

**Effect of oxide former elements on ion-irradiation response of
oxide dispersion strengthened ferritic steels**

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Chapter 1

Introduction

1.1 Advanced nuclear energy systems

Nuclear energy has been considered to reduce CO₂ emissions and alleviating global warming to a great extent by replacing with fossil power for electricity generation. From around 1942, fission reactors have experienced several development phases as shown in Fig. 1.1 [1]. The newest system (i.e. Generation IV, GIV), identified as six sorts of reactors, was proposed to deliver advances with respect to energy efficiency, safety and minimal nuclear waste. However, currently, there are 451 civil nuclear power nuclear reactors in operation around the world, most of which were light water reactors (LWRs), classified as generation II (GII) reactors [2].

Since deuterium fusion reactions were discovered in about 1933, especially $^2D + ^3T \rightarrow ^4He$ (3.5 MeV) + *neutron* (14.1 MeV), fusion energy has been recognized as a newer, cleaner and more sustainable one, together with no long-lived radioactive fission products in comparison to fission energy. International thermonuclear experimental reactor (ITER) Tokamak project started under global cooperation from 1988 [3], aiming to enable fusion energy to be accessible and to solve the energy demand completely in the future. No matter in fission or fusion reactors, candidate materials being applied in reactor components should face harsh environmental issues (varying on the components), such as high temperature, high applied stress, severe corrosion and intense irradiations, and so on.

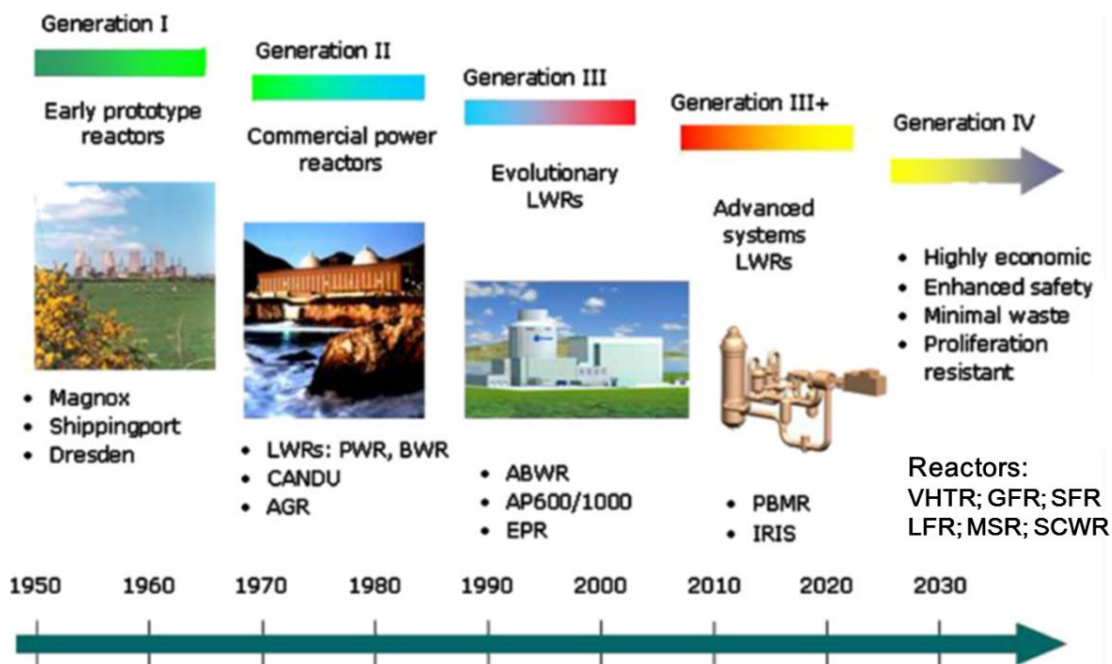
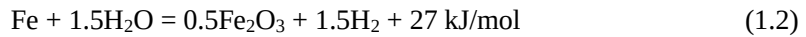
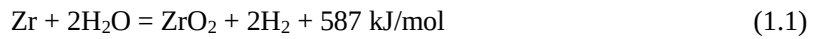


Fig. 1.1 Generations of nuclear energy systems [1].

1.2 Structural materials & fuel claddings in fission reactors

In fission reactors, taking pressurized water reactor (PWR) for an example, numerous steels or alloys were used for different roles and shown in Fig. 1.2 [4]. Austenite steels have been applied widely such as core structures and also outside components (e.g. pipes, dryers), mainly because of

their better ductility, manufacturing properties and excellent corrosion resistance compared with ferritic/martensitic (F/M) steels. Concerning the fuel cladding, it serves to contain the fuel and radioactive fission products while simultaneously efficiently transferring the intense nuclear heat from the fuel cells to the coolants (see Fig. 1.3) [2]. Under these circumstances, in most of fission reactors GI and GII, zirconium (Zr) alloys have been chosen due to the relatively low effective neutron absorption cross section, good compatibility with nuclear fuel, acceptable mechanical properties, as well as high service temperature, corrosion and radiation resistance [5]. However, there is one detrimental chemical property of the Zr-based alloys that the reaction of one mole Zr and H₂O produces more heat and H₂ than the (Fe, H₂O) reaction, as indicated in eq. 1.1 and 1.2 [6]. The produced heat and hydrogen gases led to a fuel core melting and a hydrogen explosion in Fukushima Daiichi Nuclear plant (Japan), respectively [7]. In Gen-IV reactors, high fuel burn-ups also impose stricter design constraints for the fuel cladding candidates, e.g. superior resistance to fast-neutron radiation damage and corrosion resistance, outstanding dimensional stability against thermal (500–1000 °C) and irradiation creep tolerance (doses up to 200 dpa), as shown in Table 1.1 [5]. A variety of materials like austenitic stainless steels, oxide dispersion strengthened (ODS)-F/M steels, Ni-based alloys, Zr alloys and SiC are considered to be the candidates for structural components, and the material depends on the fuel and coolants (see Table 1.1). oxide dispersion strengthened (ODS) steels (hereafter called as ODS steels) have been developed to replace austenitic stainless steels and F/M steels as fuel claddings in terms of high burn-ups and safety of Gen-IV.



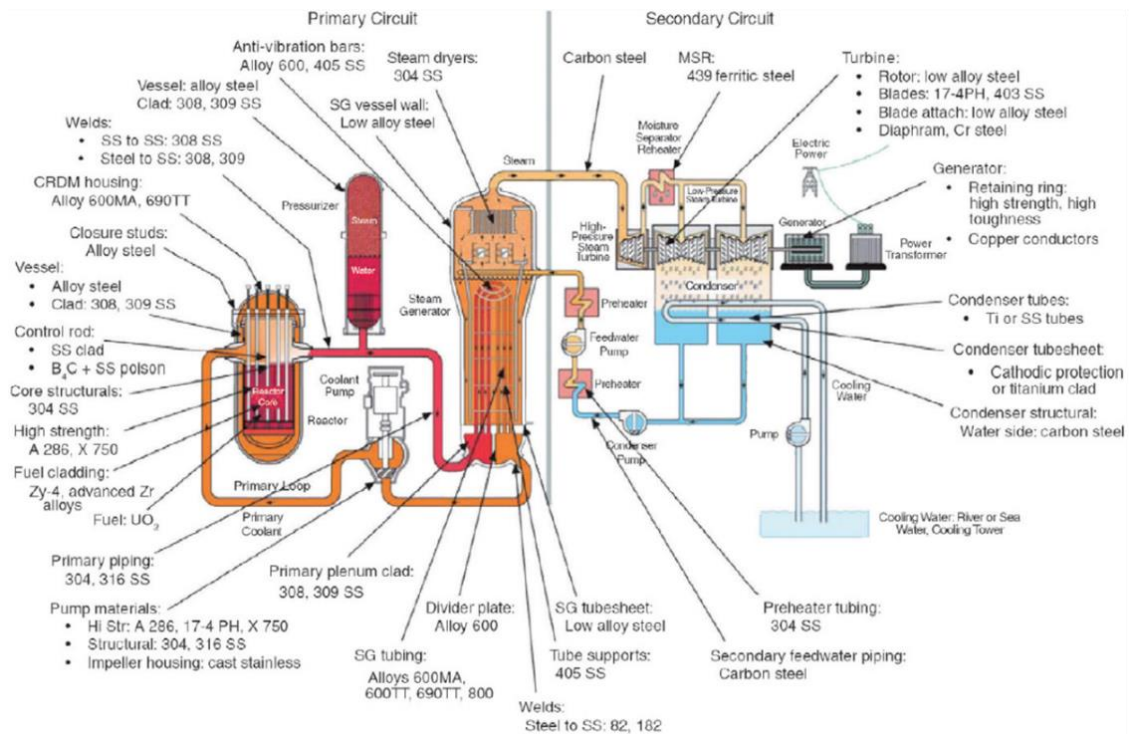


Fig.1.2 Schematic of key components utilizing structural materials in pressurized water fission reactor (PWR) [4].

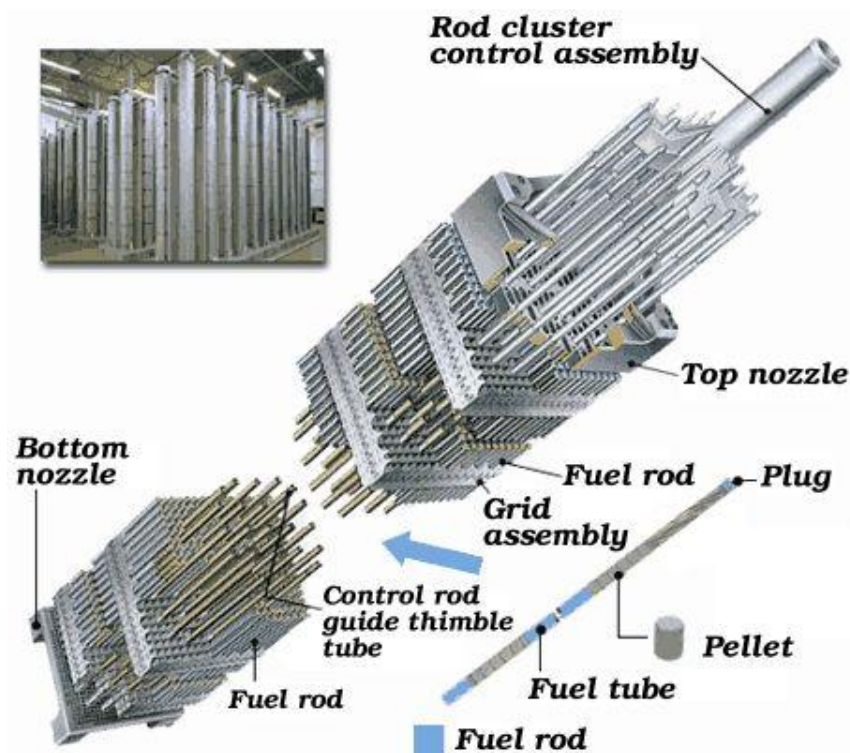


Fig. 1.3 Schematic view of PWR fuel assembly [2].

Table 1.1 Main characteristics of GIV nuclear fission reactor systems [5]

Reactor type	Fuel	Coolant	Moderator	Neutron spectrum	Core outlet temperature (°C)	Dose (dpa)	Candidate cladding material
Super critical water cooled reactor (SCWR)	UO ₂ (thermal) MOX (fast)	Water	Water	Thermal or Fast	~ 550	10–40	Zr alloys; Austenitic stainless steel; F/M steels Ni-based superalloys; ODS alloys
Sodium-cooled fast reactor (SFR)	UPuC/SiC U-Pu-Zr MOX	Liquid Na	–	Fast	~ 550	90–160	F/M steels; ODS alloys
Lead-cooled reactor (LFR)	Nitrides, MOX	Liquid Pb alloys	–	Fast	550–800	50–130	Austenitic stainless steel; F/M steels; ODS alloys SiC; Refractory alloys
Gas-cooled fast reactor (GFR)	(U, Pu)O ₂ Carbide fuel (U, Pu)	He	–	Fast	~ 850	50–90	ODS alloys; Refractory alloys; SiC
Molten salt reactor (MSR)	Salt	Molten salt	Graphite	Thermal	700–800	100–180	No cladding
Very high temperature reactor (VHTR)	TRISO UOC	He	Graphite (thermal)	Thermal or Fast	1000	7–30	ZrC coating; SiC coating

Note: TRISO means tristructural isotropic fuel, a type of micro fuel particle consisting of a fuel kernel composed of uranium oxide (sometimes uranium carbide) in the center, coated with four layers of three isotropic materials.

1.3 Structural materials in fusion reactors

There are differences in environmental operating parameters between Gen-IV fission and future fusion reactors, as shown in Table 1.2. Irrespective of fission/fusion systems, good thermal conductivity, dimensional stability and readily manufacturing property are demanded for the structural materials. In fusion reactors, the first wall/blanket (see Fig. 1.4, a water cooled ceramic breeder blanket concept) is the key component for power extraction, tritium fuel sustainability and radiation shielding and the requirements of the structural materials include the resistance to severer neutron radiation damages, transmutation effects (e.g. He effects), mechanical load and shock, and good compatibility with coolant and tritium breeders at elevated temperatures. The concept of reduced activation materials is another requirement. Under these circumstance, reduced activation ferritic steel (RAFS), V alloy and SiC/SiC composites are proposed as the leading candidate structural materials matching with each coolant and tritium bleeder as shown in Table 1.3.

The operation temperature range of fusion reactors is up to that of the structural materials, of which the lower and upper limits are generally determined by the radiation embrittlement and by the thermal creep. Furthermore corrosion issues and He/H deterioration effects of the structural materials may determine the lifetime of the blankets. In Fig. 1.5, it is shown that ODS steels possess an expanded operation temperature window in comparison to the conventional RAFS. Therefore, ODS steels are considered to be applied to the structural components of advanced blankets which require enhancing the thermal efficiency and providing more design margin of the blanket.

Table 1.2 Environmental operating parameters for fusion and fission systems [8].

Parameters	Fusion	Fission (Generation IV)
Working fluid	H ₂ O, He, Li, PbLi, FLiBe	H ₂ O, He, Na, Pb, PbBi
Energy	<14.1 MeV	<1–2 MeV (most neutron's spectrum), ~hundred MeV fission fragments (cladding)
He appm/dpa	~10–15 (first wall/blanket)	0.1–50
Heat flux, MW/m ²	1–10 (steady-state)	~1
Stresses	Moderate, slowly varying*	Moderate, slowly varying

*For normal operation. In a plasma disruption the stresses to the structure are to “high, transient”. High, for fusion, indicates stress levels that are near the allowable maximum fraction of yield stress under applicable engineering design rules. FLiBe is a LiF-BeF₂ molten salt.

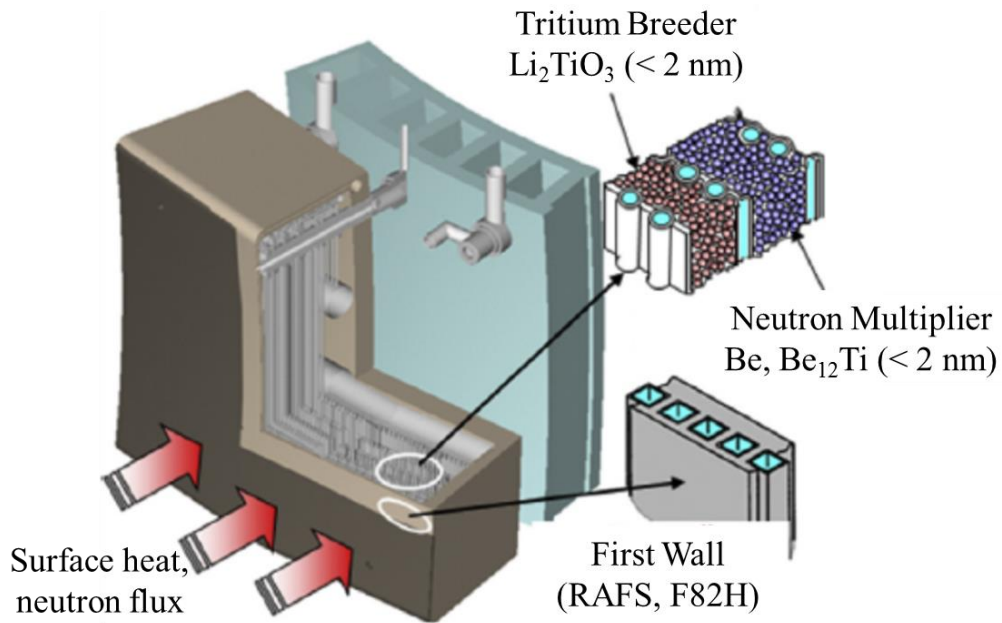


Fig. 1.4 Water cooled ceramic breeder blanket concept (pressurized or supercritical water as coolant) [9].

Table 1.3 Summary of leading proposed structural materials, coolant and tritium generation concepts for fusion energy systems. The filled cells in the table indicate material combinations that are under consideration for fusion energy blankets. FLiBe is a LiF-BeF₂ molten salt [4].

Structural Material	Coolant/Tritium Generating Material System					
	Li/Li	He/PbLi	H ₂ O/PbLi	He/Li ceramic	H ₂ O/Li ceramic	FLiBe/FLiBe
ferritic steel						
V alloy						
SiC/SiC						

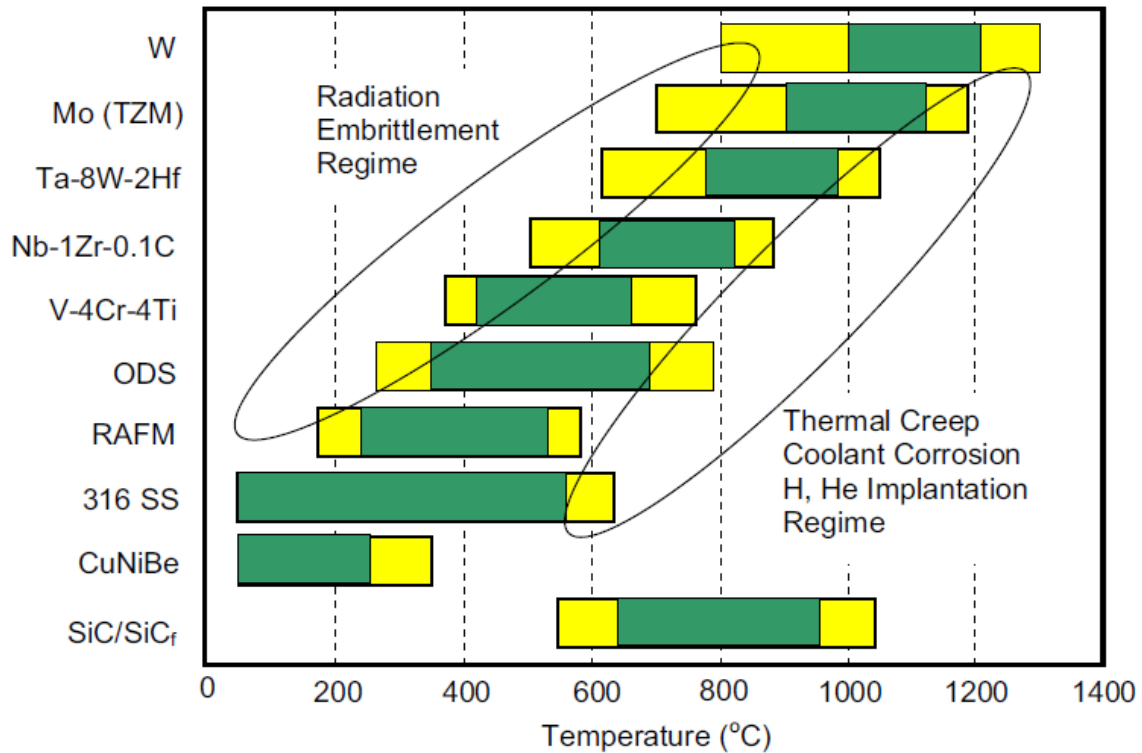


Fig. 1.5. Operating temperature windows of some candidate fusion reactor materials for the neutron irradiation giving rise to 10–50 dpa. The radiation embrittlement and thermal creep regimes delineate the minimum and maximum allowable operating temperature limits of these materials. Green (darker) areas indicate safe and yellow (lighter) areas marginal operating ranges [10].

