caused by metal carbides can explain the difference.

For Fe ion irradiation, clear bands of defects, mainly dislocations and interstitial clusters an area of 1400 nm and 1800 nm from the surface were formed in all specimens. In Fe, large dislocation loops formed in the damage peak area, while few can be found in other irradiated area near surface. In Fe-8Cr and F82H, lots of tiny dislocation loops formed in irradiated area including damage peak parts. No void can be detected by positron annihilation lifetime

measurements and corresponding cross sectional transmission electron microscopy which supports this result. It is due to that defect structure evolution by ion irradiation delays compared to neutron irradiation because of a high damage rate. The results of cross sectional transmission electron microscopy clearly show that addition of Cr can make dislocation loops more stable than that in Fe. This also supports the configuration model of Cr on void swelling resistance.

Reference (Chapter 4)

- [1] E.A. Little, Intern. Metals Rev. 21 (1976) 25.
- [2] J.D. Baird, Met. Rev. No. 149, Metals and Materials 5 (1971).
- [3] F.A. Garner, *Irradiation Performance of Cladding and Structural Steels in Liquid Metal Reactors*, in: *Nuclear Materials and Technology*, Chap. 6, Vol. 10A (1994) 419.
- [4] S.S. Huang, X.Q. Pan, K. Sato, Q. Xu, T. Yoshiie, J. Nucl. Mater. In press (2013)
- [5] D. Terentyev, P. Olsson, L. Malerba, A.V. Barashev, J. Nucl. Mater. 362 (2007) 167.
- [6] H. Trinkaus, B.N. Singh, A.J.E. Foreman, J. Nucl. Mater. 199 (1992) 1.
- [7] K. Sato, T. Yoshiie, T. Ishizaki and Q. Xu, Phys. Rev. B 75 (2007) 094109.
- [8] J.S. Koehler, J. Appl. Phys. 46 (1975) 2423.
- [9] F.A. Smidt and J.A. Sprague, Scripta Met. 7 (1973) 495.
- [10] A.H. Cottrell and B.A. Bilby, Proc. Phys. Soc. (London) A62 (1949) 49.
- [11] P. Olsson, T.P. C. Klaver, C. Domain, Phys. Rev. B 81 (2010) 054102.
- [12] H. Ohkubo, Z. Tang, Y. Nagai, M. Hasegawa, T. Tawara and M. Kiritani: Mater. Sci. Eng. A 350 (2003) 95.
- [13] A. Okada, N. Kawaguchi, M.L. Hamilton, K. Hamada, T. Yoshiie, I. Ishida, E. Hirota, J. Nucl. Mater. 212–215 (1994) 382.
- [14] A. Okada, H. Maeda, K. Hamada, I. Ishida, J. Nucl. Mater. 271&272 (1999) 133.
- [15] N. Yoshida, A. Yamaguchi, T. Muroga, Y. Miyamoto, K. Kitajima, J. Nucl. Mater. 155–157 (1988) 1232.
- [16] E. Kuramoto, T. Tsutsumi, K. Ueno, M. Ohmura, Y. Kamimura, Comput. Mater. Sci. 14 (1999) 28.
- [17] S.S. Huang, S. Kitao, Y. Kobayashi, T. Yoshiie, Q. Xu, K. Sato, M. Seto, to be published.
- [18] D. Terentyev, L. Malerba, A.V. Barashev, Philos. Mag. 88 (2008) 21.
- [19] D. Terentyev, M. Klimenkov, L. Malerba, J. Nucl. Mater. 393 (2009) 30.
- [20] M. Klimenkov, M. Rieth, U. Jäntschi, A. Möslang, G. Schuhmacher, *TEM characterization of Au-implanted Fe–Cr* P. J. Barton, B. L. Eyre and D. A. Stow, J. Nucl. Mater., 67 (1977) 181. single crystals, EFDA Report, No. 309 (2007).
- [21] T. Yoshiie, Y. Hayashi, S. Yanagita, Q. Xu, Y. Satoh, H. Tsujimoto, T. Kozuka, K. Kamae, K. Mishima, S. Shiroya, K. Kobayashi, M. Utsuro, Y. Fujita, Nucl. Inst. Meth. Phys. Res., A498 (2003) 522.
- [22] P. J. Barton, B. L. Eyre and D. A. Stow, J. Nucl. Mater., 67 (1977) 181.

Chapter 5 Short range ordering in irradiated F82H and its model alloys

5.1 Property of Fe-Cr alloys

The Fe-Cr system is a very interesting physical object. Various physical properties result from specific features of the bcc lattice [1-4], the electronic structure of 3d-transition metals and ferromagnetism. Concerning the point defect properties, it is known that ferromagnetism is the origin of the unusually high migration energy of interstitials in Fe, as compared to other fcc and bcc metals. The unusual properties of interstitials in Fe-Cr alloys are also believed to be the result of ferromagnetism [5]. Since ferromagnetism and electronic structure have a quantum nature described on the atomic scale while the description of defect migration involves typical distances larger by several orders of magnitude, the proper understanding of physical mechanisms of irradiation damage in this class of alloys requires simultaneously taking into consideration of the processes occurring on quite different physical scales and described in quite different physical approaches. It has been shown that the addition of small amounts of chromium (up to 0.1 at.%) to Fe brings about the change in configuration of interstitials, viz. [6] the formation of mixed FeCr dumbbells, whose mobility is similar or even higher than that of self-interstitials in Fe. A further increase in the Cr concentration above ~1 at.% leads to the capture of these mixed dumbbells by configurations consisting of several Cr (configuration trapping) [6,7]. As a result, the interstitial migration and recombination at stage I temperatures (up to 130 K) are progressively suppressed with increasing Cr concentration. Therefore, Frenkel pairs (FPs) survive at stage I as entities, including close pairs with Cr concentrations at above 10%.

5.2 Short range ordering

The interaction at atomic level in Fe-Cr alloys has not been understood, especially from the view of magnetism. As short-range order (SRO) is important to evaluate microstructural evolution at atomic level, several studies [8-10] have been done on the SRO in Fe-Cr alloys. Understanding of the microstructure of these alloys was made through neutron diffraction measurements [10], which showed (1) negative Cowley SRO parameters at small Cr concentrations indicating strong SRO of Cr and (2) an inversion of the sign of these parameters with increasing Cr concentration, which seems to imply a change of SRO in the solid solution as it approaches the solubility limit. The implications of these discoveries for the interpretation of creep resistance and embrittlement are apparent since SRO is known to affect the mobility of dislocations [11] and precipitation plays a role in intergranular cracking [12]. Nonetheless, the

understanding of the atomistic details of the complex behavior of this alloy is still incomplete.

On the other hand, even with low irradiation dose, Cr segregation happens in Fe-Cr alloys with more than 7.4 wt. % Cr content [13]. It follows that swelling and segregation are interrelated and any swelling reduction which is induced by solute effect is likely to be modified by the concomitant solute redistribution [14]. The physical basis of the swelling resistance in these materials has not been understood yet [15]. To embrace the combined effects of point defect trapping and solute segregation offers the most promising means of predicting the swelling behavior of complex alloy systems. Our positron annihilation lifetime spectroscopy (PALS) studies on F82H and its model alloys in swelling incubation period showed that solute atoms and carbides play key roles to prevent the growth of vacancy clusters [16,17]. The application of additional methods to assess such behavior is essential for better understanding of these damage mechanisms at microstructural level. Very few techniques are capable to detect of defects at the atomic level, moreover, it is extremely difficult to study the interaction of defects and the contribution of alloying elements to the kinetics of irradiation damage at the experimental base.

The Mössbauer spectroscopy (MS) is a very suitable tool to study a local environment of the Mössbauer atoms. Solute atoms in the vicinity of the Mössbauer probe change the Mössbauer spectral parameters. An existence of vacancy or large solute atom in the nearest neighborhood of the Mössbauer probe leads broadening of line-width of spectrum components as a result of magnetic field distribution caused by local lattice distortion. In this work, MS was conducted on F82H and its model alloys before and after neutron irradiation. The obtained hyperfine parameters were analyzed by combining with the previous PALS data.

5.3 Spectrum analyses

Neutron irradiation at 573K to a dose of 5.3×10^{-3} dpa and that at 363 K to a dose of 0.015 dpa were conducted on prepared specimens (see Section 2.1) in Research Reactor Institute, Kyoto University. The same specimens were also irradiated in BR-2 of SCK•CEN at 363 K to a dose of 0.2 dpa. Mössbauer spectra were recorded by a constant acceleration method with a source of ^{57}Co at room temperature (typically 287-293 K) for the specimens before and after irradiation. Gamma-rays were perpendicular to the foil plane. The spectrometer was calibrated with respect to Fe. All quoted isomer shifts δ were relative to $\alpha\text{-Fe}$.

To analyze Mössbauer spectra, some approximations should be considered. Martensite cannot be distinguished from ferrite by MS [18]. Martensite structure is tetragonal bct; however, under normal circumstances, it is difficult to detect any tetragonality of martensite in steels with less

than 0.2 wt. %C. In present case, F82H has a low C and N content steel (Table 1-1). So, the matrix was analyzed as bcc Fe as a whole.