1.4 Radiation effects on solids

1.4.1 Radiation defects, hardening and swelling

Energetic neutrons transfer most of their energy to primary knock-on atoms (PKAs) during the collisions with the target atoms. Meanwhile, the PKA atom would bring about collision cascade in solid, which is shown in Fig. 1.6. An atom-depleted zone surrounded by the ejected interstitials is temporary formed to be cascade and the subsequent cascade quenching and defect migrations results in the formation of point defects like vacancies and interstitial atoms, and their clusters including two-dimensional defects like dislocation loops and three dimensional defects like voids and stacking fault tetrahedral (SFTs). If alloying elements are involved in the processes, the second phase precipitates and phases (e.g. Cr α' phase, similar lattice constants with bcc ferritic phase) would be formed in the matrix and alloy element segregation would occur on grain boundaries, both of which the processes depend on the irradiation parameters such as the temperature and displacement rate. In addition, He and H are possibly produced by the corresponding transmutation reactions (n, α) and (n, p), and consequently He-vacancy clustering and H segregation at grain boundaries (GB) often occurs.

Radiation-induced defects, precipitates and phases in grains can impede dislocation motion,

leading to an increase in the strength accompanied by reduction in ductility of the solid materials, which is called as radiation hardening/embrittlement. Fig. 1.7 shows the schematic view of the microstructures after fusion neutron irradiation, where He bubbles or voids, dislocation loops existing in one grain of oxide dispersion strengthened (ODS) F/M steels. It is reasonable to say that strengthening effects of radiation defects should be superposed on the strength contributors of dislocation lines, oxide particles and precipitates existing in the grain prior to irradiations. Accompanied by the radiation hardening, the ductility is possibly reduced by the dislocation channeling mechanism due to defects, which can be reflected by the shift of the ductile-brittle transition temperature (DBTT) towards higher temperatures.

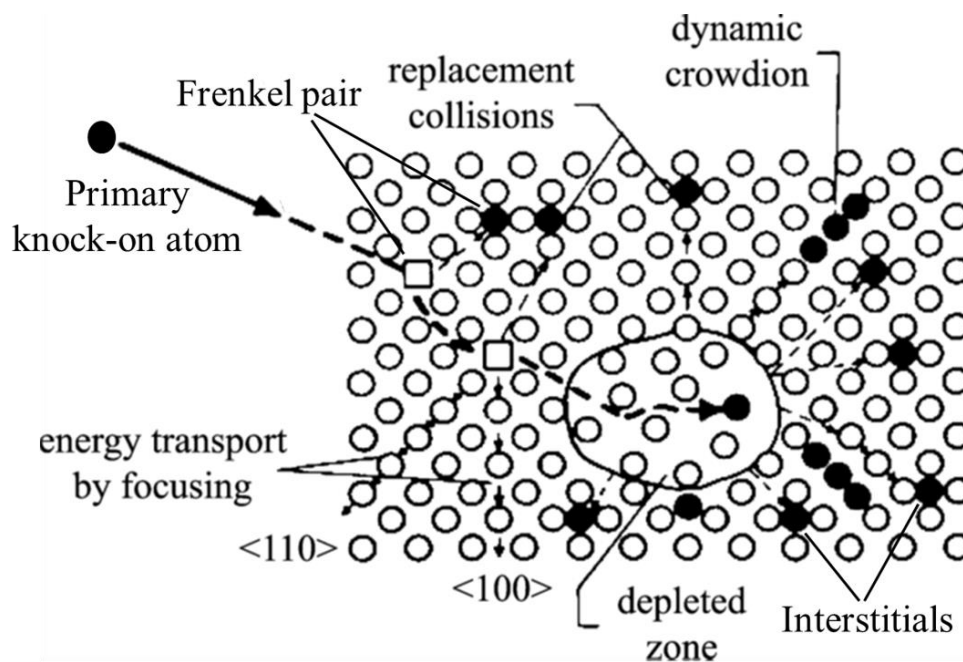


Fig. 1.6 Schematic of one cascade collision caused by one PKA atom [11].

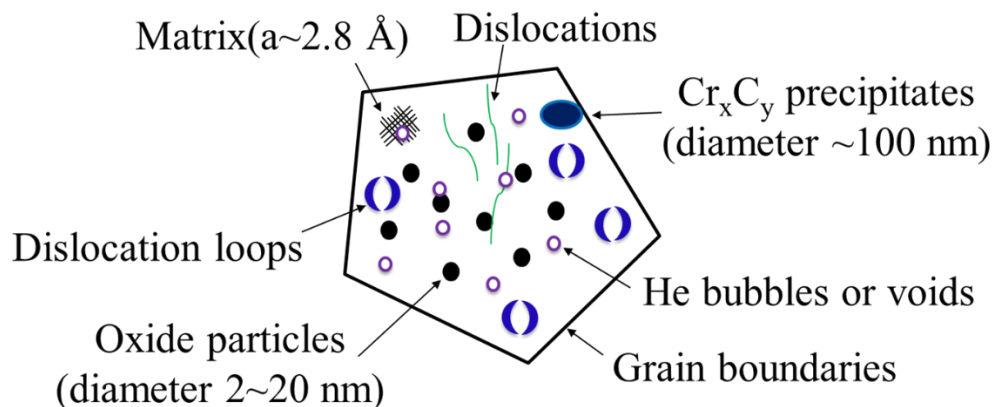


Fig. 1.7 Dislocation loops, He bubbles or voids existing in one grain of ODS steels.

Vacancy clusters (voids) and He-vacancy clusters (pressurized He bubbles) in structural materials can cause the volume expansion, finally influencing the dimensional stability of the structural components. The void swelling can be represented in terms of the void size distribution and defined as the following equation [11]:

$$\frac{\Delta V}{V} = \frac{4\pi}{3} \int_0^{\infty} r^3 N(r) dr \quad (1.3)$$

where r is the void radius and $N(r)dr$ is the number of voids per unit volume with radii between r and $r + dr$. The void swelling of structural materials is affected by many factors, including irradiation temperatures, the He appm/dpa values and the material characters like intrinsic sinks in (e.g. dislocations, precipitates or nanoclusters, GB areas), alloy solutes. Fig. 1.8 shows the swelling of FeCr alloys as a function of Cr content after ion irradiations at 13 appm He/dpa up to 128 dpa at 773 K. It is clearly noted that with increasing Cr content, the variation of void swelling is non-monotonic, with an initial drop by the addition of 3–5 wt.% Cr followed by a local swelling maxima around 9–10 wt.% Cr [12]. The strong initial decrease of swelling by the addition of only few percent of Cr can be explained by dislocations (lines and loops) formed after irradiations, which act as sinks for point defects nucleation or recombination. But the non-monotonic swelling at higher Cr levels is still an open to debate [12].

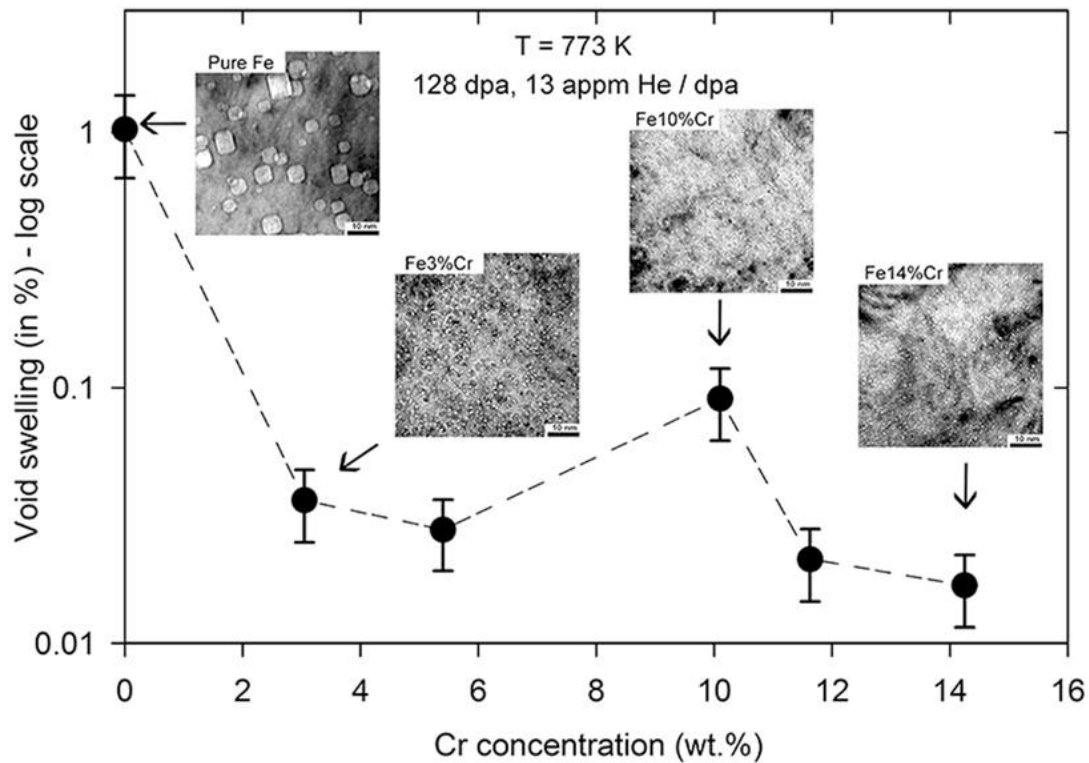


Fig. 1.8 Effect of Cr on cavity swelling in ion irradiated FeCr alloys [12].

1.4.2 Difference in damage morphology among irradiation particles

Neutron irradiation effects often compared with the effect of the other particles irradiation, electron and ion. The displacement morphology is significantly affected by mass of particles irradiated and displacement rate, which is described briefly in Table 1.4 [13]. It can be said that neutron irradiation experiments are time consuming and it needs special attention to the irradiation conditions especially temperature and dose. Moreover, the irradiated specimens are with high level radioactivity, which does not benefit for post-irradiation characterizations.

Electrons: Electron produces a few widely spaced Frenkel pairs (FPs) that have low probability of recombination. The displacement efficiency, which is defined as the fraction of the Frenkel pairs surviving after the cascade quenching, is high.

Protons: Proton produces small widely spaced cascades and many isolated Frenkel pairs.

Neutrons and heavy ions: Neutron and heavy ion produce dense cascades that result in substantial recombination during the quenching process, with a low displacement efficiency. However, as for the heavy ion irradiations, the displacement rate produced by all collisions is generally 3–6 orders of magnitude higher than the counterpart of neutron irradiations (see Table 1.4).

Therefore, the heavy ions irradiation is time-saving and economic way for reaching the comparable displacement levels, possibly being utilized to simulate neutron irradiations for assessing radiation tolerance of the candidate materials, while the damage rate effect should be considered.

Table 1.4 Comparison of different particle irradiation experiments [13].

Particle type	Energy, MeV	Irradiation temperature, °C	Efficiency	Displacement rate, dpa/s	
				Reported	Real
Electrons	1.0	450	1.0	1.9×10^{-3}	1.9×10^{-3}
Protons	3.4	400	0.2	7.0×10^{-6}	1.4×10^{-6}
Ni ²⁺ ions	5.0	500	0.04	5.0×10^{-3}	2.0×10^{-4}
Neutrons	Fission reactor	288	0.02	4.5×10^{-8} ($E > 1$ MeV)	9.0×10^{-10}

1.5 Current status of oxide dispersion strengthened (ODS) steels

1.5.1 Methods of manufacturing

As described in the previous sections 1.2 and 1.3, the ODS steels have been considered to be applied to the fuel cladding of fission reactors and the first wall/blanket structural components of fusion reactors. In addition to the improvement in high-temperature strength, radiation and corrosion resistance, the manufacturing method for large scale ODS steels is also under exploration. Generally, ODS steels are produced by powder metallurgy method involving mechanical alloying (MA) of Y₂O₃ and pre-alloyed or elemental metallic powders, followed by consolidation techniques, such as hot

isostatic pressing (HIP) or hot extrusion. However, spark plasma sintering (SPS) method is adopted as more cost-effective way in comparison with HIP, while during the latter very high pressures (several hundred MPa) and long soak times (several hours) are necessary to obtain high density bulk ODS alloys [14]. Particularly, SPS offers the potential for scale-up beyond the laboratory scale on ODS steels. It was reported that the Ti, Y-added ODS ferritic steel was fabricated by SPS subsequent to MA, possessing a high density (99.6%) and uniformly dispersed $\text{Y}_2\text{Ti}_2\text{O}_7$ nanoclusters of < 5 nm in diameter and high number density of $1.04 \times 10^{23} \text{ m}^{-3}$ [14].

1.5.2 Oxide particles, high-temperature strength and corrosion resistance

Yttria (Y_2O_3) was generally selected as the reinforcement particle because it was more stable thermodynamically than nitrides and carbides [15]. Meanwhile, Ukai et al. first recognized the importance that adding Ti can effectively refine the size of the Y_2O_3 -like dispersoids [16]. As a result, the majority oxide particles in ODS steels became Y-Ti complex oxides according to the two types of combination, i.e. $\text{Y}_2\text{O}_3 + \text{TiO}_2 \rightarrow \text{Y}_2\text{TiO}_5$ and $\text{Y}_2\text{O}_3 + 2\text{TiO}_2 \rightarrow \text{Y}_2\text{Ti}_2\text{O}_7$. Both Y-Ti complex oxides are thermodynamically stable at elevated temperatures, even above 2273 K [17]. In addition, other oxides such as Y_2O_3 with cubic structure, YTiO_3 , TiCr_2O_4 , $\text{Ti}(\text{C}, \text{O}, \text{N})$ were also found in ODS steels with the Y, Ti addition [18]. However, there are some evidences to support the possible existence of non-stoichiometry (Y, Ti) oxides with the oxygen deficiencies [19] and (Y, Ti) oxides surrounded by Cr-shell [20].

The nano-oxide particles dispersed in the steel matrix can act as obstacles to dislocation glide and also suppress their recovery at elevated temperatures. The interaction between oxide particles and dislocations were confirmed to be the Orowan by-pass mechanism and the cross-slip system by in situ dynamical TEM tensile test [21]. For the Orowan by-pass mechanism, an Orowan dislocation loop should be left around oxide particle assuming the particle is impenetrable, as shown in Fig. 1.9. The barrier strength factor of oxide particles depends on various factors, such as the particle type, size and the degree of coherency etc. In general, for a given volume fraction, finer oxide particles with higher number density offer to the ODS steels higher strength, especially high temperature strength (e.g. creep rupture strength). It was reported that the strengthening contributed by oxide particles was more than 45% of the measured room temperature yield stress of ODS steels [22].

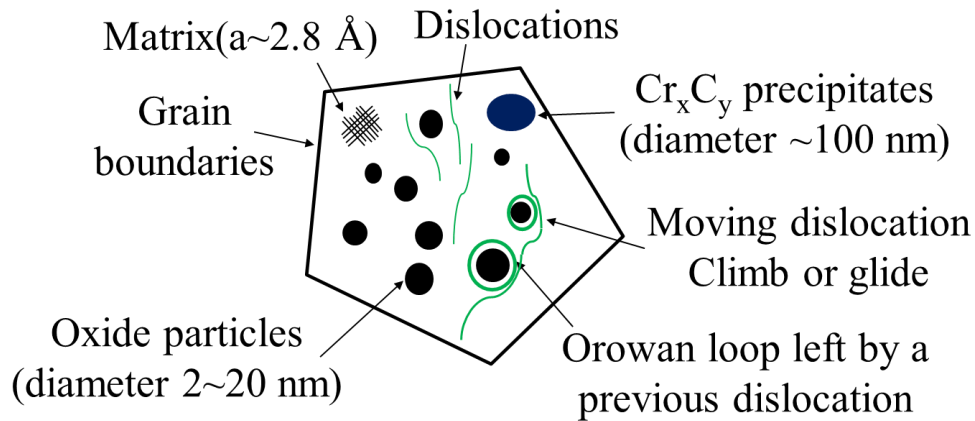


Fig. 1.9 Interaction between dislocations and impenetrable oxide particles.

Corrosion resistances of ODS steels with or without Al addition, austenitic steel and non-ODS ferritic/martensitic steel are compared in Fig. 1.10 [23]. It clearly illustrates that high Cr (10–20 wt.%) ODS alloys with Al addition possess better corrosion/oxidation resistance than other steels, mainly due to the formation of protective (Fe, Cr) oxides (e.g. spinel structure) and Al_2O_3 in corrosion environments. The high Cr-ODS steels with sufficient Al addition (> 5 wt.%) are being considered to replace Zircaloy as fuel cladding in LWRs for enhanced accident tolerance. However, the Al-addition to FeCr-ODS steels altered the main particles from (Y, Ti) oxide nanoparticles to coarser YAlO_3 (YAH, YAP) [24], which reduced the high-temperature strength of ODS steels significantly (see Table 1.5) [23]. Such reduction was effectively suppressed by a small addition of Zr or Hf to FeCrAl ODS steels where the majority of oxide particles became fine Y-Zr-O or Y-Hf-O dispersoids [25]. Besides, ODS alloys with the Cr content more than 12 wt.% are readily susceptible to aging embrittlement due to the formation of a Cr-rich α' phase in the service temperature range of ~ 400 – 550 °C, so called the 475 °C aging embrittlement [26].

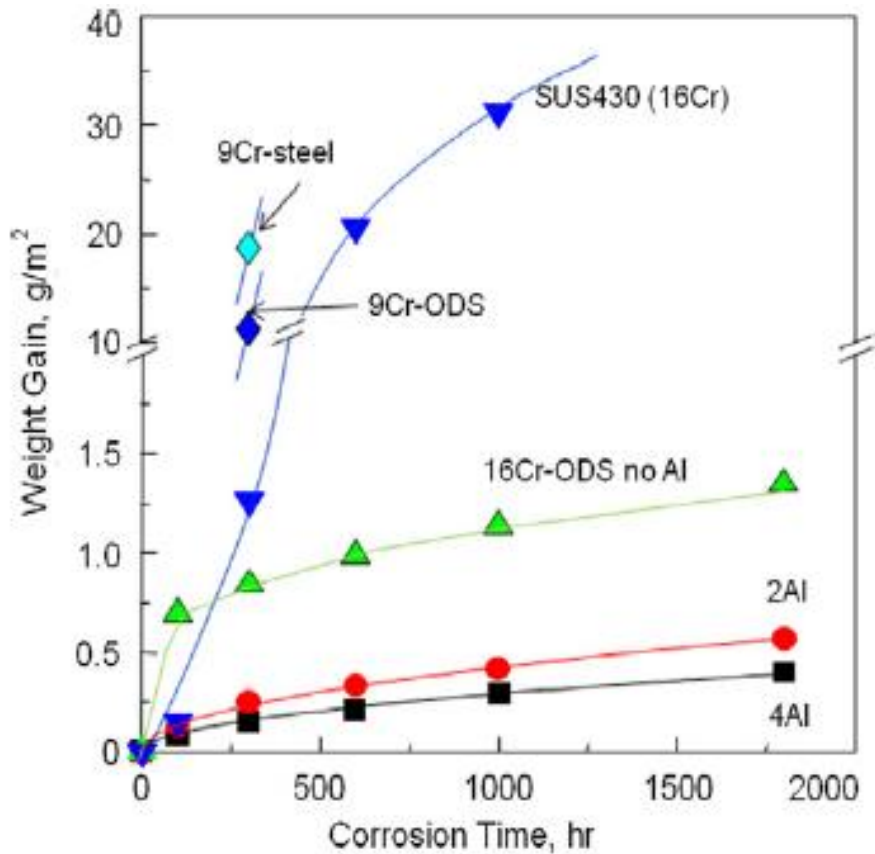


Fig. 1.10 Weight gain after corrosion tests in SCPW (783 K, 25 MPa) up to 1800 h [23].

Table 1.5 Creep test results at 973 K of each candidate ODS steels [23].

ODS steels	Creep strength (973 K, 10 kh), MPa
16Cr-ODS	100
16Cr-4Al-ODS	60
16Cr-4Al-ODS-Zr	120
16Cr-4Al-ODS-Hf	110

1.5.3 Radiation resistance

Radiation effects on ODS steels have been investigated especially on microstructures including radiation defects, phase transformation and second phase precipitation, as well as swelling and hardening behaviors under a wide variety of irradiation conditions. Table 1.6 depicts the selected results of defects in ODS alloys after particle irradiations. As for the dislocation loops induced by ion irradiation, the followings can be recognized:

- 1) The dominant dislocation loops are $1/2\langle 111 \rangle$ loops with the small fraction of $\langle 100 \rangle$ loops at lower temperatures below 300 °C, and it is only $\langle 100 \rangle$ loops at around 400 °C, and both loops disappear at above 420 °C.

- 2) At 500 °C, no loops formed in ion-irradiated ODS steels but both $\frac{1}{2}\langle 111 \rangle$ and $\langle 100 \rangle$ loops still form under neutron irradiations, demonstrating a possible positive temperature shift for ion irradiations.
- 3) Voids can form and stably exist at further elevated temperatures no matter ion or neutron irradiations.

The above temperature dependence did not always stand on under more complicated irradiation conditions. J. Chen et al. [27] reported that both the interstitial loops of $\langle 100 \rangle$ and $\frac{1}{2}\langle 111 \rangle$ type formed in PM2000 strengthened by (Y, Al) oxides after He implantations (3000 appm, 0.75 dpa) at 300, 400, 500 °C and under the applied stress of 20–250 MPa. Concerning the Cr-rich α' phase precipitates, they can be produced by neutron irradiations with low displacement rates ($\leq 10^{-5}$ dpa s⁻¹) in FeCr alloys (Cr $\geq$ ~9 wt.%) including ODS alloys, but they were seldom reported in ion irradiated ODS F/M steels or non-ODS alloys [28, 29].

Void formation behaviors in ODS F/M steels and conventional non-ODS F/M steels have been investigated in numerous studies. Fig. 1.11 shows the void formation morphologies in K3-ODS steel and in JLF-1 RAF steel after single- and dual-ion irradiations. In dual-ion irradiation with ion and He ions, much finer He-vacancy clusters were formed in the ODS steel, which resulted in a smaller swelling (see Fig. 1.12) than in RAF steel. The reason should be the significant trapping effects of oxide particles/matrix (O/M) interfaces on helium interstitials and vacancies. This phenomena has been confirmed by numerous experimental results as shown in Fig. 1.13. In addition, no DBTT shift or fracture mode change was observed in He-implanted 9Cr- and 14Cr-ODS steels whereas the DBTT shift was 70 °C for F82H RAFM steel after He implantation up to 1000 appm at around 550 °C. The DBTT shift was attributed to the formation of numerous He bubbles formation at grain boundaries [30].

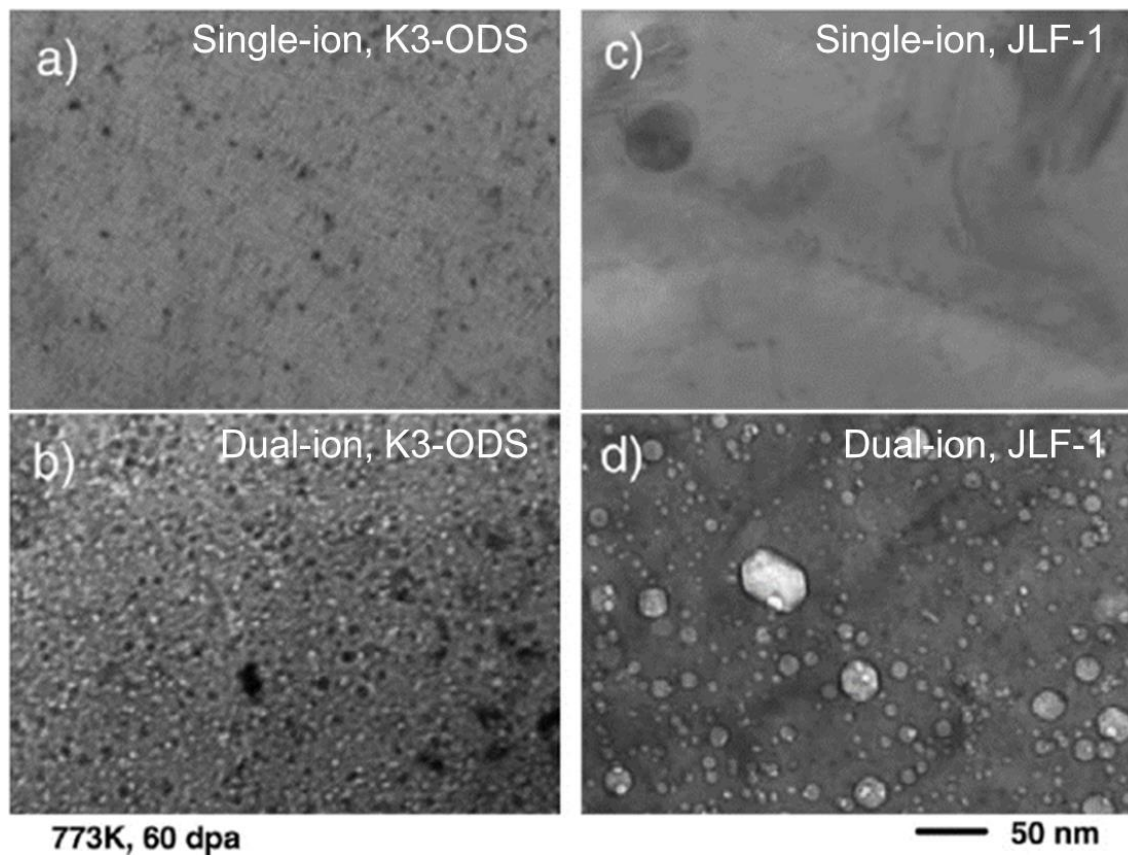


Fig. 1.11 TEM images of K3-ODS ferritic steel and JLF-1 RAF steel under single- and dual-ion irradiations at 773 K, 60 dpa [31].

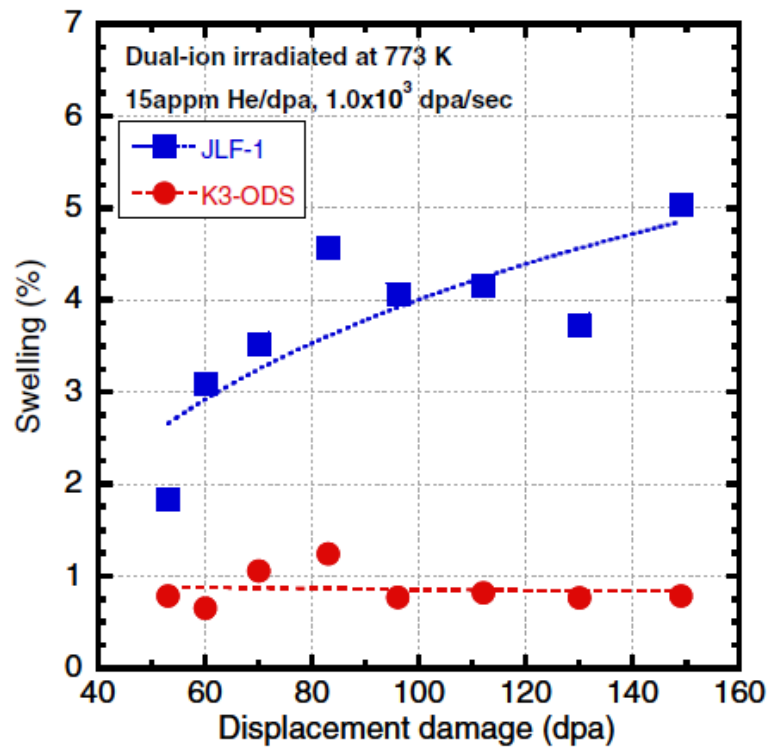


Fig. 1.12 The swelling versus dpa between K3-ODS steel and JLF-1 RAF steel after dual-ion irradiation at 773 K [31].

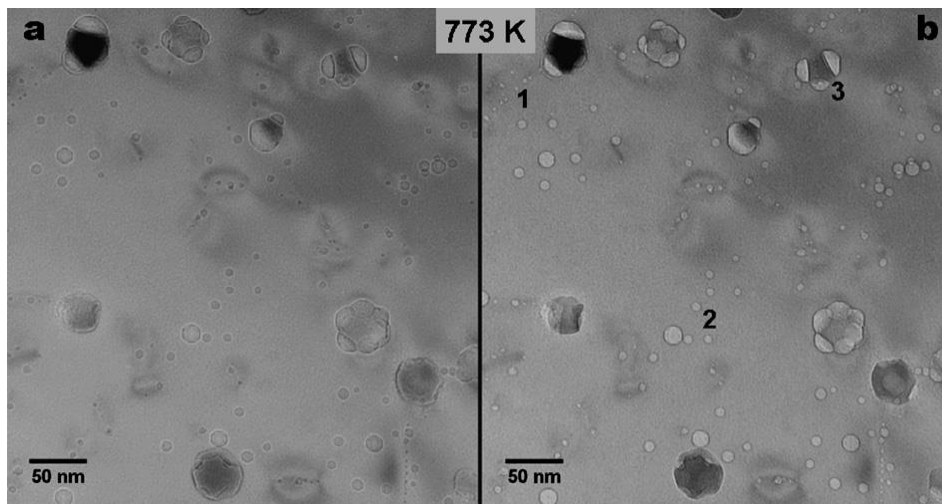


Fig. 1.13 Bubble/ODS particle complex in PM2000 ODS ferritic steel implanted with α -particles at 773 K: (a) over- and (b) under-focused [27].

Table 1.6 Radiation defects in selected ODS steels after various irradiations

ODS alloys	Main oxides	Temperature	Damage & He content	Beams	Defects	Articles
16Cr-4Al ODS	Y-(Al, Zr, Hf)-O	500 °C	10 dpa	Electrons	Dislocation loops (low number density) on oxide particles	[32]
CRPP ODS	Y-Ti-O	40 °C	1.0 dpa	Protons	Black dots of 2–3 nm	[33]
CRPP ODS	Y-Ti-O	350 °C	1.0 dpa	Protons	Loops <100> {100} with nano-cavities	[33]
MA956, MA957	Y-Ti-O	420 °C	200 dpa	Neutrons	Loops <100> and primarily 1/2 <111> network; Voids truncated between dodecahedra and cubes	[34]
PM2000	Y-Al-O	500 °C	~21 dpa	Neutrons	Loops <100> ($8.0 \times 10^{20} \text{ m}^{-3}$), 1/2<111> ($4.0 \times 10^{20} \text{ m}^{-3}$); He bubbles (~1 nm) and voids (8.8 ± 5.0) of low density (10^{21} m^{-3})	[35]
16Cr-4.5Al-ODS	Y-Al-O	300 °C	1, 10 dpa	6.4 MeV Fe	Loops <100> and 1/2 <111>, 8 nm for 1 dpa and 16 nm for 10 dpa	[36]
Eurofer-ODS	Y-Ti-O	400 °C	26 dpa	Fe	Loops <100> (over 75%) and 1/2<111>; No cavities	[36]
Eurofer-ODS	Y-Ti-O	400 °C	26 dpa	Fe, He or Fe, He, H	Loops <100> and 1/2 <111>; Cavities with low swelling (<0.1%)	[37]
MA956	Y-Ti-O	440, 570 °C	1, 5, 10 dpa	Ne-ions	Voids	[38]
16Cr-4.5Al-ODS	Y-Al-O	500 °C	60 dpa, 900 appm He	6.4 MeV Fe, 1 MeV He	Obvious cavities; No loops	[36]
16Cr-4.5Al-ODS	Y-Al-O	500 °C	20 dpa	6.4 MeV Fe	No loops observed; No cavities	[36]
12 YWT ODS	Y-Ti-O	650 °C	50 dpa, 260 appm He	3.2 MeV Fe & 330 keV He	Bubbles and voids (not bimodal size distribution); High-density dislocations, clusters; No dislocation loops	[39]

It is also expected that ODS steels perform better against irradiation hardening and He-embrittlement because the O/M interfaces work as trapping sites for point defects recombination. Nonetheless, there are some discrepancies in experimental results of the radiation hardenings of ODS F/M steels and RAFM steels. In Fig. 1.14, radiation hardening was compared between ODS F/M steels and non-ODS RAFM steels under ion irradiations [40], which showed a similar hardening potential between the ODS-Eurofer steel and the other steels. It was noted that simultaneous dual-ion (Fe, He) irradiations caused more hardening than single-ion irradiations in the steels (Fe9%Cr, T91, Eurofer97 and ODS-Eurofer).

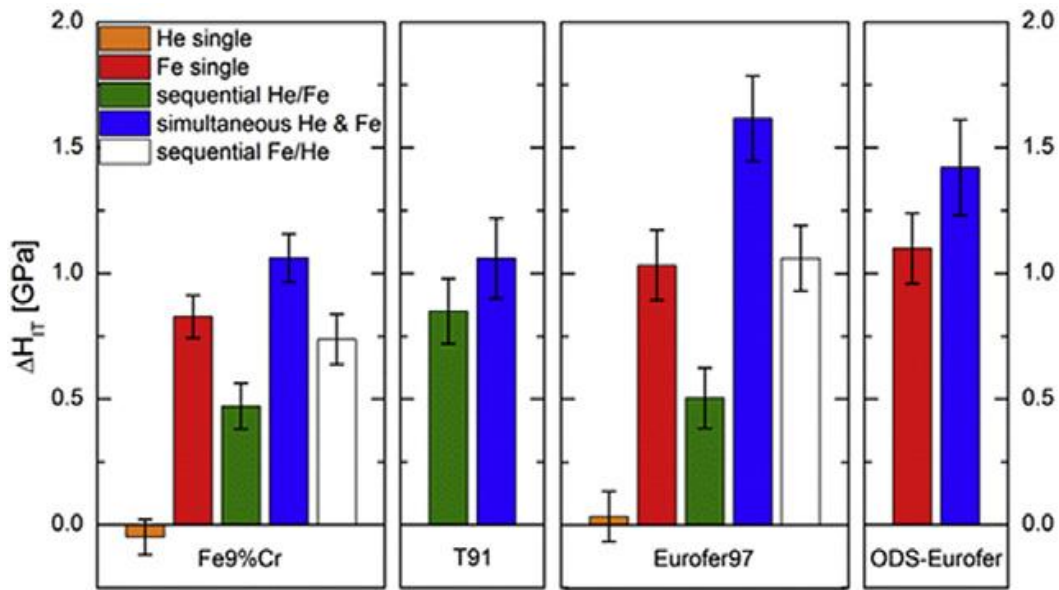


Fig. 1.14 Radiation hardening in RAFM steels (Fe9%Cr, T91, Eurofer97) and ODS-Eurofer after ion-irradiations (300 °C, up to 5 dpa, up to 100 appm He) [39].

Concerning the phase stability of ODS steels, most works focused on the complex (Y, Ti, O) oxide particles such as pyrochlore $Y_2Ti_2O_7$. The morphology, chemical compositions and crystal structure have been investigated under a wide variety of irradiation conditions. Unfortunately, the obtained results showed that there were many disagreements among the studies on the irradiation effects on the size and number density of nano-oxide particles as well as the compositions, Y/Ti and (Y+Ti)/O ratios, especially in the irradiation temperature range of 300–700 °C [41]. Such disagreement might be due to the variety in the possible mechanisms depending on irradiation conditions: ballistic dissolution by atomic displacements, Ostwald ripening, irradiation-enhanced diffusion and irradiation-induced homogeneous precipitation [14], one or the combination of which may result in a variety of influences on the phase stability of nano-oxide particles under irradiation.

The research on the roles of different type oxide particles in radiation resistance of different ODS steels was so limited, although a few study was performed to investigate the radiation-induced

defects, swelling and hardening of ODS steels strengthened by different oxide particles. In Hf- or Zr-added ODS steels, dislocation loops showed a lower growth rate and a lower number density compared with the Al-added ODS steel after the 1.25 MeV electron in situ irradiation up to 10 dpa at 773 K, which was explained by the sink effect at the O/M interface [32].

1.6 Objective of this study

As mentioned in the above sessions, the selection of oxide former elements are essential to achieve high performance properties in ODS steels. As a result of the selection, different type of oxide particles were formed with the different dispersion morphologies, degrees of coherence with the steel matrix, and even orientation relationships with the matrix. Considering the importance of oxide particles in contributing to the high-temperature strength and radiation resistance of ODS steels, it is worth to figure out the phase stability of different oxide particles in the radiation resistance for further developing the ODS steels. In this research, the radiation effects such as He bubble formation behavior, swelling, hardening and phase stability were investigated for three different type of ODS steels with different sort of complex oxides.

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Chapter 2

Materials and methodologies

2.1 Introduction

In this chapter materials, irradiation conditions and test methods used are introduced. The studied ODS steels were fabricated by Kyoto University under the cooperation with KOBELCO company. The basic properties were measured by Kyoto University.

2.2 Materials

2.2.1 Fabrication procedure

Three (14–15) Cr ferritic ODS steels, Y-Ti-ODS, Y-Al-ODS and Y-Zr-Al-ODS were produced by mechanical alloying (MA) method with elemental raw powders plus Y_2O_3 powders, of which the chemical compositions were shown in Table 2.1. The mechanically alloyed mixed powders were encapsuled in a steel capsule, followed by hot extrusion at 1150 °C into a bar with about 30 mm diameter. After hot extrusion, the bar was hot forged at 1150 °C into 5 mm thick plates except for Y-Al-ODS. The final heat treatment condition of Y-Ti-ODS and Y-Zr-Al-ODS was an annealing at 1050 °C for 1 h and air-cooled, while it was at 1150 °C for 1 h and air cooled for Y-Al-ODS. Manufacturing process of three ODS steels was shown in Fig. 2.1. More details can be found in in Ref. [1]. According to Fe-Cr binary phase diagram, above ~830 °C, Fe-Cr alloy forms a single body-centered-cubic (bcc) ferritic phase within a wide range of Cr concentrations [2].

As for Y-Ti-ODS, in order to obtain the dispersion of slightly bigger oxide particles morphology, a bulk specimen was heated at a rate of 30 °C per minute up to 1350 °C and isothermally annealed for 1 h in a vacuum condition ($\sim 1 \times 10^{-3}$ Pa) in a hot press machine (versatile high temperature furnace, FVPHP-R-5, Fuji Dempa Kogyo Co.), and then furnace cooled. The Y-Ti-ODS after recrystallization was named by Recry. Y-Ti-ODS.