We used a superposition method and a two neighbor-shells approximation [19-21]. Cr atoms situated within the first (1NN) and the second (2NN) neighbor-shell around the probe ^{57}Fe nuclei were assumed to have a measurable effect on the spectral hyperfine parameters, namely the hyperfine field (H) and the isomer shift (IS). Using the 1NN-2NN model, the effect of Cr atoms on H and IS was additive i.e.

$$X(n_1, n_2) = X(0, 0) + n_1\Delta X_1 + n_2\Delta X_2 \quad \dots (5.1)$$

where $X = H$ or IS , ΔH_k and ΔIS_k are a change of the hyperfine field and that of the isomer shift due to one Cr atom situated in 1NN ($k=1$) or in 2NN ($k=2$). The number of Cr atoms is indicated by n_1 for 1NN and by n_2 for 2NN. The spectra were analyzed assuming the following parameters to be free for each spectrum: $H(0, 0)$, $IS(0, 0)$, C_2 (Clebsch-Gordan coefficient of the second/fifth line in a sextet), $P(n_1, n_2)$ (probability of finding n_1 Cr atoms in 1NN and n_2 in 2NN). The shifts of H and those of IS , ΔH_1 , ΔH_2 , ΔIS_1 , ΔIS_2 were also treated as free but common to all spectra. For a Fe-8Cr binary alloy with a random distribution of Cr atoms, the $P(n_1, n_2)$ can be found using the binomial distribution formula. Each measured spectrum was fitted with a transmission integral for a sum of eight six-line patterns corresponding to various hyperfine fields at ^{57}Fe nuclei generated by different numbers of Fe and Cr atoms located in the first two coordination shells of the probing nuclei. The $P(n_1, n_2)$ calculated from the binomial distribution was treated as free parameters to account for a possible departure from the random distribution in the studied alloys. Good fits, in terms of χ^2 -test were obtained with the hyperfine parameters. For our Fe-8Cr specimen before irradiation, $\Delta H_1 = -3.42$, $\Delta H_2 = -2.32$, $\Delta IS_1 = -0.021$, $\Delta IS_2 = -0.008$. These values agreed well with those reported [19,20].

5.4 Measures of short-range order

Short-range order in binary alloys is conveniently measured by means of the order parameter introduced by Cowley [22] which has been widely applied in the past (see e.g., Refs. [23], [24], and [25]). The SRO parameter for the k th shell of a Cr atom is defined as

$$\alpha_{Fe}^{(k)} = 1 - \frac{Z_{Fe}^{(k)}}{Z_{tot}^{(k)}(1 - C_{Cr})} \quad \dots (5.2)$$

where $Z_{Fe}^{(k)}$ denotes the number of Fe atoms in the k th shell, $Z_{tot}^{(k)}$ is the total number of atoms in the same shell, and C_{Cr} is the overall (total) Cr concentration. It is instructive to consider several

- special cases: (1) If a Cr atom is exclusively surrounded by other Cr atoms, $Z_{\text{Fe}}^{(k)} = 0$ and $\alpha_{\text{Fe}}^{(k)} = 1$.
(2) If one has a completely random distribution, the ratio $Z_{\text{Fe}}^{(k)}/Z_{\text{tot}}^{(k)}$ equals $C_{\text{Fe}}=1-C_{\text{Cr}}$ and $\alpha_{\text{Fe}}^{(k)} = 0$.
(3) Finally, if each Cr atom is surrounded exclusively by Fe atoms $Z_{\text{Fe}}^{(k)} = Z_{\text{tot}}^{(k)}$ and therefore

$$\alpha_{\text{Fe}}^{(k)} = 1 - \frac{C_{\text{Cr}}}{1-C_{\text{Cr}}} \quad \dots (5.3)$$

which provides a lower bound to the SRO parameter; in other words, it indicates the maximum possible degree of short-range order at a given composition.

SRO parameters $\langle \alpha_1 \rangle$, $\langle \alpha_2 \rangle$ and $\langle \alpha_{12} \rangle$ for 1NN, 2NN, and 1NN–2NN were calculated after determination of Cr atom numbers in corresponding NN based on $P(n_1, n_2)$ values obtained from the analysis of the spectra. The SRO parameters for bcc lattice have the following form [22].

$$\langle \alpha_1 \rangle = 1 - \frac{\langle n_1 \rangle}{8x} \quad \dots (5.4)$$

$$\langle \alpha_2 \rangle = 1 - \frac{\langle n_2 \rangle}{6x} \quad \dots (5.5)$$

$$\langle \alpha_{12} \rangle = 1 - \frac{8\langle n_1 \rangle + 6\langle n_2 \rangle}{14x} \quad \dots (5.6)$$

Here x is solute atom concentration in alloys. 8 and 6 are the first and second near neighbors in bcc structure. The irradiation effects on the SRO parameters and on the spectral parameters are presented and discussed as below.

Fig.5-1 and Fig.5-2 shows the fitted Mössbauer spectra at room temperature obtained for Fe-8Cr before irradiation and after neutron irradiation at 363 K to 0.015 dpa. Spectra were fitted to a superposition of eight sextets with different hyperfine parameters, depending on the number of Fe neighbors of the ^{57}Fe atom.

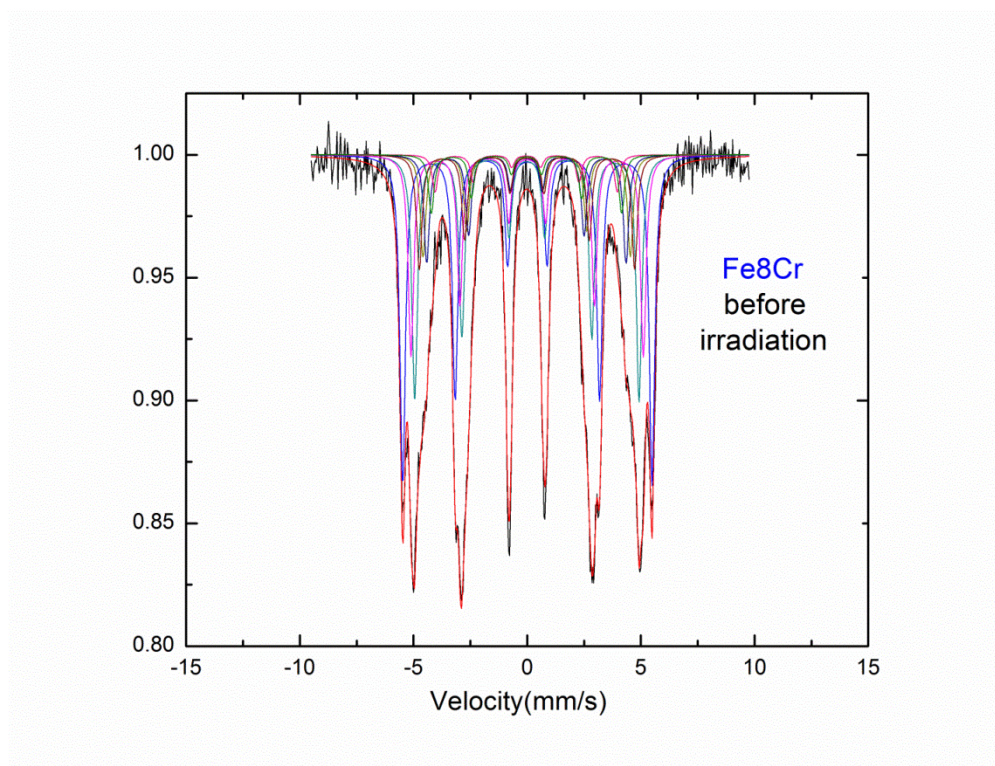


Fig.5-1 Fitted Mössbauer spectrum for Fe-8Cr before irradiation.