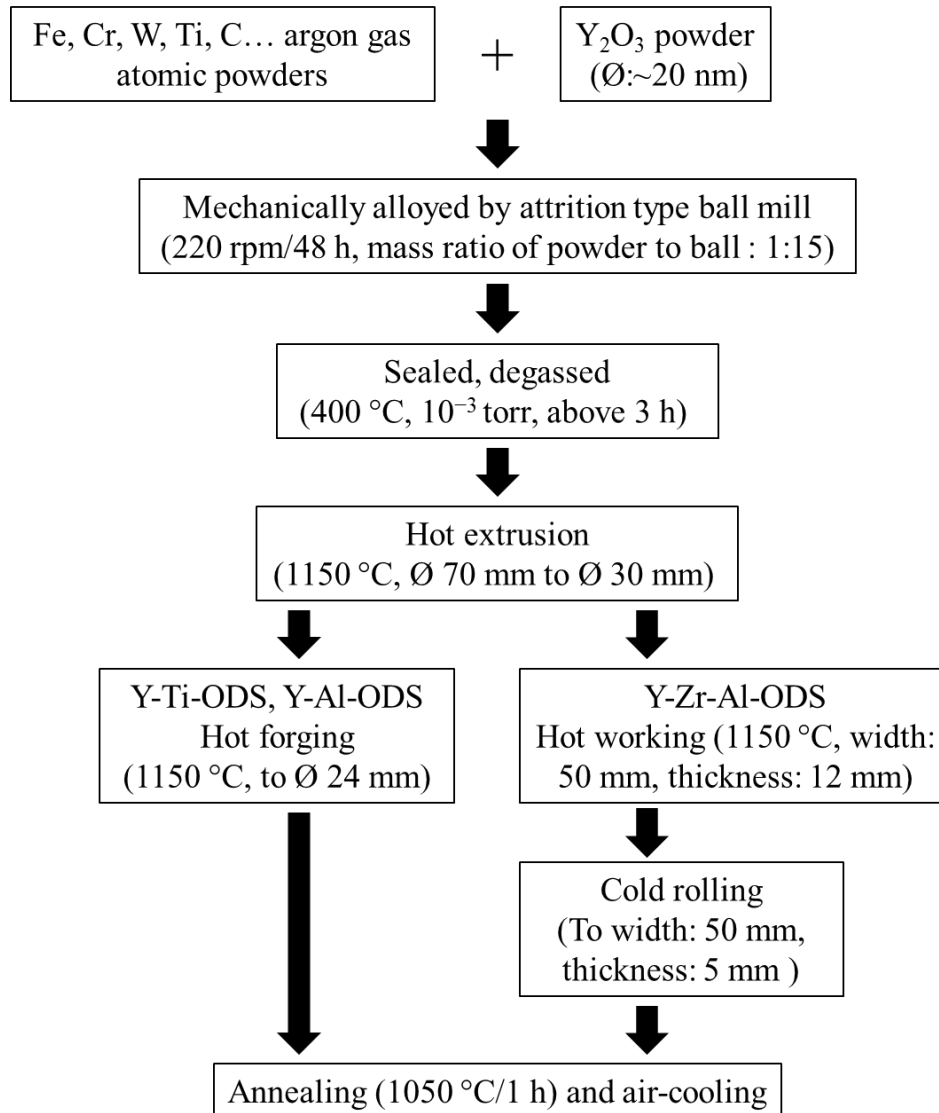


Fig. 2.1 Manufacturing process of Y-Ti-ODS, Y-Al-ODS and Y-Zr-Al-ODS steels.

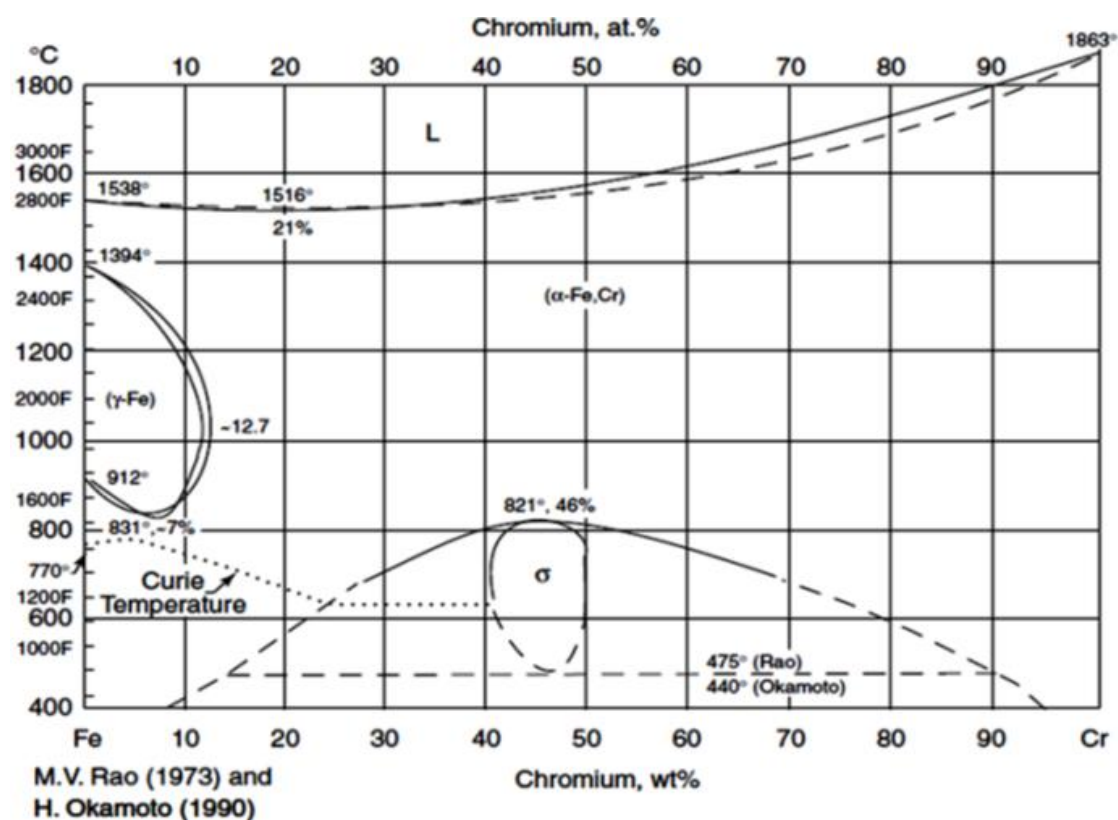


Fig. 2.2 Fe-Cr binary phase diagram [2].

Table 2.1 Resultant chemical compositions of Y-Ti-ODS, Y-Al-ODS and Y-Zr-Al-ODS steels

Elements	Chemical compositions (wt. %)		
	Y-Ti-ODS	Y-Al-ODS	Y-Zr-Al-ODS
C	0.045	0.03	0.03
Si	0.03	0.02	0.02
Mn	0.03	0.05	0.01
Cr	13.6	15.42	14.59
W	1.9	1.85	1.84
Al	0.02	3.8	3.46
Ti	0.16	0.1	0.14
Zr	-	-	0.27
Y	0.26	0.28	0.26
O	0.11	0.16	0.185
Y ₂ O ₃ (Calculated)	0.33	0.36	0.33
Ex. O (Calculated)	0.04	0.04	0.11

“-” means “not being detected”; “Ex. O” means excess oxygen concentration.

2.2.2 Grain morphology

The grain morphologies of Y-Al-Zr-ODS and Y-Ti-ODS were observed by the electron backscatter diffraction (EBSD) technique using ZEISS Ultra55 field emission scanning electron microscopy (FESEM) and the averaged grain size was estimated by averaging those of 3000 grains for each ODS steel. In Fig. 2.3, different colors represent for different grains. In Y-Al-Zr-ODS and Y-Ti-ODS steels, the grains were not homogenous and most were less than 1 μm . The grain size diameter (μm) distributions of the two ODS steels are shown in Fig. 2.4 and the averaged grain sizes were estimated to be about 0.37 μm . The grain morphology of Y-Al-ODS was characterized by scanning transmission electron microscopy (STEM) by using a 200 kV JEM 2200FS field emission microscope, and shown in Fig. 2.5. The average grain size of Y-Al-ODS was roughly 0.46 μm .

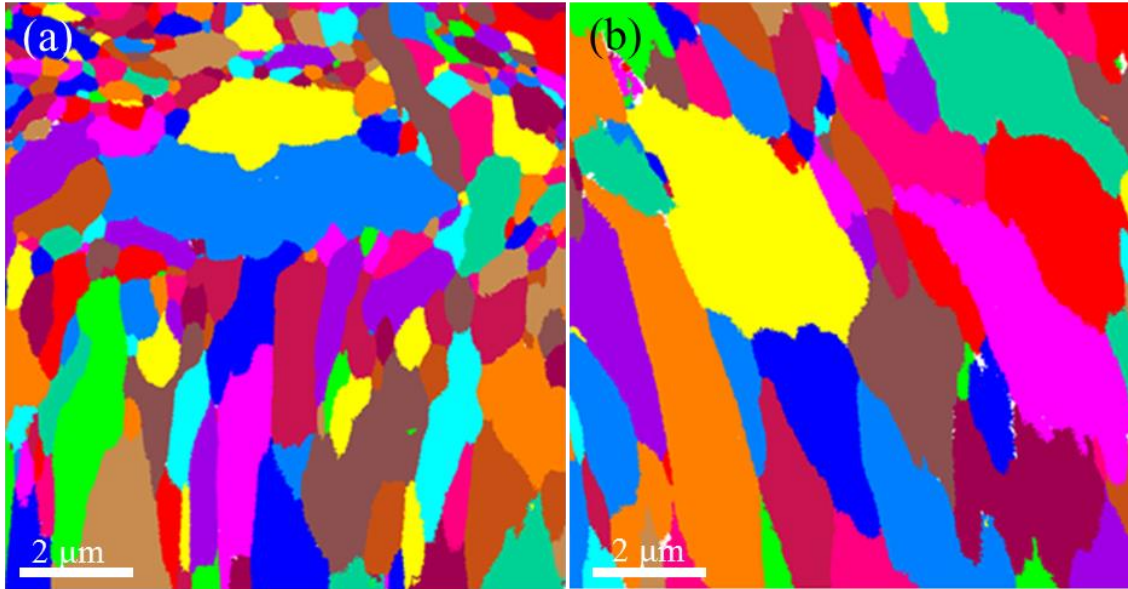


Fig. 2.3 Grain morphologies of (a) Y-Ti-ODS and (b) Y-Al-Zr-ODS.

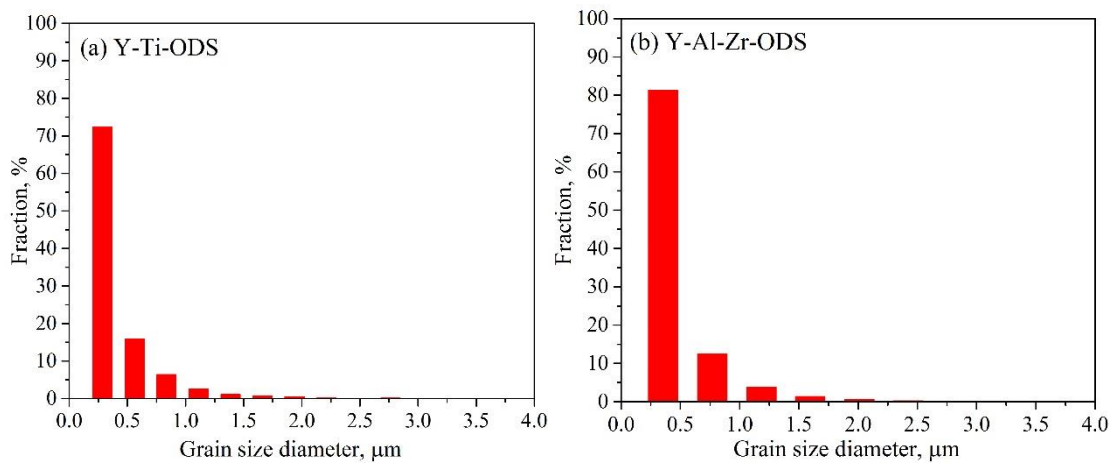


Fig. 2.4 Grain size diameter distributions of (a) Y-Ti-ODS and (b) Y-Al-Zr-ODS.

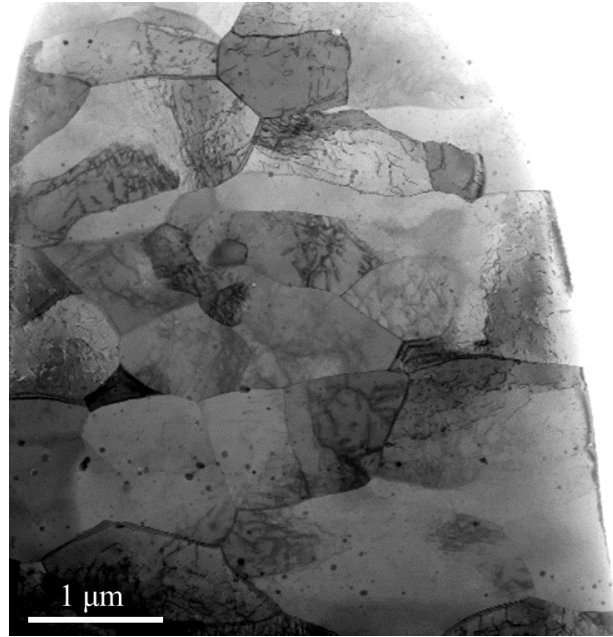


Fig. 2.5 Grain morphology of Y-Al-ODS under STEM bright filed image.

2.2.3 Surface polishing for irradiation

Specimens were sampled so that the specimen surface was perpendicular to the extrusion direction. Specimen surface was mechanically ground with SiC papers, and subsequently polished with successive grades of diamond spray down to 0.25 μm . Finally, in order to obtain an even and stress-free surface, electrolytic polishing was conducted in a solution of 10% (vol.) HClO_4 and 90% (vol.) CH_3COOH at room temperature (RT) except for Y-Al-ODS and Recry. Y-Ti-ODS.

Fig. 2.6(a) and 2.6(b) show the basic mechanism of the electropolishing process. The density of the electric current traveling along the peaks on surface is higher than the valleys. So in Fig. 2.6(a), the peak at AB can be dissolved faster than the valley at CD until a close level between both will be reached [3]. On the curve of electric current versus voltage for electropolishing in Fig. 2.6(b), there are three voltage regions: etching with an unstable dissolution (BC phase); polishing with a stable plateau (CD phase) and pitting (DE phase) [3]. Fig. 2.6(c) shows the optical micrograph of the polished surface of bulk Y-Al-Zr-ODS specimen after the electropolishing at 18 V in a solution of 10% (vol.) HClO_4 and 90% (vol.) CH_3COOH at RT for about 90 seconds, demonstrating that a successful electropolishing was done in the CD phase for Y-Al-Zr-ODS.

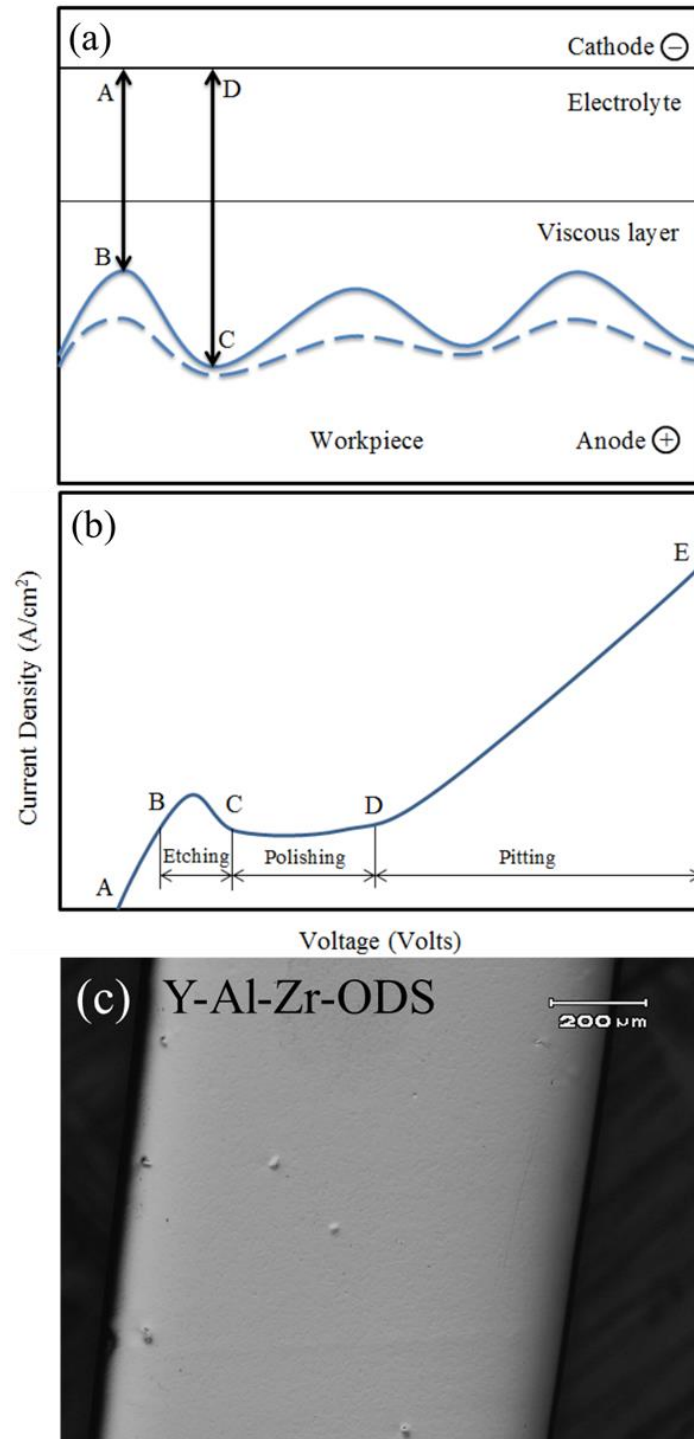


Fig. 2.6(a) Electropolishing process on the specimen surface; (b) general curve of the current versus voltage; (c) the optical image of the Y-Al-Zr-ODS specimen surface after electropolishing.

2.3 Ion irradiations

Ion irradiations were conducted at the Dual-beam facility for Energy science and Technology (DuET) in Institute of Advanced Energy, Kyoto University. According to the research purposes, various irradiation conditions including ions (Fe ion, He ions), temperatures, damage levels and He concentrations were chosen for each experiment.

2.3.1 Irradiation facilities

The DuET facility contains a 1.7 MV tandem accelerator system with a pair of ion sources (a 860A cesium sputter type heavy ion source and a model 358 duoplasmatron-type light ion source), a 1.0 MV single-end accelerator system with a light ion source (He ions) [4]. So a simultaneous irradiation of 6.4 MeV Fe^{3+} and 1 MeV He^+ ions can be done at the DuET to obtain the designed damage level and He concentration in the target materials. The beams were raster scanned at a frequency of 1000 Hz in a horizontal direction and 300 Hz in a vertical direction. The beam flux was measured by 21 small faraday cups. The target specimens were heated by infrared UHV heater and the irradiation temperature was measured by a high resolution thermography or W-Re thermocouple or both. More details of accelerators and temperature controllers were reported in Ref. [4–5].

2.3.1.1 Target station

The schematic image of target station was shown in Fig. 2.7, where solid red line and solid green line represent for Fe ions and He ions, respectively, in the dual beam (Fe, He) irradiation. The He^+ beam was inclined with 45 degrees to the normal of the specimen surface, which must pass through a rotating energy degrader before reaching the target specimens. This energy degrader was made of Al foils and the implanted He ions of four-type energies were obtained up to the Al-foil thickness, as shown in Table 2.2. A rather homogenous distribution of helium atoms in specimens can be obtained by applying the rotating energy degrader.