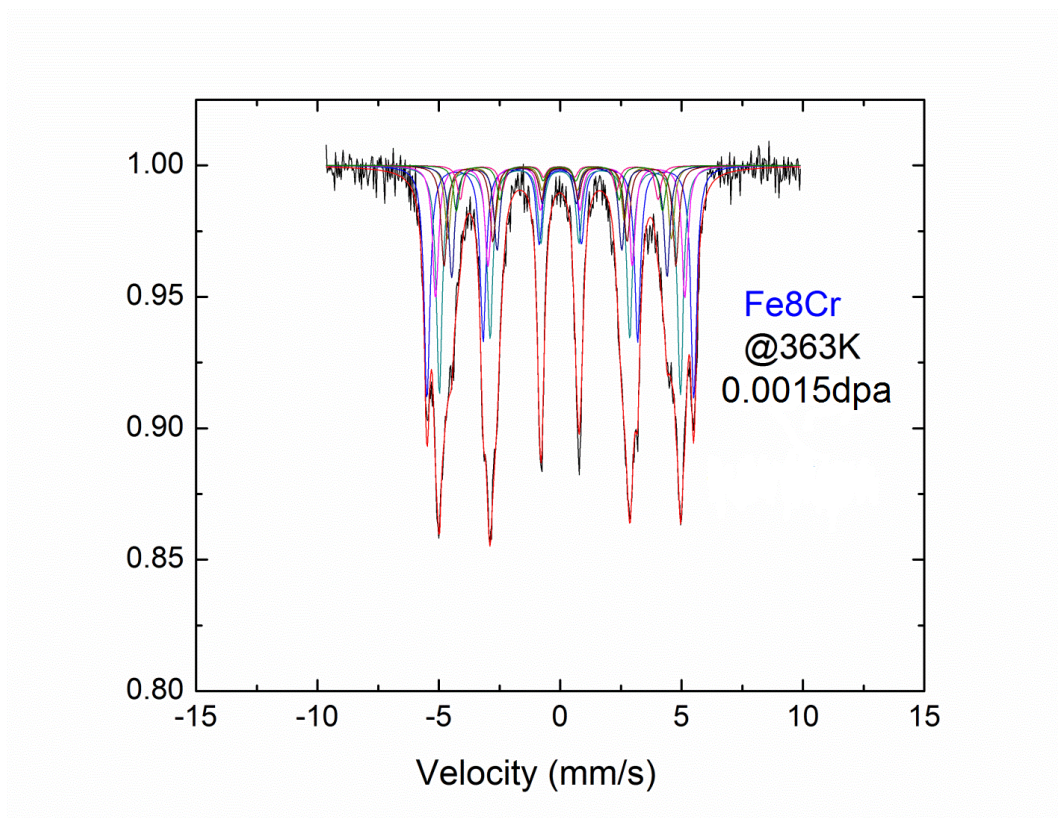


Fig.5-2 Fitted Mössbauer spectrum for Fe-8Cr after irradiated at 363 K to 1.5×10^{-3} dpa.

In disordered Fe-8Cr, the probability of randomly distributed for a configuration of (n_1, n_2) - $P_r(n_1, n_2)$ of local configuration of impurity atoms in the first and the second coordination spheres of ^{57}Fe nucleus is described by the binomial distribution:

$$P_r(n_1, n_2; x) = \binom{8}{n_1} \binom{6}{n_2} x^{n_1+n_2} (1-x)^{14-n_1-n_2} \quad \dots (5.7)$$

Fig.5-3 shows the possibilities of experimental of sub-spectra corresponding to a particular atomic configuration (n_1, n_2) compared to those of randomly distributed Fe-8Cr alloy. We can see that distribution of Cr atoms in the neighbor-shells of ^{57}Fe nuclei is not homogeneous and it cannot be described in terms of binomial distribution. SRO in this Fe-8Cr alloy can be explained in terms of electron band [3] and magnetic properties [26,27] of Fe and Cr. Single Cr atom has a negative heat of formation in Fe and thus prefers to be surrounded by Fe atoms because of a lowering of the density of states at the Fermi level. Cr atoms are distributed sufficiently far from each other to avoid magnetic frustration, i.e. ordering of the alloy.

5.5 Defect effects

A Mössbauer spectrum can show different components belonging to various sites of Mössbauer atoms with different neighborhoods. From the hyperfine interactions and the Debye-Waller factor, it is generally possible to define the defect-correlated sites. A neighboring vacancy, for instance, decreases a magnetic hyperfine field at the Mössbauer atom site.

The average hyperfine field, $\langle H \rangle$ was calculated as weighted hyperfine fields associated with particular atomic configurations,

$$\langle H \rangle = \sum_{n_1, n_2} p(n_1, n_2) H(n_1, n_2) \quad \dots (5.8)$$

where $H(n_1, n_2)$ is the hyperfine field for (n_1, n_2) atomic configuration and $p(n_1, n_2)$ is possibility obtained experimentally as shown in Fig.5-3.

Fig.5-4 shows the results of average hyperfine field of specimens before and after irradiation. Decreased magnetic hyperfine field should be due to vacancies introduced by irradiation.

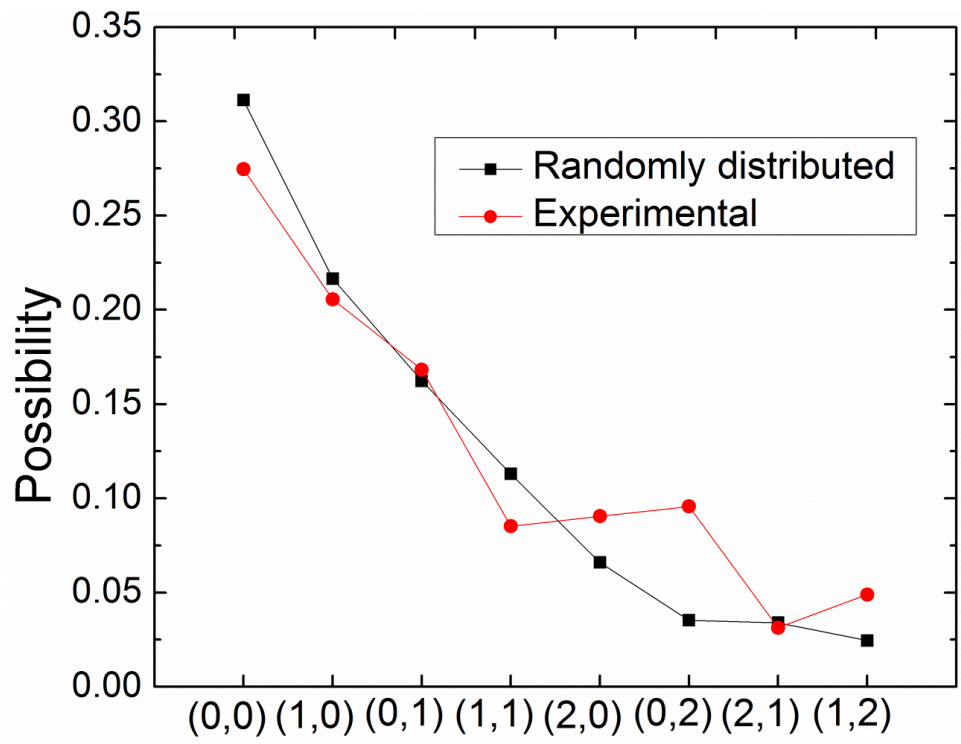


Fig.5-3 Possibilities of experimental sub-spectra corresponding to a particular atomic configuration (m_1, m_2) compared to those of randomly distributed in annealed Fe-8Cr alloy.

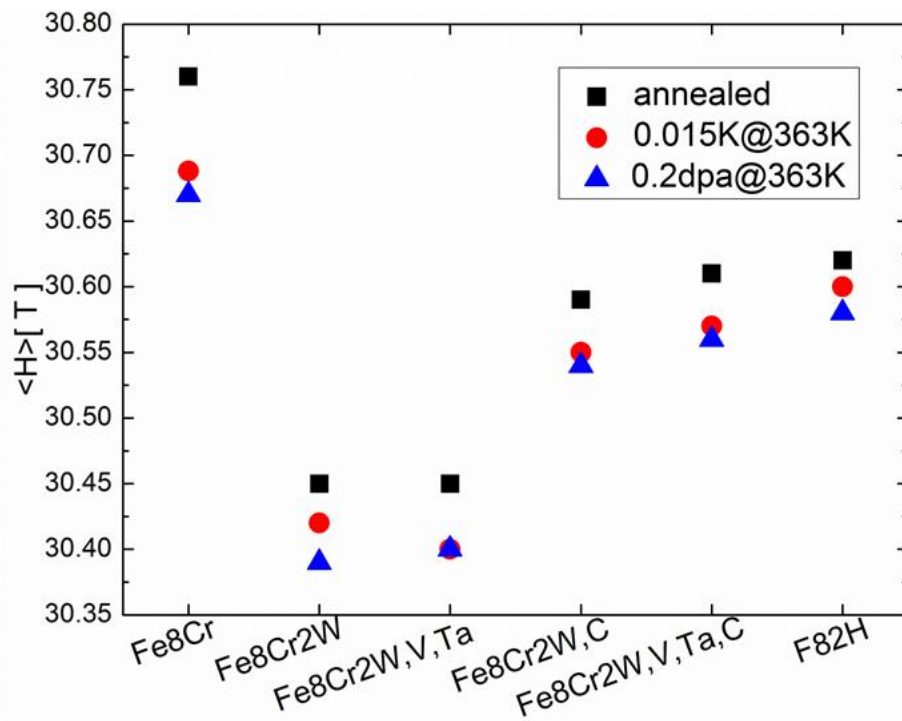


Fig.5-4 Average hyperfine field of specimens before and after irradiation.

Furthermore, broadening of full width half maximum of spectrum components as a result of magnetic field distribution caused by local lattice distortion induced by vacancies also occurred in Fe. Fig.5-5 and Fig.5-6 show Fe Subtracted spectra obtained by subtracting non-irradiated spectrums from irradiated spectrums. Table.1 also clearly shows the results. For other specimens, the broadening is not clear because of solute atom effects. Idczak *et al.* [28] conducted MS on both cold-rolled and annealed samples of pure Fe. Practically the same Mössbauer spectra showed that MS technique is insensitive to dislocations.