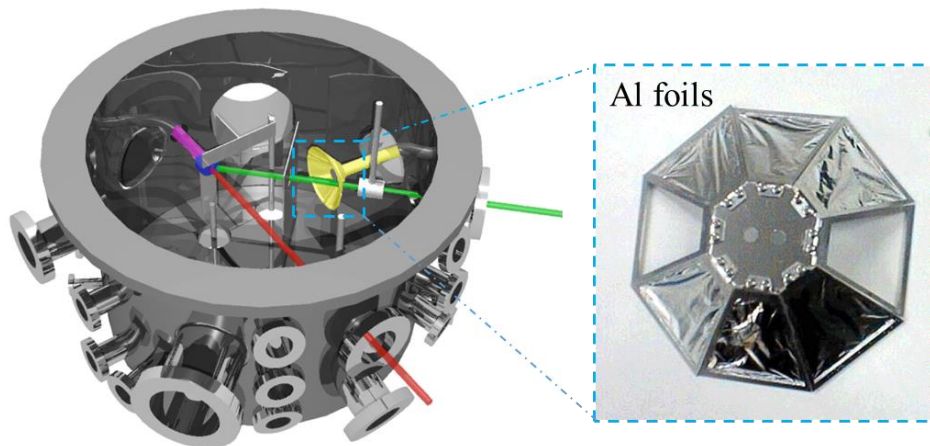


Fig. 2.7 Schematic image of target station.

Table 2.2 Al foil thickness and the corresponding energies of implanted He ions

Al foil thickness, nm	0	800	1600	2400
Implanted energy of He ions, keV	1000	737	462	201

2.3.1.2 Room temperature irradiation stage

During irradiations, in a high vacuum ($\sim 10^{-6}$ Pa) chamber, heavy ion beam irradiation results in an obvious heating of the target specimen and causes an increase in temperature. In order to maintain the specimen temperature at room temperature (RT), a copper stage was designed by ourselves in 2016, where the cooling water flows inside the tube embedded in the copper stage. The gap between the copper stage and specimens was filled with indium (In) films to enlarge the contact area for heat transportation. The front and side views of the copper stage are shown in Fig. 2.8 (a), 2.8(b) and 2.8(c), respectively. The temperature of the ODS specimen during 6.4 MeV Fe^{3+} irradiation was directly measured by thermocouple. When the beam current was 8–11 nA/mm², the measured temperature was between 26 and 28 °C, as shown in Fig. 2.9.

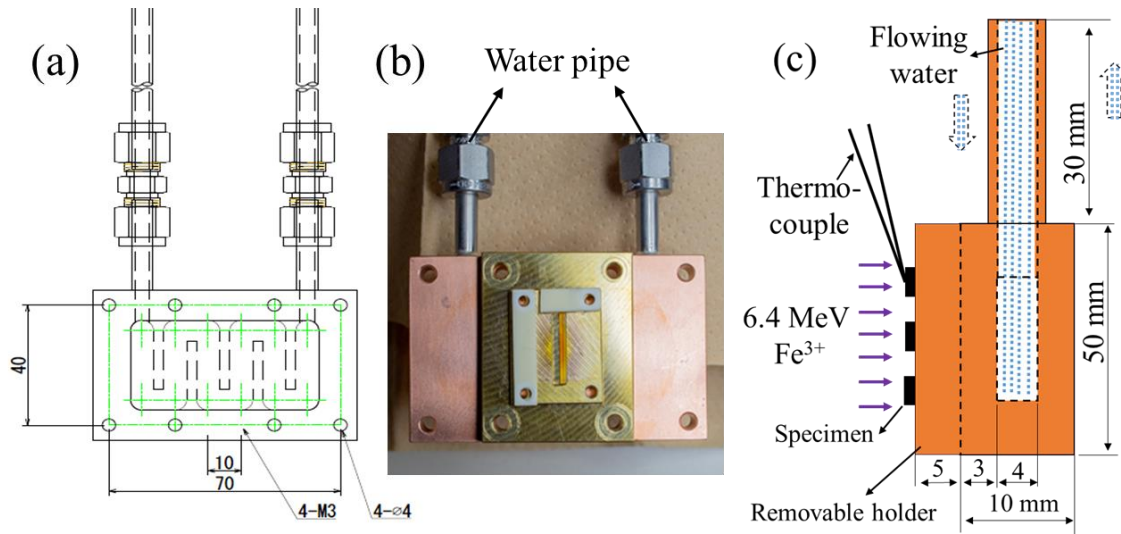


Fig. 2.8 Front view (a) and (b), as well as side view (c) images of the specimen stage for RT irradiations.

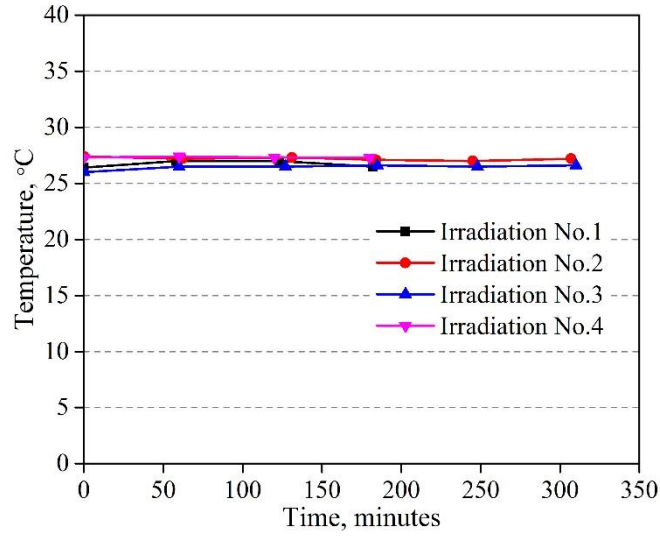


Fig. 2.9 Irradiation temperatures of the ODS specimens during 6.4 MeV Fe³⁺ irradiations.

2.3.2 Irradiation parameters

Irradiations were conducted with controlling irradiation temperature. A diagram of temperature versus the damage level (displacements per atom, dpa) was shown in Fig. 2.10. Parameters of each irradiation will be depicted in detail in the following chapters. The He concentration (appm), electronic stopping powers of 6.4 MeV Fe³⁺ ions and the injected Fe concentration of a Fe-14Cr alloy were directly obtained by SRIM [6] simulation with use of the Kinchin-Pease method, recommended by Stoller et al. [7]. The threshold displacement energies of Fe and Cr were 40 eV. The damage level (dpa) consisted of vacancies produced by energetic ions (V_{ions}) and recoil atoms ($V_{recoils}$), which was given by:

$$dpa = (V_{ions} + V_{recoils}) \times Q/N_a \quad (2.1)$$

where Q is the fluence of incident ions and N_a is the atomic density of the target material. All the profiles in depth dependence will be shown in the following Chapters 3–6.

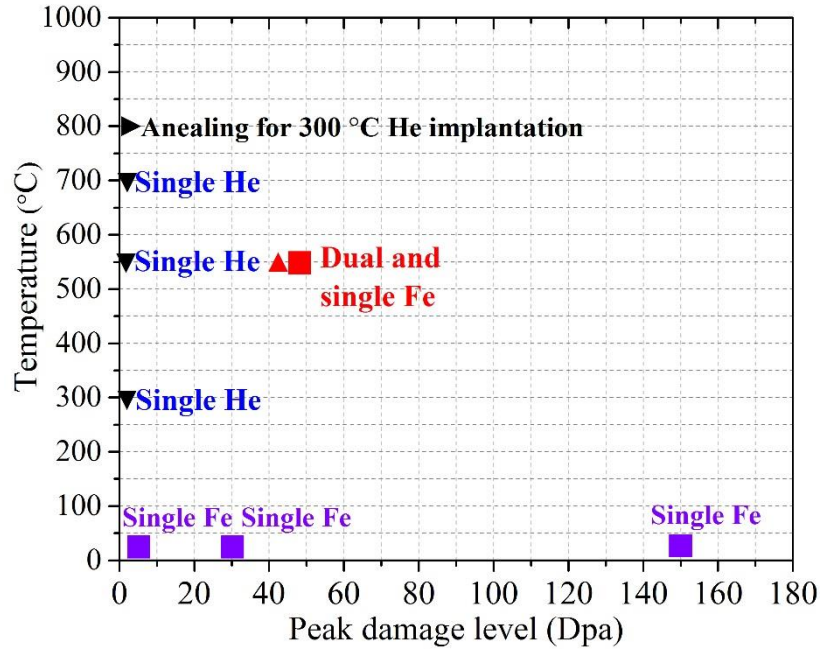


Fig. 2.10 Irradiation experimental diagram of temperature versus damage level.

2.4 Annealing experiment

As for Y-Al-Zr-ODS, the specimens of as-received condition and the as-irradiated condition of single He irradiation at 300 °C were placed in an evacuated quartz tube to roughly 6×10^{-3} Pa, measured by Pirani gauge. Specimens were rapped with Zr film for mitigating oxidation on the specimen surface. The encapsuled specimens were annealed at 800 °C for 100 h, followed by furnace-cooling. After annealing the specimens were ultrasonic cleaned in each solution, water, methanol and acetone, subsequently.

2.5 Specimen preparation for transmission electron microscopy (TEM)

Cross-sectional TEM specimens were prepared by the lift-out technique [5] using a focused ion beam (FIB), Hitachi FB 2200. In that process, the final beam used was 20 keV Ga⁺. Prior to TEM observations, flash polishing was done by using a solution consisting of 5% (vol.) HClO₄ and 95% (vol.) CH₃OH at around -35 °C for the removal of a FIB damage layer.

2.6 Transmission electron microscopy (TEM) techniques

A high energy electron beam penetrate a very thin specimen, and the electron scattering by the interaction between lattice atoms and electron cause the difference in the degree of electron penetration that give a contrast in the electron intensity. According to the interactions, the imaging contrasts can be basically divided into three types: phase contrast, strain contrast and amplitude contrast [8]. Here, the imaging features of cavities, dislocations and oxide particles are briefly

explained. In this dissertation, all TEM images were taken by using a conventional 200 kV JEOL JEM 2010 microscope with a LaB₆ electron emitter and a 200 kV JEM 2200FS field emission microscope, which was equipped with an in-column energy filter (Omega filter).

2.6.1 Cavities, dislocations and oxide particles

The contrast of cavities depends on the difference in the inner potential of the matrix and the cavity. So we can view it at out of focus condition to observe the Fresnel-fringe contrast (phase contrast); if the defocus $\Delta f < 0$, the image is a bright dot surrounded by a dark fringe; if $\Delta f > 0$, the dot is dark and the fringe is bright [8]. A representative simulated TEM image of 5-nm He bubble is shown in Fig. 2.11 [9].

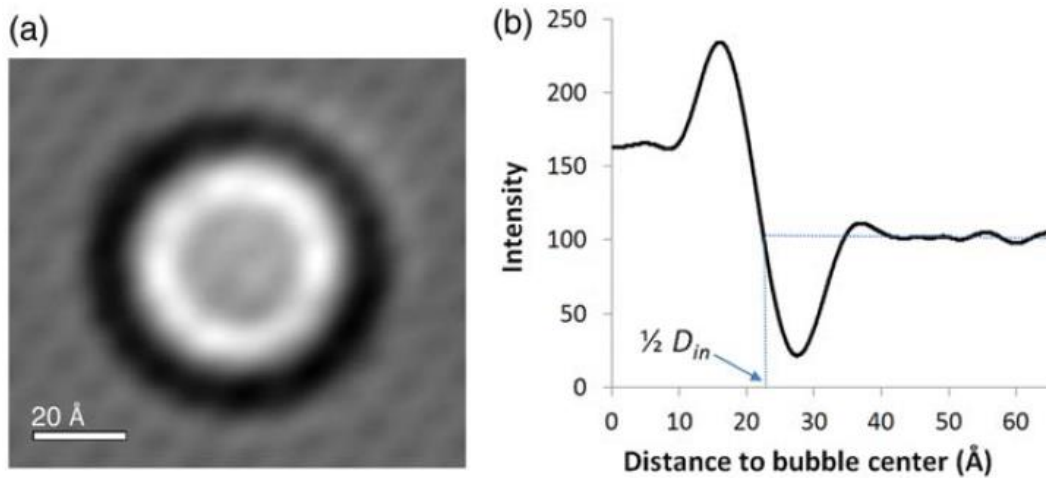
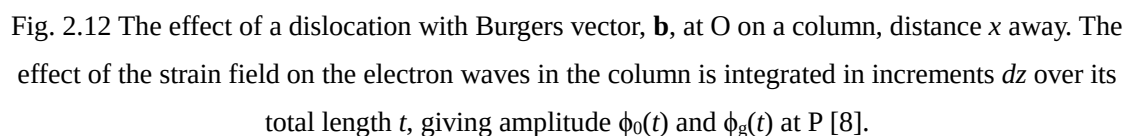


Fig. 2.11 (a) A representative simulated TEM image of a 5-nm He bubble with 200 kV, $\Delta f = -500$ nm, $C_s = 1$ mm and a deviation of illumination semi-angle of 0.5 mrad; (b) the corresponding average-intensity profile of the image [9].

Dislocations and oxide particles can be imaged by their intrinsic strain fields, according to the diffraction theory (e.g. the two-beam approach) [8]. In an isotropic solid, the displacement field $\mathbf{R}$ of the dislocation can be written as:

$$\mathbf{R} = \frac{1}{2\pi} \left(\mathbf{b}\phi + \frac{1}{4(1-\nu)} \{ \mathbf{b}_e + \mathbf{b} \times \mathbf{u} (2(1-2\nu)\ln r + \cos 2\phi) \} \right) \quad (2.2)$$

$\mathbf{R}$ is given here in polar coordinates (r and ϕ) shown in Fig. 2.12; $\mathbf{b}$ is the Burgers vector, $\mathbf{b}_e$ is the edge component of the Burgers vector, $\mathbf{u}$ is a unit vector along the dislocation line, and ν is Poisson's ratio. For the pure screw dislocation, $\mathbf{g} \cdot \mathbf{R}$ is proportional to $\mathbf{g} \cdot \mathbf{b}$. Moreover, when the grain observed is tilted slightly away from the Bragg condition, the distorted planes close to the dislocations may be bent back into the Bragg-diffraction condition, diffracting into the $\mathbf{g}$ beam.


$$\mathbf{R} = \mathbf{C}_\varepsilon r \quad (2.3)$$
$$\mathbf{R} = C_\varepsilon (r_0^3/r^2) \quad (2.4)$$
$$C_{\varepsilon} = 3K\delta/(3K+2E(1+\nu)) \quad (2.5)$$
$$A_g = \frac{i\pi}{\xi_a} A_0 \int_0^t \exp[-2\pi i(s_g z + \mathbf{g} \cdot \mathbf{R})] dz \quad (2.6)$$

41

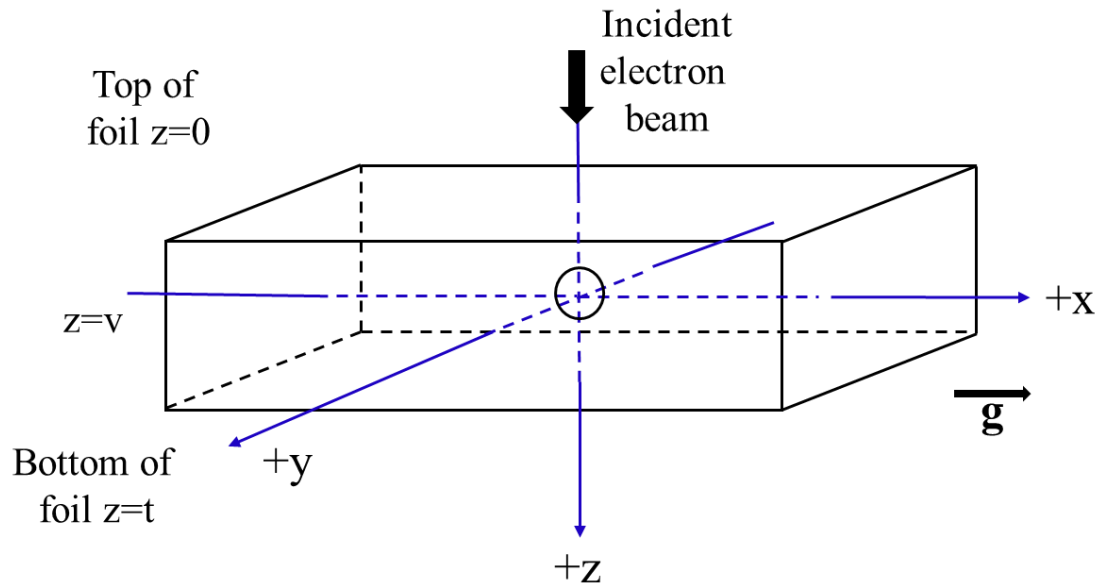


Fig. 2.13 Coordination system of a particle embedded inside a thin foil under TEM observation [10].

Fig. 2.14 shows the oxide particles and dislocations under two-beam ($s_g \approx 0$) and weak-beam dark-field imaging condition (WBDF) ($\mathbf{g}, 3\mathbf{g}$) with $s_g \neq 0$. It is easy to distinguish oxide particles and dislocations under the WBDF condition ($s_g \neq 0$) in Fig. 2.13 (b). Besides, under kinematical bright-field condition ($s_g \neq 0$), it is possible to observe cavities and dislocations/oxide particles at the same time by means of Fresnel-fringe contrast and diffraction contrast, as shown in Fig. 2.15.

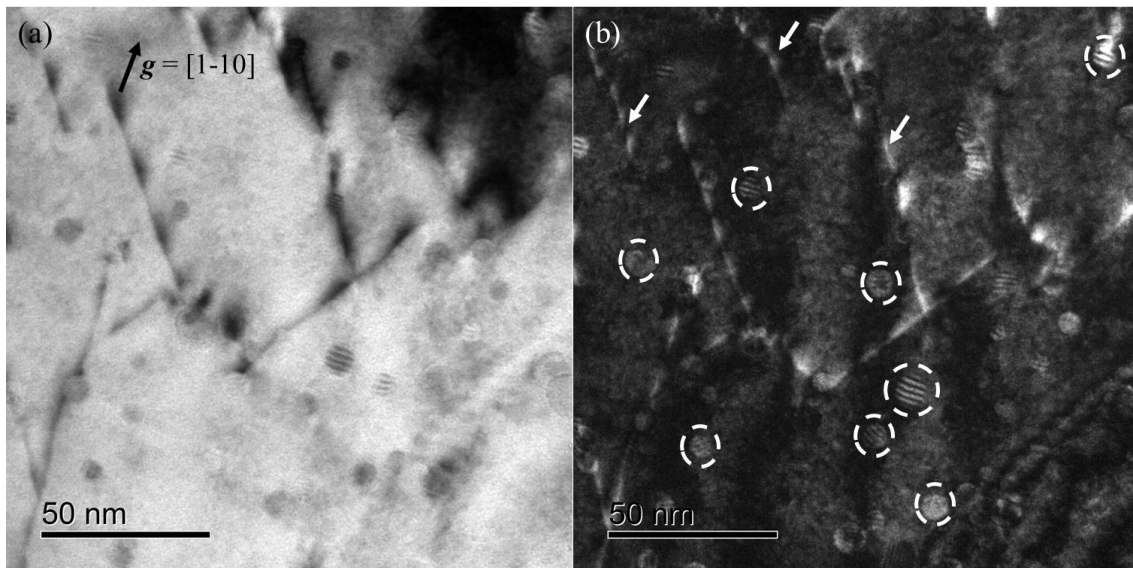


Fig. 2.14 Oxide particles (partly marked with circles) and dislocations (partly marked with arrows) in the as-received Y-Al-ODS imaged by using $\mathbf{g} = [1\bar{1}0]$ close to pole [111] under (a) two-beam dynamical condition ($s_g \approx 0$) and (b) $(\mathbf{g}, 3\mathbf{g})$ WBDF condition ($s_g \neq 0$).

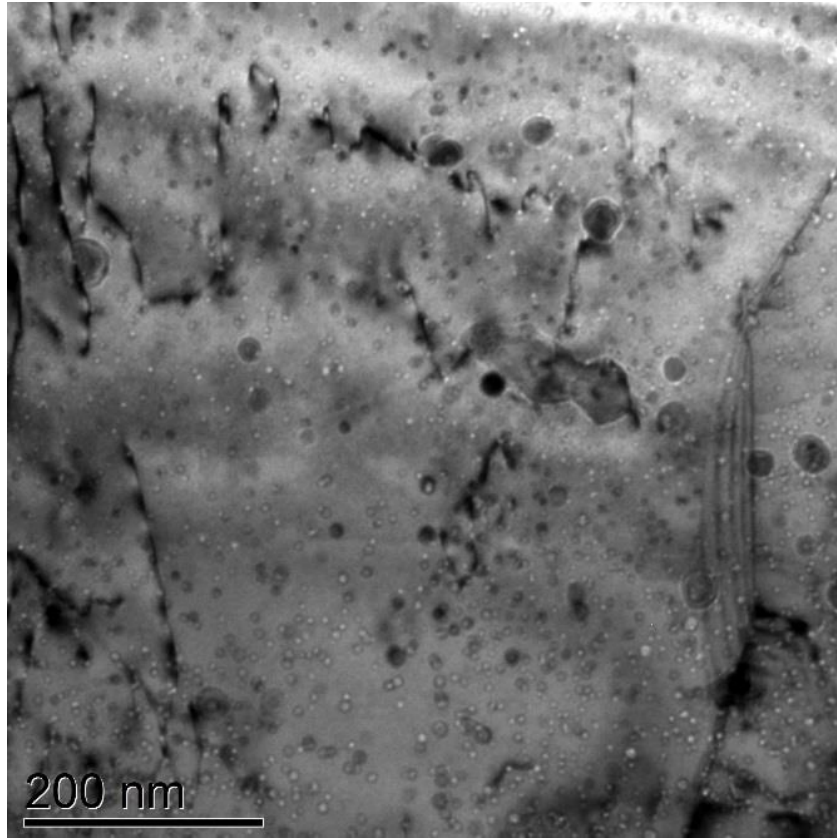


Fig. 2.15 Microstructures in Y-Al-ODS after the dual-beam irradiation at 550 °C ($\Delta f = -3744$ nm); black spots and white spots represent for oxide particles/precipitates and He bubbles, respectively.

2.6.2 Energy-filtered TEM (EFTEM)

Energy-filtered transmission electron microscopy (EFTEM) is another powerful TEM imaging technique, where images are formed by choosing a small range of inelastically scattered electrons in the energy loss spectrum with an energy-selecting slit. Usually, two-window and three-window EFTEM methods were selected. In the two-window method, the post-edge image is divided by a pre-edge image to yield the jump-ratio image. In the three-window method (see Fig. 2.16), the background can be calculated from two pre-edge (pre-edge 1 and pre-edge 2) images in front of the ionization- (core-) edge assuming an inverse power law dependence at each pixel in the image. To extrapolate the background image to the post-edge image results into a jump-ratio elemental map [11]. In this thesis, only two-window method was adopted. Fig. 2.17 shows the zero-loss image, Fe M-jump ratio image and Ti M-jump ratio image at an identical region of Y-Ti-ODS. Bright contrast features in Fig. 2.16(c) indicated the oxide particles or precipitates containing Ti.

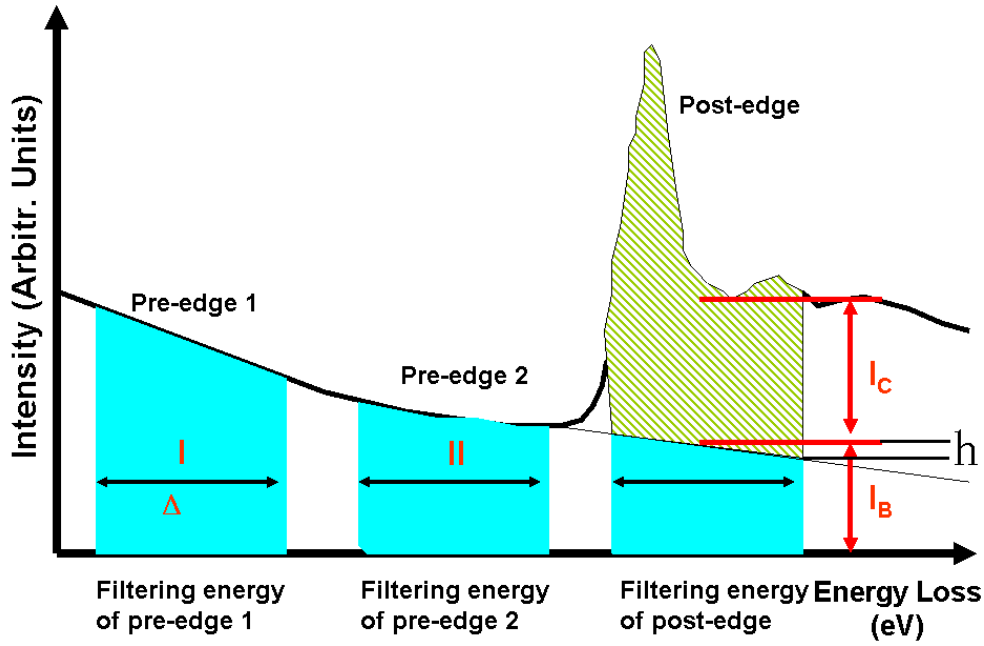


Fig. 2.16 Schematic of the three-window method [11].

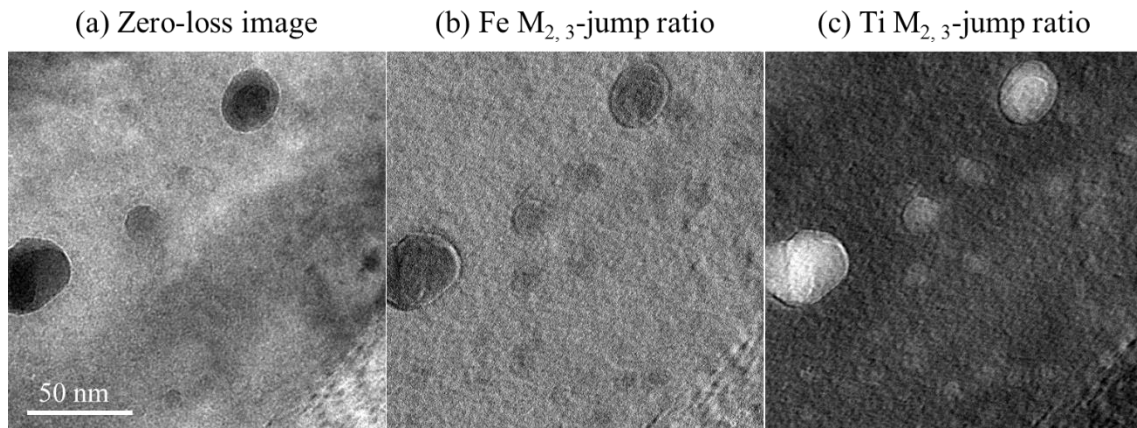


Fig. 2.17 (a) Zero-loss image; (b) Fe $M_{2,3}$ -jump ratio image and (c) Ti $M_{2,3}$ -jump ratio image at an identical region of Y-Ti-ODS

2.6.3 Thickness measurements of TEM foils

The thickness of the local region of interest in TEM foils was obtained by measuring the fringe spacing in convergent-beam electron diffraction (CBED) patterns [12] or by electron energy-loss spectroscopy (EELS) log-ratio technique [11].

In the CBED patterns, the central bright fringe is at the exact Bragg condition where $s = 0$. s_i is a certain deviation for the i^{th} fringe ($i = 1, 2, 3, \dots$) when the diffracting hkl plane, the d_{hkl} spacing and the de Broglie wavelength of electrons are given. The foil thickness t can be calculated by the following equation:

$$\left(\frac{s_i}{n_k}\right)^2 + \left(\frac{1}{n_k}\right)^2 \left(\frac{1}{\zeta_g}\right)^2 = \frac{1}{t^2} \quad (2.7)$$

where ζ_g is the extinction distance for the hkl plane; n_k is an integer (k is an integer identical to i or differing from i).

In the EELS log-ratio technique, the ratio of TEM foil t to the characteristic mean free path λ for inelastic scattering for the material is given by:

$$\frac{t}{\lambda} = \ln \left(\frac{I_t}{I_0} \right) \quad (2.8)$$

where I_t is the total number of electron in the EELS spectrum and I_0 is the number of electrons having no energy loss (the zero-loss peak); λ is a function of the atomic number Z of the material, the incident electron energy E_0 and the spectrum collection semi-angle β [11]. In spite of the accuracy in each thickness measurement, the same measurement was adopted to achieve a meaningful comparison between different irradiation conditions.

2.5 Hardness measurements

2.5.1 Vickers hardness

Vickers hardness was measured for as-received ODS bulk samples using a diamond indenter with a Vickers hardness tester (HMV-G21, Shimadzu). The sample surface tested was perpendicular to the extrusion direction. Vickers hardness, HV is defined as:

$$HV = F/A_c \quad (2.9)$$

$$A_c = \frac{d^2}{2\sin(136^\circ/2)} \quad (2.10)$$

where F is the load in kgf; d is the average length of the diagonal left by the indenter in millimeters; A_c is the contact surface area in square millimeters. The load and dwell time were 1 kg and 10 s, respectively. 10 tests were done for each sample and the averaged values were obtained, as shown in Table 2.3.

Table 2.3 Vickers hardness, HV of the studied ODS steels

HV	Y-Ti-ODS	Recry. Y-Ti-ODS	Y-Al-ODS	Y-Al-Zr-ODS
in kgf/mm ²	367.8 ± 4.4	254.3 ± 4.0	305.1 ± 4.4	340.3 ± 5.5
in GPa	3.60 ± 0.04	2.49 ± 0.04	2.99 ± 0.04	3.34 ± 0.05

2.5.2 Nanoindentation hardness

Nanoindentation testing was performed on as-received and irradiated samples by using a nanoindenter (Agilent G200) equipped with a Berkovich tip. A continuous stiffness measurement (CSM) was adopted to obtain continuous hardness and elastic modulus as a function of indentation depth. Before testing, the indenter tip geometry was calibrated by indenting a fused silica reference sample with known mechanical properties. Other main testing parameters were depicted as follows: the maximum indentation depth was 2000 nm, the strain rate was 0.05 s^{-1} , the harmonic displacement was 1 nm, and the Poisson's ratio was 0.3. For each specimen, 24 testing points (60 μm between two adjacent points) were chosen and the averaged hardness was obtained by calculating the measured hardness data of roughly 20 tests after several test results were omitted because of the significance in the data scattering.

In the dynamic indentation testing, the harmonic contact stiffness $S(h)$ is directly measured, which is also a key parameter of influencing the contact depth h_c , the combined modulus E^* and the measured hardness H of the specimen through the following equations:

$$h_c = h_{\max} - \varepsilon \frac{P_{\max}}{S(h)} \quad (2.11)$$

$$E^* = \frac{1}{2} S(h) \frac{\sqrt{\pi}}{\sqrt{A(h)}} \quad (2.12)$$

$$H = \frac{P_{\max}}{A(h)} \quad (2.13)$$

where $h_{\max}$ and the load $P_{\max}$ can be known by the instrument; ε is a constant, about 0.72 for the case of a conical indenter; E^* should be a constant for a standard fused silica; An indenter geometry $A(h)$ can be generally expressed as a mathematical function of the depth h_c beneath the contact and given by:

$$A(h) = C_1 h_c^2 + C_2 h_c + C_3 h_c^{1/2} + \dots + C_7 h_c^{1/32} + C_8 h_c^{1/64} \quad (2.14)$$

where eight coefficients can be calculated on the standard fused silica according to eq. (2.12). For an ideal Berkovich indenter, the projected area $A(h)$ of the indentation is written as:

$$A(h) = 24.5 h_c^2 \quad (2.15)$$

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Chapter 3

He bubble formation behavior in ODS ferritic steels under single-He implantations

3.1 Introduction

In comparison to the leading candidate blanket structural material, reduced activation ferritic/martensitic (RAFM) steels, ODS steels possess outstanding creep strength at elevated temperatures up to about 700 °C, and overcome radiation tolerance after neutron irradiation up to 50 dpa [1, 2]. Therefore, ODS steels are another possible candidate structural materials to expand the design margin of the blanket and to improve thermal efficiency of future fusion reactors. Concerning the materials issues of blanket structural materials, the effects of transmuted helium, such as bubble formation and grain boundary He precipitation, are unavoidable. Therefore, a profound understanding of helium effects is essential for improving the performance of the candidate blanket structural materials.

In conventional RAFM steels, helium is possibly trapped by lattice defects and microstructures involving dislocations, lath boundaries, grain boundaries and interfaces of precipitates/matrix or carbides/matrix. Kimura et al. investigated the helium desorption behaviors for RAFM steels and ODS F/M steels by using thermal helium desorption spectra (THDS) [3]. It was reported that there were various He trapping complexes: (i) desorption from the surface, 100 °C; (ii) detrapping from helium-vacancy pairs, 450 °C; (iii) detrapping from dislocations, 550 °C; (iv) α - γ phase transformation related desorption, 900 °C; (v) desorption by He bubble migration, 1100 °C [3]. Meanwhile, no desorption peaks were directly attributed to the oxide particles, although it might happen at temperatures above 1100 °C. Moreover, T. Yamamoto et al. have obtained strong evidence for the existence of a high number density of ultrafine He bubbles trapped on nano-sized (Y,Ti) oxide particles at 500 °C [4]. However, few studies reported He bubble formation behaviors in ODS steels with temperature dependence.

As for swelling in ODS steels, several ODS steels have been studied under single heavy ion irradiation, single He ion irradiation and multi-beam ion irradiation [5–9]. M.B. Toloczko [5] has demonstrated the excellent swelling resistance of ODS ferritic alloy MA957 by showing its low void swelling of only 4.5 % even after ion irradiation to 500 dpa at 450 °C. Under Fe/He dual-ion irradiation, ODS alloys were more resistant to void swelling than non-ODS RAFM steels because of a lower dislocation bias and a high number density of fine oxide particles acting as effective traps for He atoms and vacancies [6, 7]. Furthermore, much lower void swelling was found in tempered martensite grains than ferrite grains for 12Cr ODS ferritic-martensitic alloy after 800 dpa iron-ion irradiation, which should stem from the high density internal boundaries of tempered martensite [8]. Accordingly, it was summarized that in ODS steels microstructures, such as oxide particles, dislocations and grain boundaries, played a vital role in suppressing void swelling. Unlike heavy ion irradiation, He ion implantation generally produces a smaller number of atomic displacements thus causing fewer damage structures. With regard to swelling behavior of ODS steels under helium irradiation, W. Xu et al. elucidated a relationship between oxide particle and He bubble induced

swelling of ODS alloys at the He implantation temperature of 500 °C, that the swelling went up with oxide particle diameter [9]. Nonetheless, the temperature dependent swelling in ODS steels is limited.

The Al-containing ODS steels might not be adequate for the application to fusion blanket which demands reduced activation [10]. However, the simultaneous addition of Al and Zr to 16Cr-ODS steels improved not only corrosion resistance but also high-temperature strength up to the almost same level with 16Cr-ODS steels [1]. Actually, the changes in strength were due to the alteration of the sorts of the oxide particles, which resulted in a dispersion morphology change of the oxide particles. It is also expected that the He bubble formation and swelling behavior are influenced by the sort of dispersed oxide particles.

The objective of this chapter is to investigate the role of nano-scaled oxide particles in the temperature dependent He bubble formation and swelling behavior of two 14.5Cr ODS ferritic steels with and without the co-addition of Al and Zr, which alters the oxide particle dispersion morphology.

3.2 Materials and experimental methods

The materials used in this work were two 14.5Cr ODS ferritic steels, designated as Y-Ti-ODS and Y-Al-Zr-ODS. The chemical compositions of the Y-Ti-ODS and Y-Al-Zr-ODS are shown Chapter 2. The Y-Al-Zr-ODS steel contains 3.5 wt.% Al and 0.27 wt.% Zr as alloying elements. The main fabrication process and specimen preparations for He irradiation are also described in detail in Chapter 2.

He-irradiation experiments were carried out at the DuET facility at Kyoto University by using 1 MeV He⁺ ions, whose energy was separated into 201 keV, 467 keV, 737 keV and 1 MeV by a rotating energy degrader made of thin Al foils, then injected into the samples to form a homogenous He atoms distribution. The fluence was roughly 4.5×10^{20} ions m⁻² and the corresponding flux was about 6.2×10^{16} ions m⁻² s⁻¹. The irradiation temperatures were 300 °C, 550 °C and 700 °C with a temperature fluctuation of ± 10 °C, which was measured by a thermo-couple and an infrared thermography. At each temperature, the two ODS specimens were irradiated simultaneously for about 2 hours.

The He concentration and damage level as a function of the He-ions penetration depth were obtained by SRIM simulation [11], as shown in Fig. 3.1. For the depth ranging from 1000 to 1300 nm, the He concentration remained stable around 3500 appm. The corresponding nominal damage level was about 0.2 dpa. Main parameters are presented in Table 3.1.

The cross sectional specimens for transmission electron microscopy (TEM) observations were fabricated by the lift-out technique using a Focused Ion Beam (FIB), then treated by flash polishing or low energy Ar ion sputtering to eliminate FIB damage. TEM observation was done using a conventional 200 kV JEOL JEM 2010 microscope. The thickness of all TEM samples was acquired based on the measurement of fringe spacing in convergent beam electron diffraction (CBED) patterns.

Table 3.1 Parameters of single He ion irradiations

Materials	Ions	Dose, ions m^{-2}	Local He content, appm	Local damage, dpa	Temperatures, $^{\circ}\text{C}$
Y-Ti-ODS,	energy degraded	$\sim 4.5 \times 10^{20}$	~ 3500	~ 0.2	300, 550, 700
Y-Al-Zr-ODS	He^+ ions				

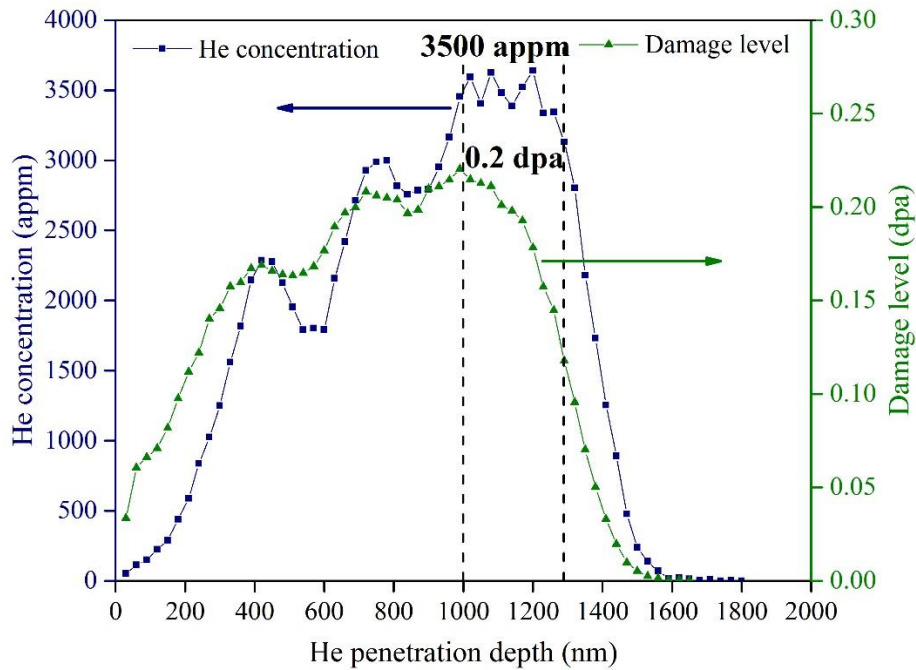


Fig. 3.1. Depth profiles of damage level (in units of displacements per atom, dpa) and He atom concentration (appm) calculated with SRIM code.