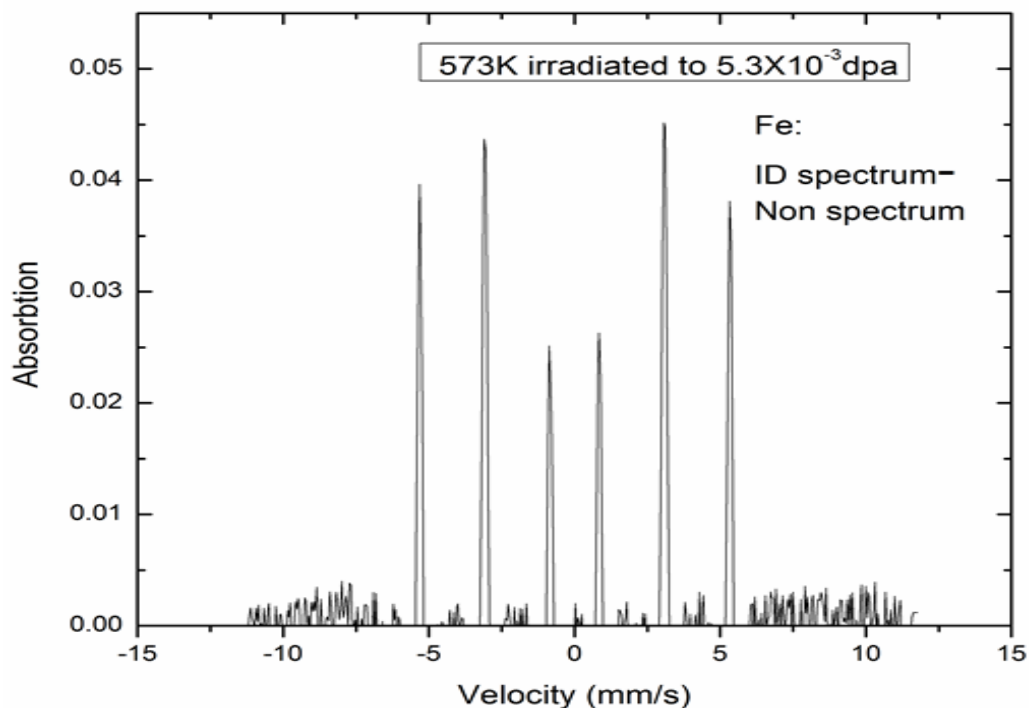


Fig.5-5 Fe Subtracted spectra obtained by subtracting non-irradiated spectrums from 573 K irradiated spectra.

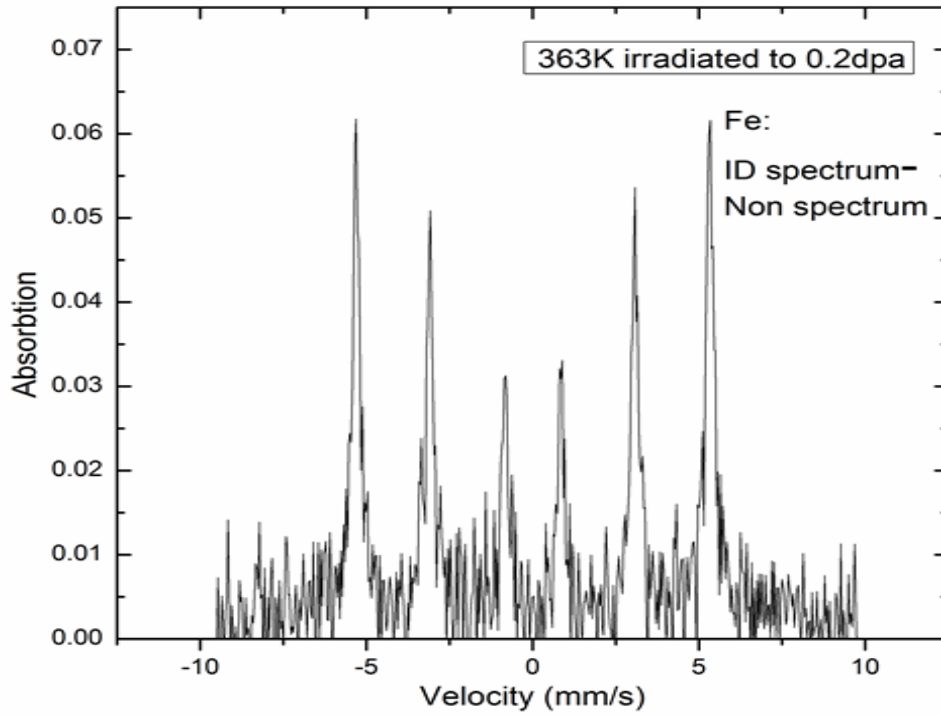


Fig.5-6 Fe Subtracted spectra obtained by subtracting non-irradiated spectra from 573 K irradiated spectra.

Table.1 Line-width of Fe MS spectrum before (BI) and after irradiation (AI) at 363 K.

Condition (Fe, 363K)	Line-width (BI) [mm/s]	Line-width (AI) [mm/s]
0.015dpa	0.271	0.294
0.2dpa	0.274	0.302

5.6 Solute atom effects

5.6.1 Cr effect

A graphical presentation of $\langle \alpha_1 \rangle$, $\langle \alpha_2 \rangle$ and $\langle \alpha_{12} \rangle$ is displayed in Fig.5-7 and Fig.5-8 respectively. Concerning the primary solute concentration, the role of Cr among in the effects of alloying elements should be the principle one. Different SRO parameters than zero means the distribution of Fe/Cr atoms is not random. Concerning the 1NN-shell, positive $\langle \alpha_1 \rangle$ means that the number of Cr situated in this shell is lower than the one expected for the random case. The under population of Cr in the 1NN-shell means that Fe and Cr being the first-nearest neighbors with each other repulse themselves. On the other hand, an opposite SRO parameter as negative

$\langle\alpha_2\rangle$ was obtained for the 2NN-shell. The negative $\langle\alpha_2\rangle$ indicates that the potential between Fe and Cr being the second-nearest neighbors is attractive leading to the over population of Cr in the 2NN-shell. These indicate that $\langle 100 \rangle$ direction Fe-Cr is more stable in Fe rich alloys.

The overall effect within the 1NN–2NN can be quantitatively expressed in terms of $\langle\alpha_{12}\rangle$. The negative average SRO parameter for NN shells indicates that more Cr in NN shells exist than expected for the random case. In terms of interactions, Fe and Cr being the second-nearest neighbors is attractive. For interstitial, Cr can form stable mixed Fe-Cr dumbbell, suppressing one-dimensional (1-D) mobility of interstitials to prevent void swelling (configuration trapping model [29]). Furthermore, irradiation can accelerate short range order in these Fe-8Cr based alloys in the form of more negative $\langle\alpha_{12}\rangle$ parameters than those of annealed ones. This should be due to repelling interaction among Cr in Fe. Irradiation accelerates diffusion and resulting in a redistribution of Cr in Fe matrix. As the vacancies generated during the irradiation can accelerate Cr diffusion by vacancy diffusion mechanism. This is in agreement with experiments by Mirebeau *et al.* [30] and Sagaradze *et al.* [31] which showed ordering at low Cr concentrations. Sagaradze *et al.* [31] found that Fe-Cr alloys with 5 and 9 wt. % Cr indeed show ordering after thermal annealing and electron irradiation, while alloys with Cr concentrations of 13% or higher show the formation of a Cr-rich phase. It means that at low concentration, Cr in Fe repel each other, causing ordering. Irradiation accelerates this ordering. Note that, concerning the parameters of high temperature irradiated specimens, the more negative value indicated SRO parameters to be very sensitive to temperature as shown in Fig.5-8. Solute atom diffusion was accelerated by increasing temperature.