The cross sectional specimens for transmission electron microscopy (TEM) observations were fabricated by the lift-out technique using a Focused Ion Beam (FIB), then treated by flash polishing or low energy Ar ion sputtering to eliminate FIB damage. TEM observation was done using a conventional 200 kV JEOL JEM 2010 microscope. The thickness of all TEM samples was acquired based on the measurement of fringe spacing in convergent beam electron diffraction (CBED) patterns.

3.3 Results and discussion

3.3.1 Grain morphology, oxide particles and dislocations

The mean grain size of each ODS steel was estimated to be about 0.37 μm by using EBSD (see Chapter 2). Although the irradiation temperature was elevated to 700 $^{\circ}\text{C}$ in this work, no grain coarsening occurred because the grain boundaries were pinned down by fine oxide particles, which agrees with the previous work by Y. Ha [12] who reported that no recrystallization or evolution of oxide particles occurred in Al-added and Al-free ODS steels after annealing up to 1350 $^{\circ}\text{C}$.

Dispersion morphologies of oxide particles in both ODS steels were observed by TEM using $\mathbf{g} = (1\bar{1}0)$ at the kinematical bright field (KBF) imaging condition with the deviation vector $\mathbf{s}_{\mathbf{g}} \neq 0$, and shown in Fig. 3.2. The corresponding size distributions are presented in Fig. 3.2(c). For Y-Al-Zr-ODS, the mean diameter of oxide particles was 6.2 nm and the number density was $3.5 \times 10^{22} \text{ m}^{-3}$. For Y-Ti-ODS, smaller oxide particles of 3.0 nm were observed with a higher number density of $1.1 \times 10^{23} \text{ m}^{-3}$. In Zr-free 15Cr-ODS steels, the Al addition resulted in the alteration of oxide particles from nanoscale (Y, Ti) oxides (e.g. cubic pyrochlore $\text{Y}_2\text{Ti}_2\text{O}_7$) to larger yttrium aluminum perovskite (YAP, YAlO_3) and yttrium aluminum hexagonal (YAH, YAlO_3) oxides [13]. The simultaneous addition of Al and Zr, however, suppressed the nucleation of (Y, Al) oxides and enhanced the formation of (Y, Zr) oxides [1]. As for the effect of irradiation on the oxide particles in this work, the dispersion morphologies were not changed by irradiation, which was also consistent with the previous work indicating that they remained stable even after irradiation up to 150 dpa at 670 $^{\circ}\text{C}$ [14].

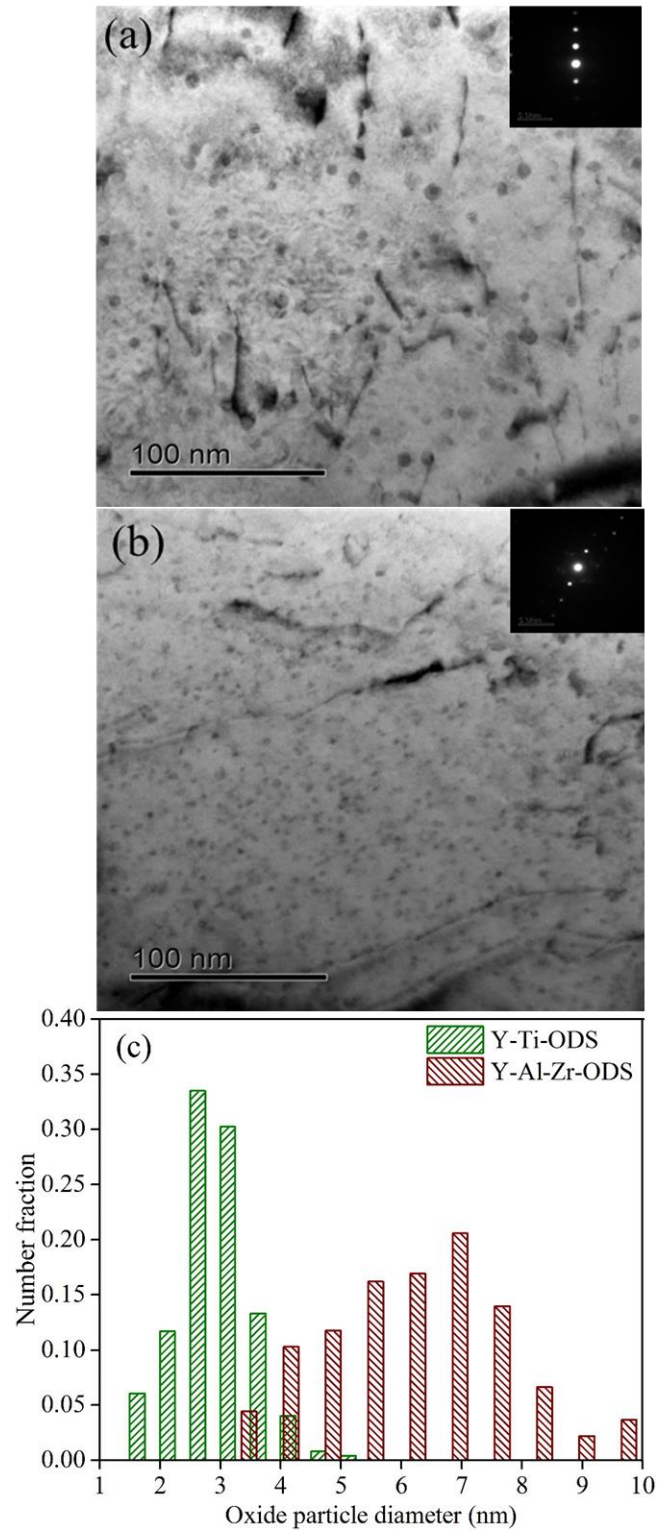


Fig. 3.2 Bright-field images of dislocations and oxide particles in (a) Y-Al-Zr-ODS, (b) Y-Ti-ODS taken under a two-beam diffraction condition by using $\mathbf{g} = [1\bar{1}0]$ and (c) size distribution histogram of oxide particles

The dislocations before irradiation were observed by TEM using vector $\mathbf{g} = \langle 1\bar{1}0 \rangle$ under pole [001] and could be seen in Fig. 3.2 (a) and (b). After the He ion irradiations at 300 and 550 °C, dislocations were observed in a depth range of 1000 to 1300 nm, as shown in Fig. 3.3. The dislocation density was obtained by measuring the dislocation length in a unit volume. The corresponding numerical values before and after irradiation are displayed in Table 3.2, indicating no significant changes among them for a damage level of about 0.2 dpa. Above 300 °C (greater than 0.2 T_M , where T_M is the melting temperature), vacancies detrapped from impurities and might accelerate mutual annihilation with interstitial atoms. As a result, few defects survived to form dislocation structures after collision cascades [15].

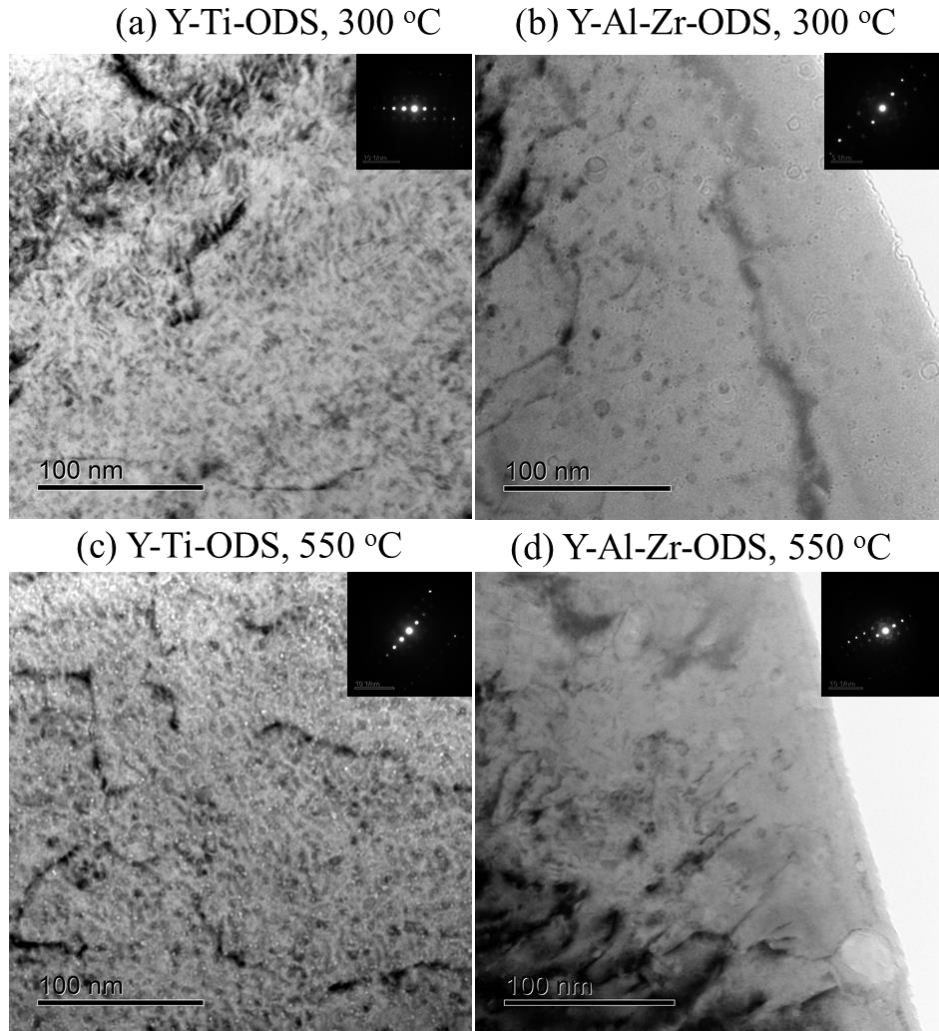


Fig. 3.3 Dislocations in a depth range of 1000 to 1300 nm observed by using $\mathbf{g} = \langle 1\bar{1}0 \rangle$ close to zone [001] in Y-Ti-ODS (a) and (c), as well as in Y-Al-Zr-ODS (b) and (d) after the He ion irradiations at 300 ((a) and (b)) and 550 ((c) and (d)) °C .

Table 3.2 Dislocation densities (m^{-2}) of unirradiated samples and He-ions irradiated samples at 300 °C, 550 °C with a damage level of 0.2 dpa.

	Un-irradiated	300 °C	550 °C
Y-Al-Zr-ODS	1.4×10^{14}	1.3×10^{14}	0.8×10^{14}
Y-Ti-ODS	1.2×10^{14}	0.7×10^{14}	1.2×10^{14}

3.3.2 He bubbles

The depth profile of He bubble distribution morphology of Y-Al-Zr-ODS irradiated at 700 °C is shown in Fig. 3.4. As the depth increased, He bubbles generally became larger in size and number density, most of which were distributed in the depth range of 700–1600 nm. This phenomena is in agreement with the He concentration depth profile of SRIM simulation results. He bubbles in the depth range from 1000 to 1300 nm were observed at under-focused conditions (see Fig. 3.5). The corresponding size distributions of He bubbles are shown in Fig. 3.6. Meantime, the irradiation temperature dependences of mean diameter and number density of He bubbles are displayed in Fig. 3.7 (a) and (b), respectively. In both steels, the bubble size and number density increased and decreased, respectively, with increasing irradiation temperature. Moreover, the bubble size distribution became broader as the temperature elevated.

At 300 °C, some tiny spherical bubbles were nucleated along dislocation lines as shown in Fig. 3.5(a), implying that He atoms were trapped at dislocations. In Fig. 3.5(d), only the isolate spherical He bubbles existed. For both the ODS ferritic steels, the average diameter of He bubbles was about 1.6 nm. Actually, at 300 °C, He-vacancy clusters smaller than He_3V_5 were mobile but their diffusion coefficients were at least two orders of magnitude lower than that of a mono vacancy [16].

At 550 °C (over $0.3 T_M$), He bubbles grew up evidently and were of mean diameter 5.0 nm with some loss of spherical shape in Y-Al-Zr-ODS (in Fig 3.5(b)). No obvious size difference was found between intragranular and intergranular bubbles. In Y-Ti-ODS, bubbles grew very slightly (see Fig. 3.5(e) and Fig. 3.6(c)) with increasing temperature.

At 700 °C, He bubble size became the largest. In Fig. 3.5(f), intergranular bubbles (near the black dash) were bigger than intragranular bubbles in Y-Ti-ODS steel, indicating that the bubble growth on grain boundary was more favorable than in the grain. Under high temperature conditions (more than $0.5 T_M$), He-vacancy complexes smaller than the critical size were not thermally stable. Furthermore, more vacancies flew readily to stable He bubbles, which had the size bigger than the critical value. As a result, He bubbles grew up with a lower number density.

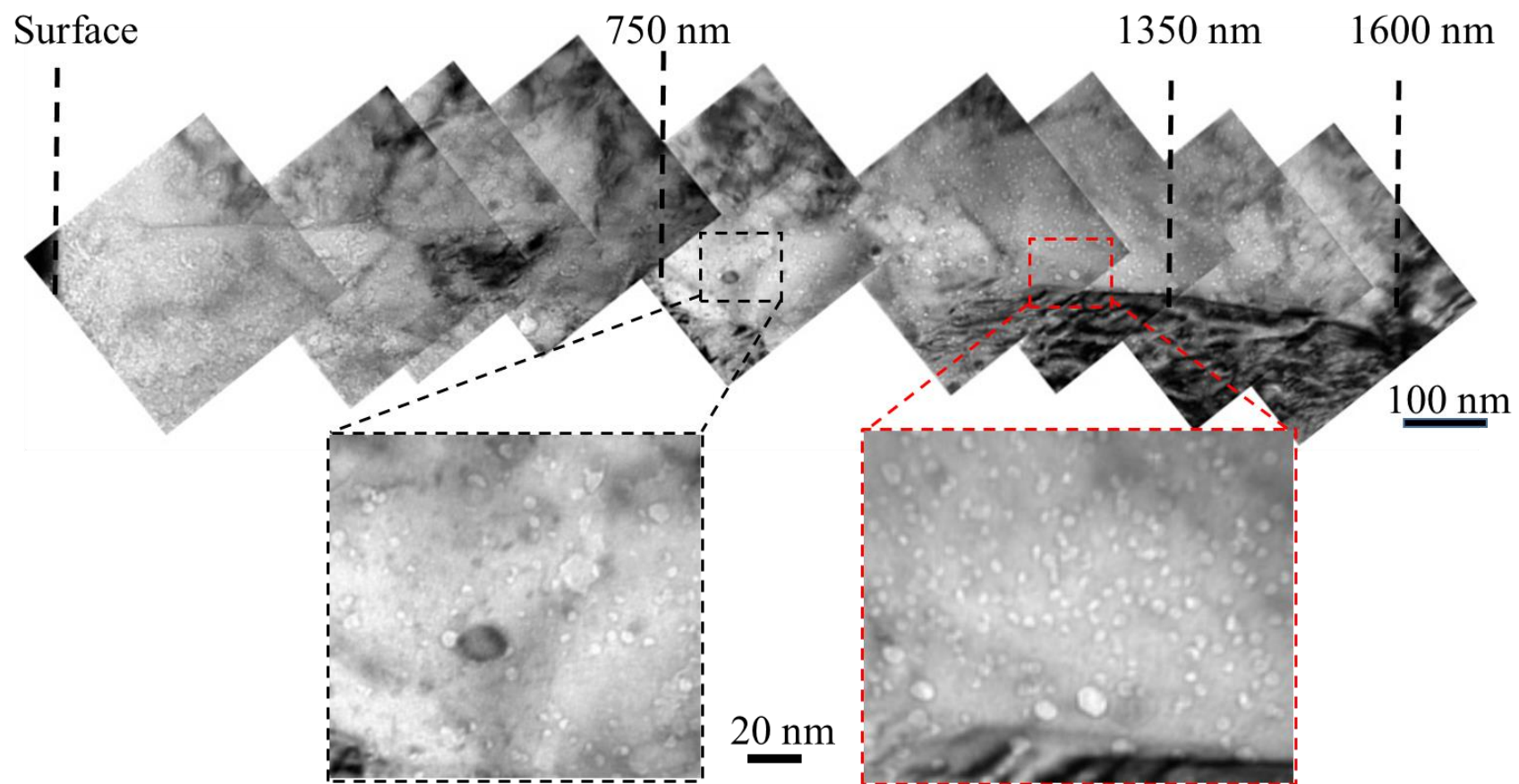


Fig. 3.4 Depth profile of He bubble distribution morphology in Y-Al-Zr-ODS irradiated at 700 °C.

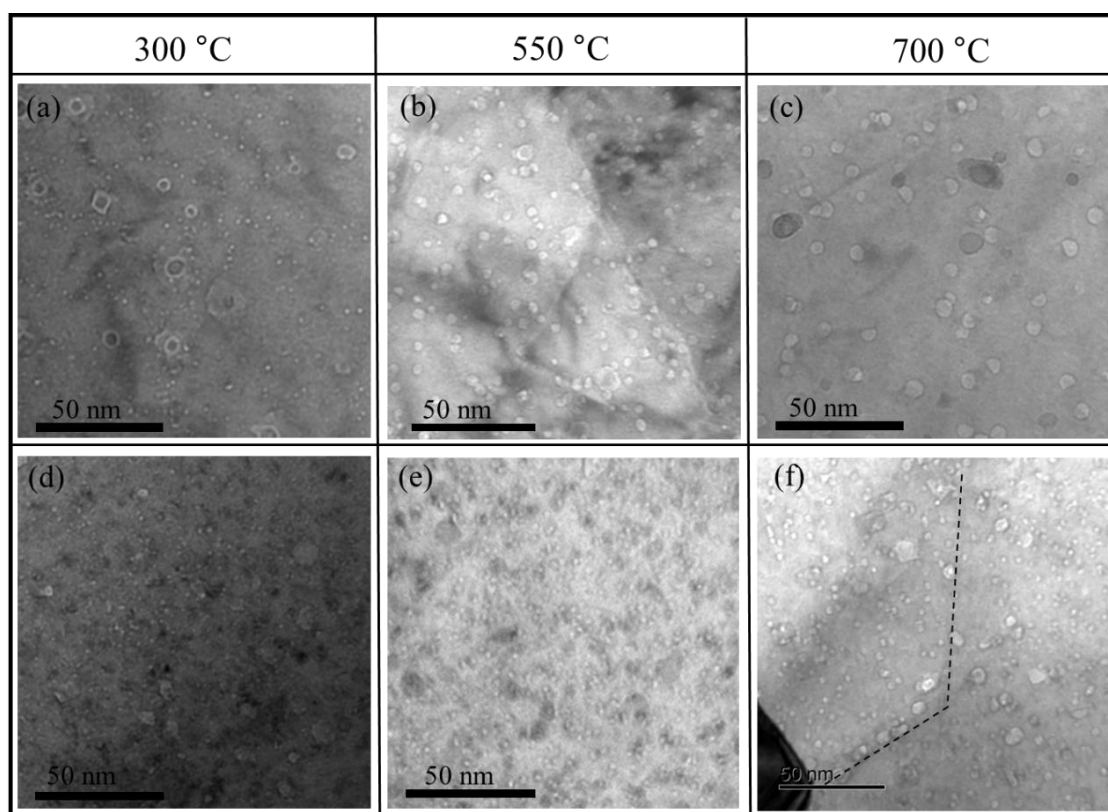


Fig. 3.5 TEM micrograph of He bubbles in Y-Al-Zr-ODS (a) to (c) and Y-Ti-ODS (d) to (f) taken at under-focus conditions, the He concentration of around 3500 appm; Dash line in 3.5(f) means grain boundary.