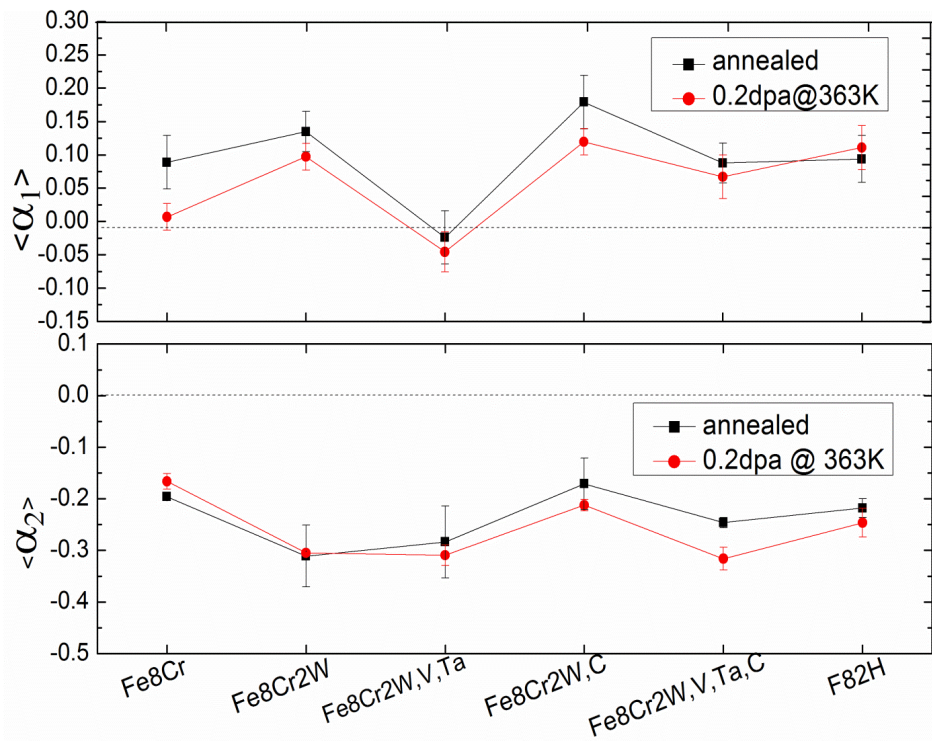


Fig.5-7 α_1 and α_2 parameters for all the specimens before and after irradiation at 363 K to a dose of 0.2 dpa.

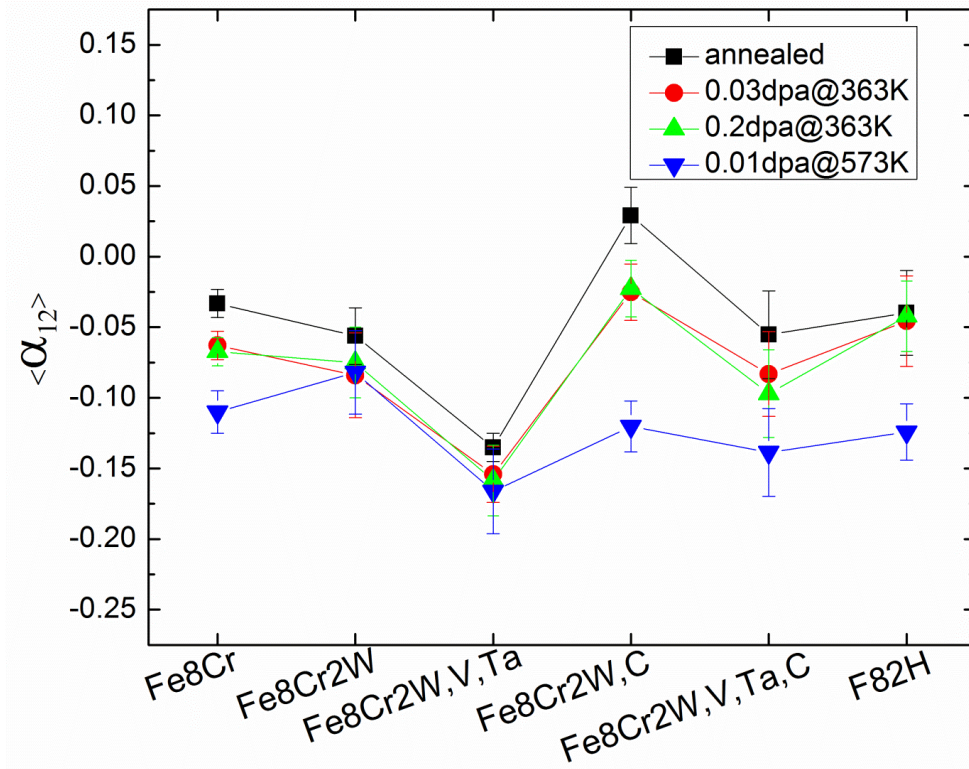


Fig.5-8 α_{12} parameters for all the specimens before and after irradiation.

The reasons that short range order in dilute FeCr based alloys are as follows. In terms of electron band and magnetic properties of Fe and Cr, the single Cr has a negative heat of formation and thus prefers to be surrounded by Fe atoms because of a lowering of the density of states at the Fermi level, i.e. the total energy [3]. In addition, in their respective ground-states, pure Fe is ferromagnetic and pure Cr can be described as antiferromagnetic [26,27]. Thus, if a single Cr is inserted in the Fe matrix, its magnetic moment will be antiparallel to that of the surrounding Fe. However, if a second Cr is introduced nearby, a situation of ‘magnetic frustration’ is produced, because either Cr tends to have its magnetic moment antiparallel to both that of the surrounding Fe and to that of the other Cr. When many Cr are close to each other in Fe, since this is impossible, different magnetic configurations can result from the competition [26], but in practice the energetically most favorable situation is obtained when Cr is distributed sufficiently far from each other to avoid magnetic frustration, i.e. ordering the alloy. Furthermore, spinodal decomposition is usually related to Cr with high concentration at high temperature. As shown in Fig.5-9.

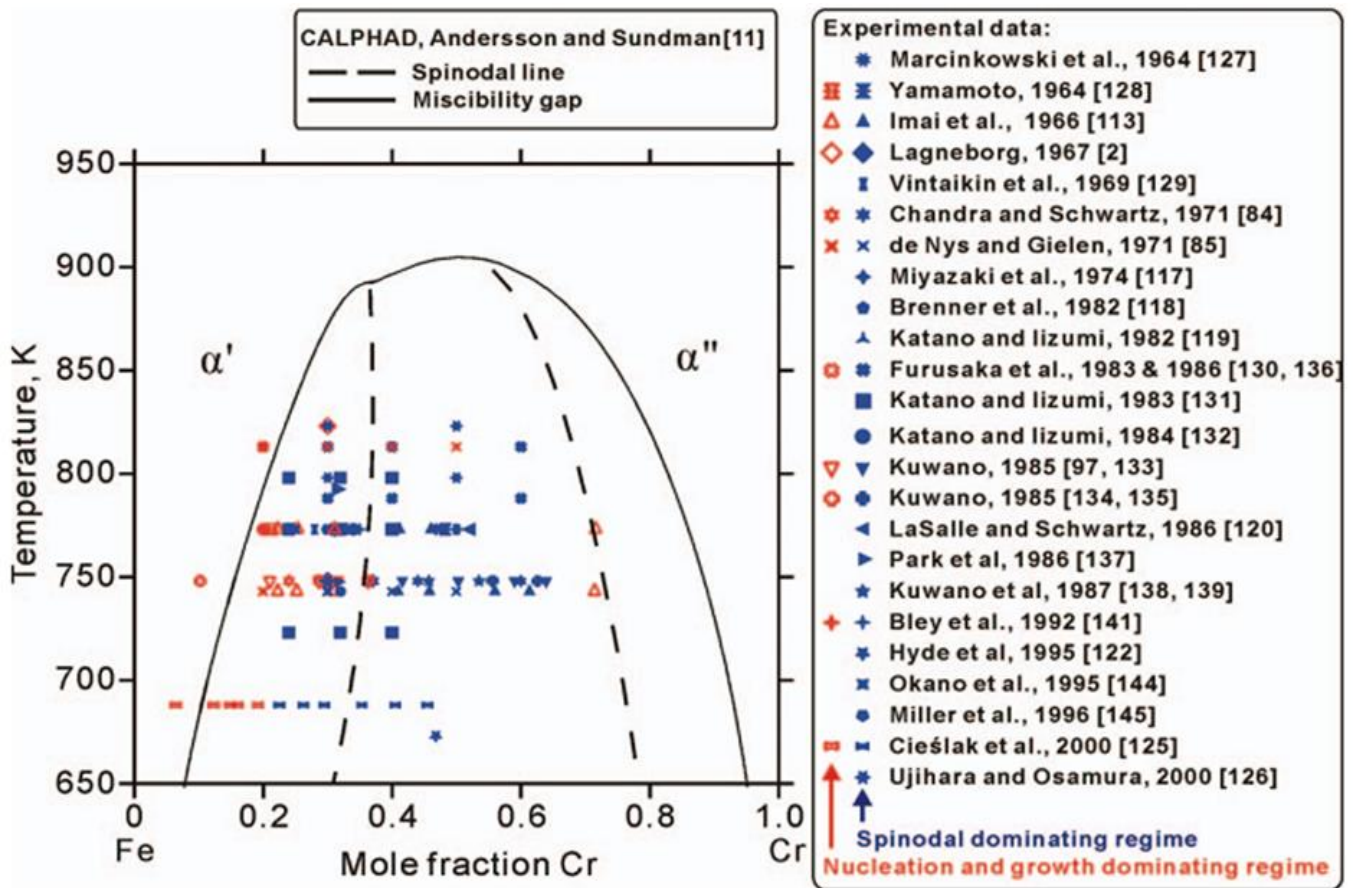


Fig.5-9 Spinodal decomposition region in the Fe-Cr system [32].

5.6.2 W and other solute atom effects

In Chapter 4, results showed that W, V and Ta together with dislocations can effect of irradiation defect evolution (dislocation interaction model) [17]. However, as mentioned above, MS is insensitive to dislocations. We do not say any more here at this point. Even so, at NN shells level, we can see from Fig.5-8 that addition of W can accelerate the short range order compared to Fe-8Cr alloy. This should be due to the relative bigger atom size of W than that of Fe inducing a local lattice distortion. Solute atom effects of V and Ta can be explained in the same way.

5.6.3 Metal carbides effect

Metal carbides in steels have been studied by several researchers by MS [33,34]. Based on Principi [33], $M_{23}C_6$ -type precipitates appear in the Mössbauer spectrum as a single line with a IS value of 0.06 mm/s and line width of 0.4mm/s. The transmission of valley appeared near 0mm/s in the specimens containing C should due to $M_{23}C_6$ -type precipitates as shown in Fig.5-10.

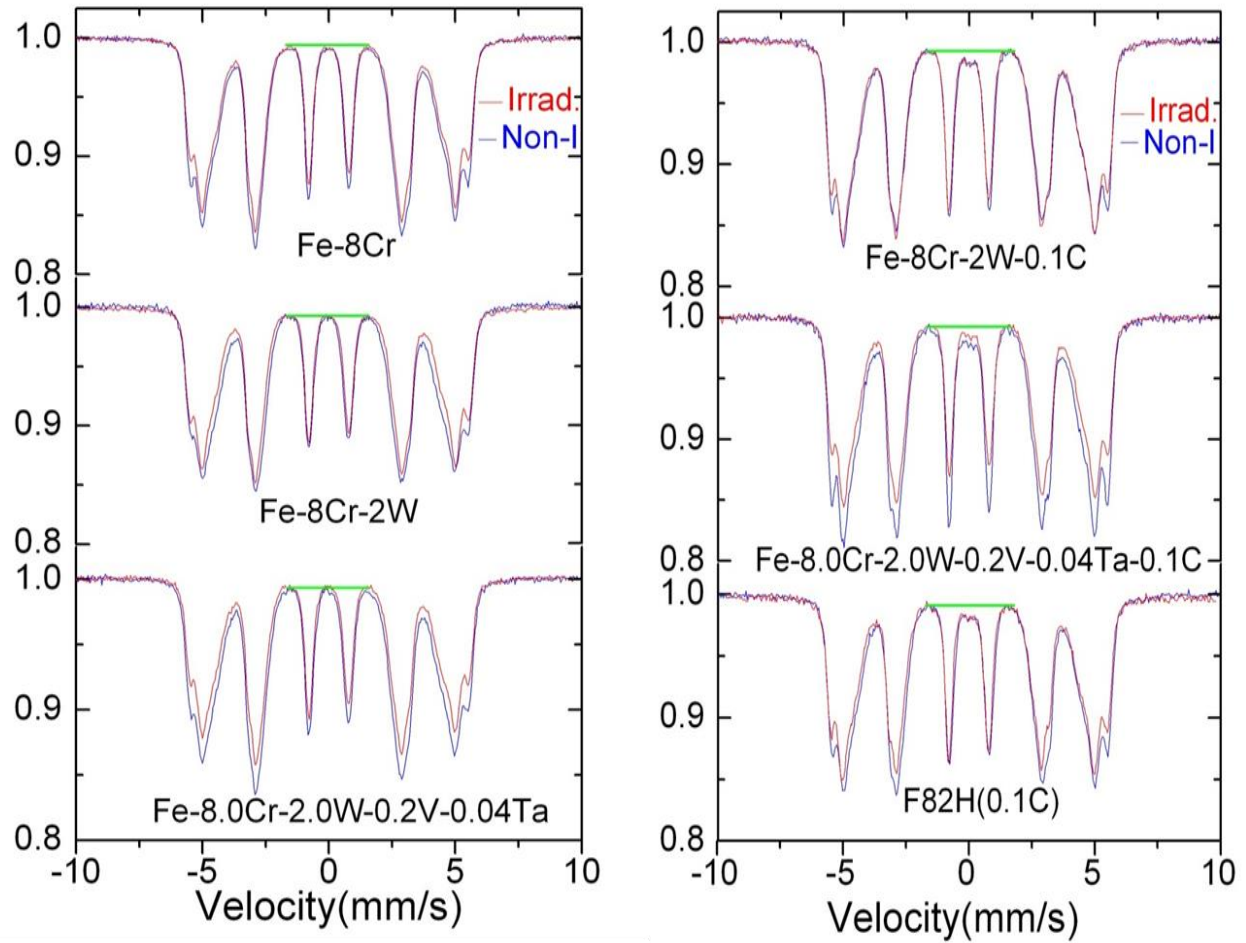


Fig.5-10 Mössbauer spectrum for model alloys (Non-I: non irradiated, Irrad: irradiated at 573 K to 5.3×10^{-3} dpa) Left: specimens not containing C, Right: specimens containing C.

Fig.5-11 shows clear characteristic of $M_{23}C_6$ in Mössbauer spectrum of F82H before irradiation. By best fitting Mössbauer spectra, we can evaluate area of $M_{23}C_6$ in C including specimens before and after irradiation.

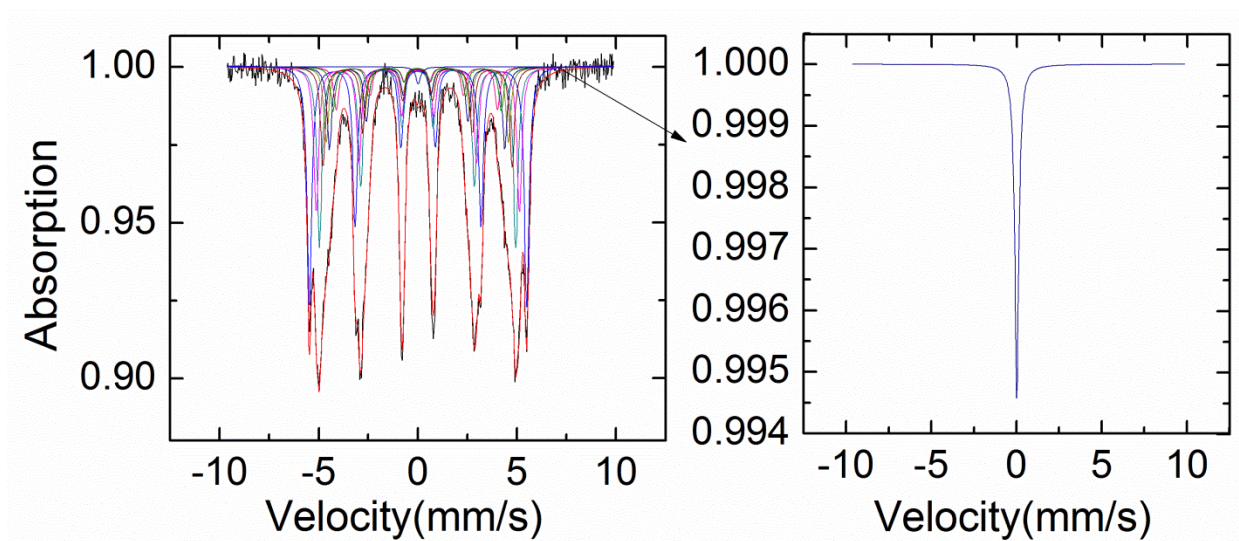


Fig.5-11 Fitted Mössbauer spectrum and characteristic Mössbauer spectrum of $M_{23}C_6$ in F82H before irradiation The right figure is 0 velocity line.

The amount of $M_{23}C_6$ increases after irradiation as shown in Fig.5-12. Note that, our positron annihilation lifetime result [17] (see Fig.5-13) showed that the intensity of $M_{23}C_6$ decreased and positron lifetime (long lifetime component) increased after corresponding irradiation. It only means the decrease of the concentration and increase of the size of carbide, and the increase of total amount of carbide was not obvious. Characteristic of $M_{23}C_6$ in Mössbauer spectra of C containing alloy clearly indicated that irradiation promotes the growth of $M_{23}C_6$.

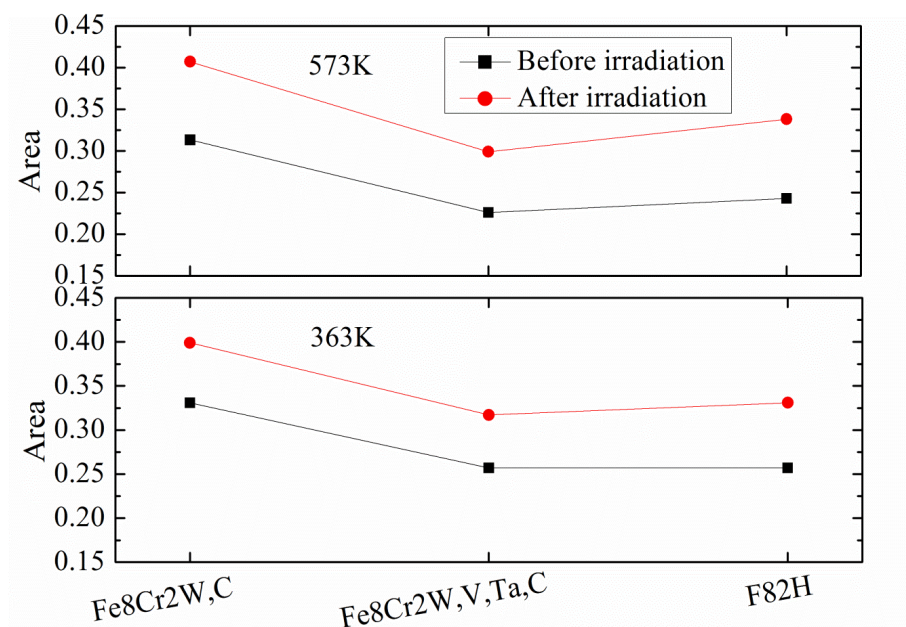


Fig.5-12 Area of $M_{23}C_6$ in C including specimens before and after irradiation.

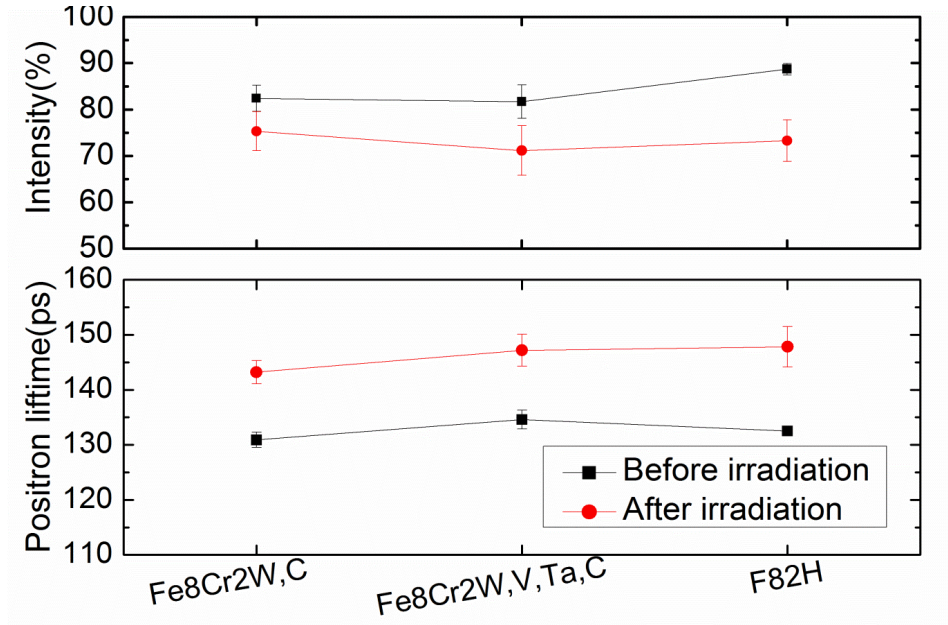


Fig.5-13 Positron annihilation spectroscopy results in C including specimens before and after irradiation at 573 K to 5.3×10^{-3} dpa.

5.7 Conclusions

Before irradiation, Cr atoms in NN of Fe in Fe-8Cr based alloys are not homogeneous. Short range order in the alloys can be explained in terms of electron band and magnetic properties. Vacancies are detected with a broadening line-width in irradiated Fe MS. Decreased average hyperfine fields in all specimens after irradiation are also detected. SRO parameters show that Fe-Cr pairs of $\langle 100 \rangle$ direction is more stable in Fe rich alloys. Negative average SRO parameter for the 2NN shells indicates the interaction between Fe and Cr in 2NN is attractive. This can be explained by configuration trapping model. Irradiation accelerates SRO in Fe-8Cr based alloys. This should be due to repelling interaction among Cr in Fe; irradiation accelerates diffusion resulting in a redistribution of Cr in Fe matrix. Characteristic of $M_{23}C_6$ in MS of C containing alloy indicates that irradiation promotes the growth of $M_{23}C_6$.

Reference (Chapter 5)

- [1] J. Wallenius, P. Olsson, C. Lagerstedt, et al., Phys. Rev. B 69 (2004) 094103.
- [2] P. Olsson, J. Wallenius, Ch. Domain, et al., Phys. Rev. B 72 (2005) 214119.
- [3] P. Olsson, I.A. Abrikosov and J. Wallenius, Phys. Rev. B 73 (2006) 104416.
- [4] Yu.Yu. Tsiovkin, A.N. Voloshinskii, V.V. Gapontsev, et al., Phys. Rev. B (2005) 722240204.
- [5] H. Abe and E. Kuramoto, J. Nucl. Mater. 271–272 (1999) 209.
- [6] F. Maury, P. Lucasson, A. Lucasson, et al., J. Phys.: Met. Phys. (1987) 171143.
- [7] A.L. Nikolaev, J. Phys.: Condens. Mat. (1999) 118633.
- [8] Paul Erhart, Alfredo Caro, Magdalena Serrano de Caro, and Babak Sadigh, Physical Review, B77 (2008) 134206.
- [9] S. M. Dubiel and J. Cieslak Phys. Rev. B 83 (2011) 180202(R).
- [10] I. Mirebeau, M. Hennion, and G. Parette, Phys. Rev. Lett. 53 (1984) 687.
- [11] E. Rodary, D. Rodney, L. Proville, Y. Brechet, and G. Martin, Phys. Rev. B 70, (2004) 054111.
- [12] R. L. Klueh and D.R. Harries, High-Chromium Ferritic and Martensic Steels for Nuclear Applications ASTM, West Con-shohocken, PA, (2001).
- [13] H. Kuwano, Y. Hamaguchi. J. Nucl. Mater. 155-157 (1988) 1071.
- [14] E.A. Little, J. Nucl. Mater. 87 (1979) 11.
- [15] Z. Yao, M. Hernandez-Mayoral, M.L. Jenkis, M.A. Kirk, Philos. Mag. 88 (2008) 2851.
- [16] S.S. Huang, T. Yoshiie, Q. Xu, K. Sato, T.D. Troev, J. Nucl. Mater. 440 (1-3) (2013) 617.
- [17] S.S. Huang, X.Q. Pan, K. Sato, Q. Xu, T. Yoshiie, J. Nucl. Mater. In press (2013).
- [18] Y. Jirásková, J. Svoboda, O. Schneeweiss, W. Daves, F.D. Fischer, Appl. Surf. Sci. 239 (2005) 132.
- [19] S.M. Dubiel, G. Inden, Z Metallkde 78 (1987) 544.
- [20] S.M. Dubiel, J. Cieslak, H. Reuther, J. Nucl. Mater. 434 (2013) 235.
- [21] R. Idczakn, R. Konieczny, J. Chojcan, J. Phys. Chem. Solids. 73 (2012) 1095.
- [22] J. M. Cowley, Phys. Rev. 77 (1950) 669.
- [23] I. Mirebeau, M. Hennion, and G. Parette, Phys. Rev. Lett. 53 (1984) 687.
- [24] V. V. Ovchinnikov, N. V. Zvigintsev, V. S. Litvinov, and V. A. Osminkin, Fiz. Met. Metalloved. 42, (1976) 310.
- [25] V. V. Ovchinnikov, B. Y. Goloborodsky, N. V. Gushchina, V. A. Semionkin, and E. Wieser, Appl. Phys. A: Mater. Sci. Process. 83 (2006) 83.
- [26] T.P.C. Klaver, R. Drautz, M.W. Finnis, Phys. Rev. B 74 (2006) 094435.
- [27] J.H. Shim, H.J. Lee, B.D. Wirth, J. Nucl. Mater. 351 (2006) 56.

- [28] R. Idczakn, R. Konieczny, J. Chojcan, Solid State Commun, 152 (2012) 1924–1928
- [29] D. Terentyev, P. Olsson, L. Malerba, A.V. Barashev, J. Nucl. Mater. 362 (2007) 167–173.
- [30] I. Mirebeau, M. Hennion, and G. Parette, Phys. Rev. Lett. 53 (1984) 687-690.
- [31] V. V. Sagaradze, I. I. Kositsyna, V. L. Arbuzov, V. A. Shabashov, and Y. I. Filippov, Phys. Met. Metallogr. 92 (2001) 505.
- [32] T. P. C. Klaver, R. Drautz, M. W. Finnis. Physical review B 74, 094435(2006)
- [33] G. Principi, R.Frattini, M.Magrini, Gazz. Chim. Ital. 113 (1983) 281.
- [34] G. Brauer, W. Matz, Cs. Fetzner, Hyperfine Interact. 56 (1990) 1563-1568.

Chapter 6 Summary

In this study, defect evolution in F82H and its model alloys by irradiation damage were investigated mainly focusing on initial stage of period to explore the mechanism of void swelling resistance in ferritic/martensitic steels. For this purpose, defects were introduced by different kinds of irradiation as electron irradiation, neutron irradiation and ion irradiation. Transmission electronic microscopy and positron annihilation spectroscopy were employed as experimental techniques. The internal atomic forces on the defects evolution were also studied for these alloys by using Mössbauer spectroscopy.

In chapter 1, the background of this study was presented. The importance of ferritic/martensitic alloys, lattice defects and irradiation damages are explained.

In chapter 2, the experimental techniques employed in this study were introduced. Irradiation methods, transmission electron microscopy, positron annihilation spectroscopy and Mössbauer spectroscopy are mentioned.

In chapter 3, defect evolution by isolate point defects induced by electron irradiation in F82H steel and its model alloys were investigated. Additive solute atoms and their synergistic effects on vacancy cluster evolution during an incubation period were systematically analyzed for the first time. The results clearly demonstrated void swelling resistance in Fe-Cr based alloys. The trapping of vacancies at interstitial-type dislocation loops is proposed as the mechanism responsible for the observed void swelling resistance at higher temperatures. During the incubation period, elements such as W, V, and Ta had little effect on the evolution of point defect clusters. During the recovery stage of alloys containing C, the release of vacancies from the complicated $M_{23}C_6$ /matrix interface were detected, indicating that metal carbides have a strong effect on void swelling resistance.

In chapter 4, for the study of defects behavior by irradiation cascade, neutron irradiation and Fe ion irradiation were conducted. Results showed that Cr has a consistent effect on void swelling resistance compared to electron irradiation. For neutron irradiation performed at 363K, no interstitial-type dislocation loops are detected in Fe, while for Fe-Cr alloy, the short lifetime corresponding to the vacancies at the dislocation sites was detected. This supports the configuration trapping model of Cr on void swelling suppression. In cascade damage induced by neutron irradiation, solute atoms V, Ta and especially W significantly affect the vacancy cluster evolution. The results of two types of irradiation, electron and neutron irradiations, support the solute and dislocation interaction model. The effects on metal carbides ($M_{23}C_6$) were investigated

using neutron irradiation and electron irradiation. For neutron irradiation, the solute effect may be the dominating factor compared to the effects of the $M_{23}C_6$. Solute depletion caused by metal carbides can explain the difference.

For 6 MeV Fe ion irradiation, clear bands of defects, mainly dislocations and interstitial clusters an area of 1400 nm and 1800 nm from the surface were formed in all specimens. In Fe, large dislocation loops formed in the damage peak area, while few can be found in other irradiated area near surface. In Fe-8Cr and F82H, lots of tiny dislocation loops formed in irradiated area including damage peak parts. No void can be detected by positron annihilation lifetime measurements and corresponding cross sectional transmission electron microscopy supports this result. This should be due to that defect structure evolution by ion irradiation delays compared to neutron irradiation because of a high damage rate. The results of cross sectional transmission electron microscopy clearly show that addition of Cr can make dislocation loops more stable than that in Fe. This also supports the configuration trapping model of Cr on void swelling resistance.

In chapter 5, Short range ordering in F82H and its model alloys by neutron irradiation at different temperatures was studied. Before irradiation, Cr atoms in NN of Fe in Fe-8Cr based alloys are not homogeneous. Short range order in the alloys can be explained in terms of electron band and magnetic properties. Vacancies are detected with a broadening line-width in irradiated Fe Mössbauer spectrum. Decreased average hyperfine fields in all specimens after irradiation are also detected. SRO parameters show that Fe-Cr pairs of $\langle 100 \rangle$ direction is more stable in Fe rich alloys. Negative average SRO parameter for the 2NN shells indicates the interaction between Fe and Cr in 2NN is attractive. This can be explained by configuration trapping model. Irradiation accelerates SRO in these alloys. This should be due to repelling interaction among Cr in Fe; irradiation accelerates diffusion resulting in a redistribution of Cr in Fe matrix. Characteristic of $M_{23}C_6$ in Mössbauer spectra of C containing alloy indicates that irradiation promotes the growth of $M_{23}C_6$.

Acknowledgements

First of all, I would like to express my thanks to Prof. T. Yoshiie. Without his support for my visit to Japan, this dissertation would not have been possible. I would also like to express my deep appreciation to my adviser Prof. Q. Xu for his valuable advisement to my study. I would sincerely like to thank Prof. Y. Shirai and Prof. T. Fukunaga for their useful criticism and revising of my thesis. I am also grateful to all the professors, assistants, students and clerks in the Department of Mechanical Engineering, Kyoto University.

These studies have been mainly made in the Research Reactor Institute of Kyoto University. I would like to thank all the staffs in the Institute, in particular, I wish to express my deep appreciation to Prof. K. Sato and Dr. M. Horiki for their instruction in performing researches. I am grateful to the students in the Institute, in particular, I would like to thank Mr. S. Kawamoto, Mr. Y. Sugiura, Mr. R. Tamiya for their help during my experiments and my daily life. I would like to express my gratitude to Mr. K. Ikemura, Mr. T. Yokotani and Mr. R. Ishibashi, they helped me a lot in my daily life, which is very beneficial to my concentration on my studies.

I would like to express my gratitude to the research group in Division of Nuclear Radiation Physics in this Institute for using their Mossbauer spectroscopy measurement. I am very grateful to Professors S. Kitao, Y. Kobayashi and M. Seto for the help during the MS experiment and giving so much meaningful instructions. Regarding the Fe ion irradiation, I would like to thank Professors H. Tsuchida and A. Itoh in Quantum Science and Engineering Center, Kyoto University for using their tandem Pelletron accelerator.

I appreciate the kind cooperation of Mr. Q.Zhang and Mr. X.Q.Pan in National Key Laboratory on Reactor Fuel & Materials, Nuclear Power Institute of China for the TEM observation. I would also like to express my gratitude to Prof. T. Troev of Bulgarian Academy of Sciences for the valuable instruction and discussion about the positron annihilation measurement results. I would like to express my gratitude to Prof. A. Kimura in Institute of Advanced Energy, Kyoto University for his encouragement and comment to my study.

I am very grateful to my friends Ms. M. Mikura, Ms. C. Nakamura, Dr. Shimatsu, Ms F. Mary. Thanks to them, the research life here in Japan was full of happiness and interesting things. I would also like to thank friends Dr. J.B. Lagrange and Ms. K. Nadège for their encouragements and thoughtful discussion with my research. Thank you to Prof. X.Z. Shen for his encouragement, time and help.

Prof. F.R. Wan in University of Science and Technology, Beijing and Prof. S.Ohnuki in

Hokkaido University are gratefully appreciated for their encouragement and support to my study.

My study belongs to “National construction of high-quality University projects of graduates” of China. I would like to express my gratitude to the China Scholarship Council for supplying me living expenses and also tuition fee in Kyoto University.

Finally, I would like to dedicate this work to Ms. J.Huang, my parents, brother and relatives.

January, 2014

List of publications

• Journal

- (1) “Positron annihilation studies of electron-irradiated F82H model alloys”

S.S. Huang, T. Yoshiie, Q. Xu, K. Sato, T.D. Troev

Journal of Nuclear Material. 440 (1-3) (2013) 617–621.

- (2) Early stage irradiation effects in F82H model alloys

S.S. Huang, X.Q. Pan, K. Sato, Q. Xu, T. Yoshiie

Journal of Nuclear Material, in press (2013).

- (3) Effects of alloying elements on defect structures in the incubation period for void swelling in austenitic stainless steels

M. Horiki, T. Yoshiie, **S.S. Huang**, K. Sato, X.Z. Cao, Q. Xu, T.D. Troev

Journal of Nuclear Material, 442 (2013) 813-816.

- (4) Vacancy migration process in F82H and Fe-Cr binary alloy using positron annihilation lifetime measurement

K.Sato, Q.Xu, D.Hamaguchi, **S.S. Huang**, T.Yoshiie

Journal of Physics: Conference Series Volume 443, Issue 1, 2013, Article number 012031

• Proceedings

- (1) Defect Structures during Incubation Period of Void Swelling in Austenitic and Ferritic Alloys Studied by Positron Annihilation Spectroscopy

S. S. Huang, K. Miyawaki, K. Tsujikawa, M. Horiki, T. Yoshiie, K. Sato, Q. Xu and T.D. Troev

Materials Research Society (MRS) Proceedings, 1526 (2013),

mrsf12-1526-tt01-04 doi:10.1557/opl.2013.594.

(2) Study of neutron irradiated F82H steel and its model Fe-Cr alloy by Mössbauer spectroscopy

S. S. Huang, S.Kitao, Y.kobayashi, T. Yoshiie, Q. Xu, K. Sato, M. Seto

Specialist Research Meeting on Physical properties of applied research and Science of unstable nuclei, December 19, 2012, Research Reactor Institute, Kyoto University, p.26

(3) Defect structural evolution in ferritic alloys

S.S.Huang, K.Sato, Q.Xu, T.Yoshiie, H.Tsuchida, A.Itoh

The 14th open symposium in Quantum Science and Engineering Center, Kyoto University, October 18-20, 2013 Kyoto University, p.10