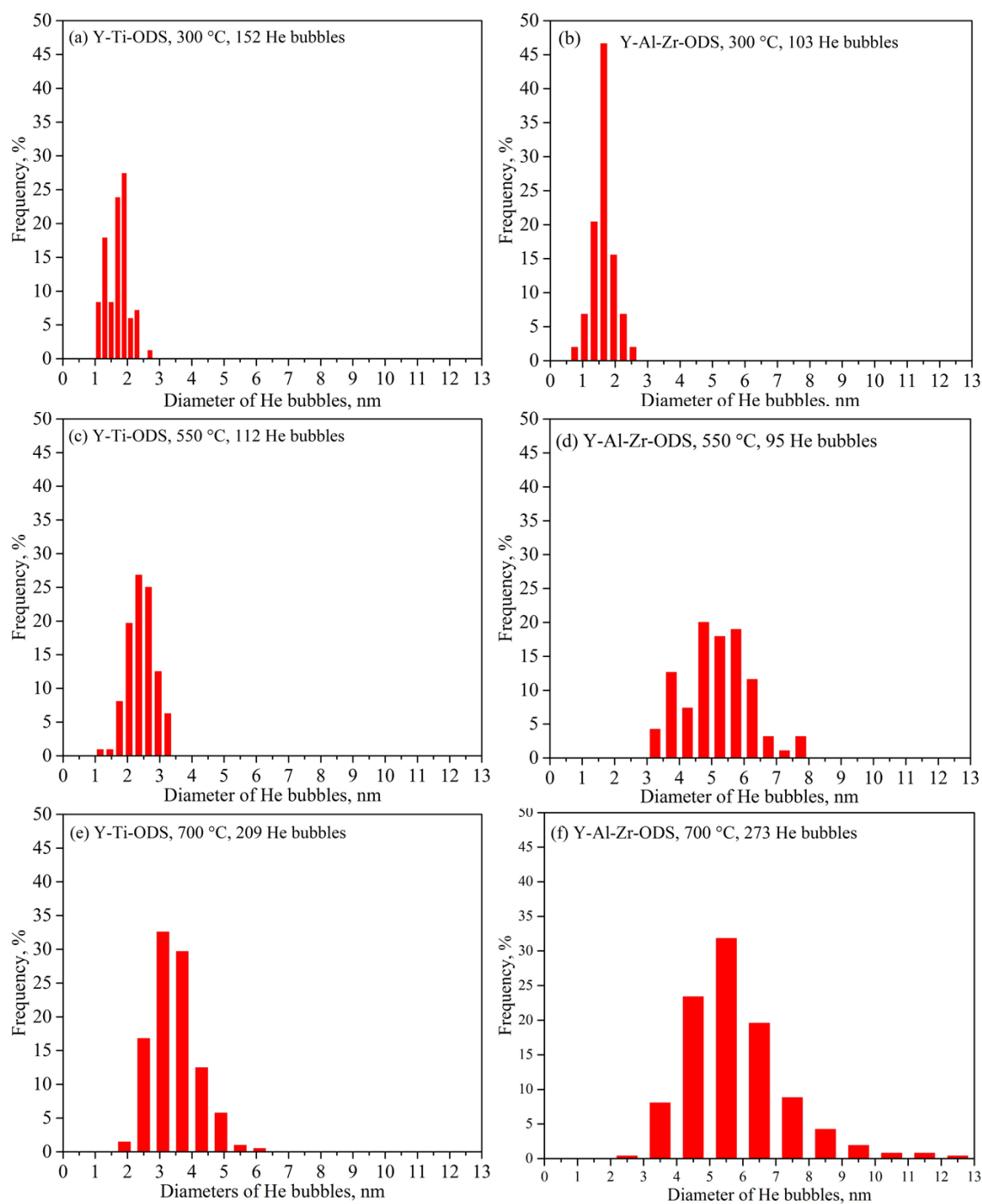


Fig. 3.6 Size distribution of He bubbles in Y-Ti-ODS (a), (c), (e) and Y-Al-Zr-ODS (b), (d), (f) at the He concentration of around 3500 appm.

3.3.3 Swelling behavior

In the depth range of 1000 to 1300 nm, the local swelling ($\Delta V/V$) induced by He bubbles can be approximately defined as follows:

$$\frac{\Delta V}{V} = \frac{4\pi}{3} \bar{r}^3 N_b \quad (3.1)$$

where $\bar{r}$ and N_b are the average radius and the number density of He bubbles, respectively [17]. All swelling values of ODS ferritic steels are shown in Fig. 3.7(c) as a function of irradiation temperature. At 300 °C, both ODS steels exhibited a near-zero swelling. As the temperature increased, the swelling of Y-Ti-ODS steel tended to be saturated but that of Y-Al-Zr-ODS steel continued to increase. The largest swelling of the latter steel was less than 0.7% at 700 °C, which is in accordance with the largest value of 0.5% in 15CRA3 ODS alloy irradiated to about 3300 appm He at 500 °C [18]. At each irradiation temperature, the swelling was smaller in Y-Ti-ODS steel than Y-Al-Zr-ODS steel.

Microstructures, including dislocations, dislocation loops, grain boundaries, and oxide particles may contribute to swelling resistance by playing a role as sinks for radiation induced damage structures. The sink strength of dislocation lines for point defects is approximately estimated as the dislocation density (about $1.4 \times 10^{14} \text{ m}^{-2}$), whilst that of oxide particles Z_s is expressed by $4\pi r_s N_s$ [19], where r_s is the mean radius and N_s is the number density. Accordingly, the sink strengths of oxide particles in Y-Al-Zr-ODS and Y-Ti-ODS steels were $1.4 \times 10^{15} \text{ m}^{-2}$ and $2.1 \times 10^{15} \text{ m}^{-2}$, respectively. In general, dislocations can preferentially absorb interstitials (He or Fe atoms) over vacancies. This effect could become more efficient especially at lower temperatures. However, in this work, when compared to the capture efficiency of oxide particles, the dislocation bias effect was rather negligible. In terms of the influence of grain boundaries on swelling resistance, M.B. Toloczko et al. discovered distinguishable void-denuded zones near grain boundaries, which led to a reduction of the overall swelling of MA957 ODS at 500 dpa [5]. But void-denuded zones were not observed in the current work. Taking into account the similar grain morphologies of both steels and larger intergranular bubbles in the Y-Ti-ODS steel, oxide particles should play a crucial role in causing discrepancies in swelling resistance for these two ferritic ODS steels.

In addition, it was elucidated by kinetic rate theory that void swelling was characterized by a peak at an intermediate irradiation temperature. Meanwhile, temperature sensitive parameters, the vacancy diffusion coefficient and the equilibrium vacancy concentration, controlled the process of void growth [17]. This phenomenon was also observed in He or Fe ions irradiated ODS steels and non-ODS steels [5, 18, 20]. In other words, similar to void swelling, it was possible for He bubble swelling to have an analogical dependence on temperature. At low temperatures, the mobility of vacancies and their clusters and He-vacancy complexes was so limited to retard the growth of bubbles, then suppressing swelling. With increasing temperature, vacancies became mobile and the swelling might reach its maximum value. For ODS steels, oxide particles trapped He atoms and vacancies

keeping the size of He bubbles small by acting as sinks for He and vacancies. In our work, the saturation temperature of swelling tended to be higher for the Y-Al-Zr-ODS ferritic steel than for Y-Ti-ODS ferritic steel. This might be related to the higher capture efficiency of oxide particles in Y-Ti-ODS ferritic steel. Therefore, controlling the dispersion morphology of oxide particles with a high sink strength is necessary to enhance swelling resistance.

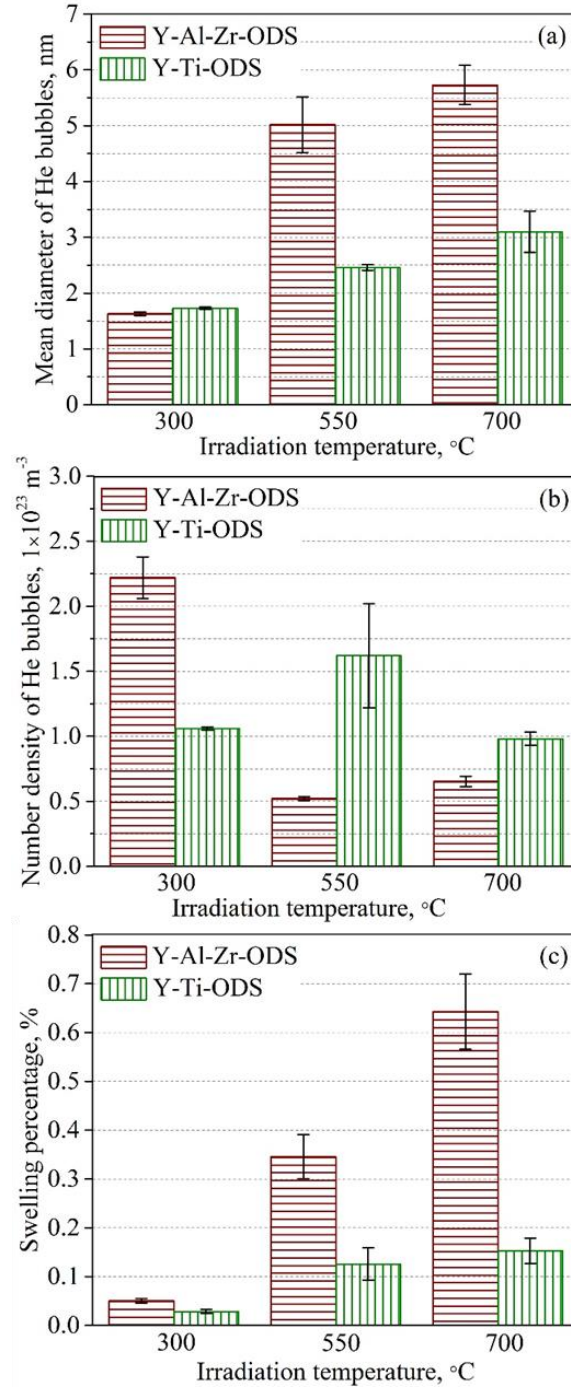


Fig. 3.7 The mean bubble size, number density and void swelling as a function of irradiation temperature for two ODS ferritic steels.

3.4 Conclusions

He bubble formation behaviors were compared between two ODS ferritic steels with and without simultaneous addition of Al and Zr after irradiation with 3500 appm He ions up to 0.2 dpa at 300 °C, 550 °C, 700 °C. The obtained main results are as follows:

- 1). In both steels, the grain sizes were not homogenous and the mean grain size of each ODS steel was estimated to be about 0.37 μm . For Y-Al-Zr-ODS, the mean diameter of oxide particles was 6.2 nm and the number density was $3.5 \times 10^{22} \text{ m}^{-3}$, while in Y-Ti-ODS, smaller oxide particles of 3.0 nm existed with a higher number density of $1.1 \times 10^{23} \text{ m}^{-3}$.
- 2). Dislocation densities were mostly similar both before and after irradiation.
- 3). In both steels, the bubble sizes and number densities increased and decreased, respectively, with increasing irradiation temperature. At 300 °C, some tiny spherical bubbles were nucleated along dislocation lines, implying that He atoms were trapped at dislocations. At 550 °C, He bubbles grew to 5.0 nm in diameter. At 700 °C, He bubble size became the largest.
- 4). At 300 °C, two ODS steels exhibited a near-zero swelling. As the temperature increased, the swelling of the Y-Ti-ODS steel tended to be saturated but that of the Y-Al-Zr-ODS steel continued to increase. The largest swelling of the latter steel was less than 0.7% at 700 °C. At each irradiation temperature, the swelling was smaller in Y-Ti-ODS steel than in Y-Al-Zr-ODS steel.
- 5). Taking into account the similar grain morphologies of both the steels and larger intergranular bubbles in the Y-Ti-ODS ferritic steel, oxide particles played a crucial role in causing discrepancies in swelling resistance for these two ferritic ODS steels. Therefore, controlling the dispersion morphology of oxide particles with a high sink strength is necessary to enhance swelling resistance.

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Chapter 4

Post He-implantation annealing effects on cavity evolution and hardening in ODS steel

4.1 Introduction

Oxide dispersion strengthened (ODS) steels have been considered as a candidate structural material of first wall/blanket for future fusion reactors because of their outstanding mechanical properties, especially high-temperature strength [1–2], and acceptable corrosion resistance against coolants [1], as well as excellent radiation tolerance such as low swelling and hardening [2–3]. In the fusion structural material, numerous helium (He) atoms are produced by (n, α) nuclear reactions. Moreover, the formation of He-Vacancy (He-V) clusters, involving nanosized He bubbles, cavities and large voids, may lead to swelling, hardening, embrittlement and reduction in creep properties [4].

In the conventional ferritic/martensitic (F/M) steels, He-induced hardening is still a matter of discussion. P. Jung et al. investigated the effect of the implanted He on tensile properties of 9Cr-martensitic steels (EM10 and T91) using an ion accelerator at temperatures from 150 °C to 550 °C with He concentrations between 1250 and 5000 appm at 0.2 and 0.8 dpa, respectively [5]. Based on the dependence of irradiation hardening on He concentration and dpa, they attributed the hardening to He bubbles without TEM examinations [5]. J. Henry et al. [6] performed TEM examinations and SANS analysis for the same steels as those in Ref. [5] implanted with 5000 appm He. Indeed, they concluded again that the evident hardening was attributed to He bubbles at the implantation temperatures between 250 and 550 °C, although no He bubbles but dot shaped small defect clusters, probably dislocation loops, were observed by TEM in the steel implanted with 5000 ppm He at 250 °C. Additionally, they mentioned that the barrier hardening model with a strength factor of 0.4 gave an insufficient hardening by small defect clusters. K. Farrell et al. [7] compared the tensile properties of F/M steels irradiated in HFIR and LANSCE spanning the dose range 0.01–24 dpa up to about 1000 appm He. As a result, there was no sign of a large hardening contribution attributable to the presence of He at the irradiation temperatures below 160 °C. Furthermore, J. Henry et al. [8] reported on tensile properties of 9Cr-1Mo (EM10) tempered martensitic steel irradiated in spallation conditions (133–301 °C, 4–11 dpa, 150–890 appm He, 1270–4800 appm H) and after the irradiation with fission neutrons in OSIRIS reactor (325 °C, ~1–9.3 dpa) that the amount of irradiation hardening showed a similar trend of dose dependence. Y. Dai et al. [9] investigated the dpa dependence of irradiation hardening of T91 irradiated at below 300 °C in SINQ Target-3, and reported that the dpa dependence of hardening was changed over 5.9 dpa (He = 390 appm) above which He bubbles contributed to an additional hardening. More recently, Y. Dai et al. reported that an evident hardening ($\Delta HV = \sim 80 \text{ kg/mm}^2$) was left in the post-irradiation annealed (600 °C/2 h) F/M steels after the irradiation in SINQ (1175 appm/11.3 dpa), which was attributed to the contribution of He bubbles [10].

As for the ODS F/M steels, the ODS F/M steel with He ion implantation (3360 appm/0.84 dpa) also presented a temperature dependent hardening behavior: declining from ~15% at 100 °C to ~3.5% at 500 °C [11], which might be accompanied by cavity evolution [12]. Nevertheless, some discrepancies still exist for the He induced hardening in ODS F/M steels. Roldán et al. reported that

the implantation of about 750 appm He brought about a 21% hardening in Eurofer ODS at 70 °C [13], while at 30°C/9 at.% He/3 dpa, a 31% hardening was produced in the same ODS steel [14]. At such low temperatures, it is difficult to separate the pure hardening contribution of He bubbles from those of fine defect clusters or dislocation loops.

Post-implantation annealing (PIA) may be an effective way to distinguish the contributions of dislocation loops and He-V clusters, and possibly lead to an assessment of the pure bubble hardening. In a 14Cr-YWTi nanostructured ferritic alloy with 12–14 at.% He implantation at 400 °C, the mean cavity size increased from 2.2 nm in the as-implanted case to 2.7 nm after the PIA at 750 °C/100 h [15]. The corresponding number densities of cavities increased from $\sim 8 \times 10^{23} \text{ m}^{-3}$ to $\sim 12 \times 10^{23} \text{ m}^{-3}$ after the PIA [16]. Nevertheless, hardening was not addressed in those works [15–16].

Therefore, the work in this chapter, at first, aimed to investigate the effect of high concentration He implantation at various temperatures. Second, the post-implantation annealing behavior of hardness and the microstructure evolution process were examined to assess the contribution of cavities to the hardening.

4.2 Material and methods

The material used in this chapter was a 14.5Cr-ODS ferritic steel (Y-Al-Zr-ODS) which was produced by mechanical alloy processing, followed by hot extrusion and forging at 1150 °C. The final heat treatment was an annealing at 1150 °C for 1 h followed by air-cooling. The resultant compositions (wt.%) were Fe-14.59Cr-1.84W-0.14Ti-3.46Al-0.27Zr-0.33Y₂O₃. The averaged grain size of the studied ODS steel was estimated to be about 370 nm based on electron backscatter diffraction (EBSD) measurements. More details have been described in the Chapter 2.

Specimens were irradiated with 1 MeV He⁺ at the DuET facility in Kyoto University [17]. The beams were by the raster scan at a frequency of 1000 Hz in a horizontal direction and 300 Hz in a vertical direction. He⁺ beam was inclined with 45 degrees to the normal of the specimen surface and a rotating energy degrader foil was applied for obtaining a rather homogenous distribution of helium atoms in the specimens. The averaged flux of He⁺ ions was $1.7 \times 10^{16} \text{ ions m}^{-2} \text{ s}^{-1}$. The injected helium concentration and displacement damage (displacements per atom, dpa) were obtained by SRIM [18] simulation with use of the Kinchin-Pease method (shown in Fig. 4.1), recommended by R.E. Stoller et al. [19]. At the region 1000 to 1300 nm from the specimen surface, the He concentration was about 3500 appm and the corresponding damage level was approximately 0.2 dpa. Main parameters are shown in Table 4.1.

The specimen as irradiated at 300 °C, which was placed in one evacuated quartz tube with Zr thin films for mitigating the surface oxidation of the specimen, was annealed at 800 °C for 100 h in a vacuum of $6 \times 10^{-3} \text{ Pa}$ followed by furnace-cooling. In order to eliminate the effect of aging itself, as-received specimen was also aged at 800 °C for 100 h and compared with the He-implanted

specimen.

Cross-sectional transmission electron microscopy (TEM) specimens were fabricated by the lift-out technique using a Focused Ion Beam (FIB). Prior to TEM observations, flash polishing was done by using a solution of 5% (vol.) HClO₄ and 95% (vol.) CH₃OH at approximately –35 °C for the removal of FIB damage layer. Subsequently, the microstructure was observed by using a conventional 200 kV JEOL JEM 2010 microscope. Further, cavities were imaged by the Fresnel contrast and the cavity size was carefully measured one by one according to the edge dark fringe (under-focus) or bright fringe (over-focus) of cavities.

Nanoindentation (NI) tests were carried out by using a nanoindenter (Agilent G200) equipped with a Berkovich tip at 20 °C. Continuous stiffness measurement (CSM) was adopted to obtain the profiles of continuous hardness and elastic modulus versus indentation displacement. Before testing, the indenter tip geometry was calibrated by indenting a standard material fused silica. Key testing parameters were as follows: the strain rate was 0.05 s⁻¹, the harmonic displacement was 1 nm and the testing Poisson's ratio of ODS samples was 0.3. For each specimen, 24 testing points (50 µm between two adjacent points) were chosen and the averaged hardness was obtained by calculating the measured hardness data of roughly 20 tests.

Table 4.1 Main irradiation parameters and the post-irradiation annealing (PIA) condition for the 300 °C irradiation

Material	Ions	Local He content	Local damage	Temperatures	PIA condition @ 300 °C irradiation
Y-Al-Zr-ODS	energy degraded He ⁺ ions	3500 appm	0.2 dpa	300, 550, 700 °C	800 °C/100 h

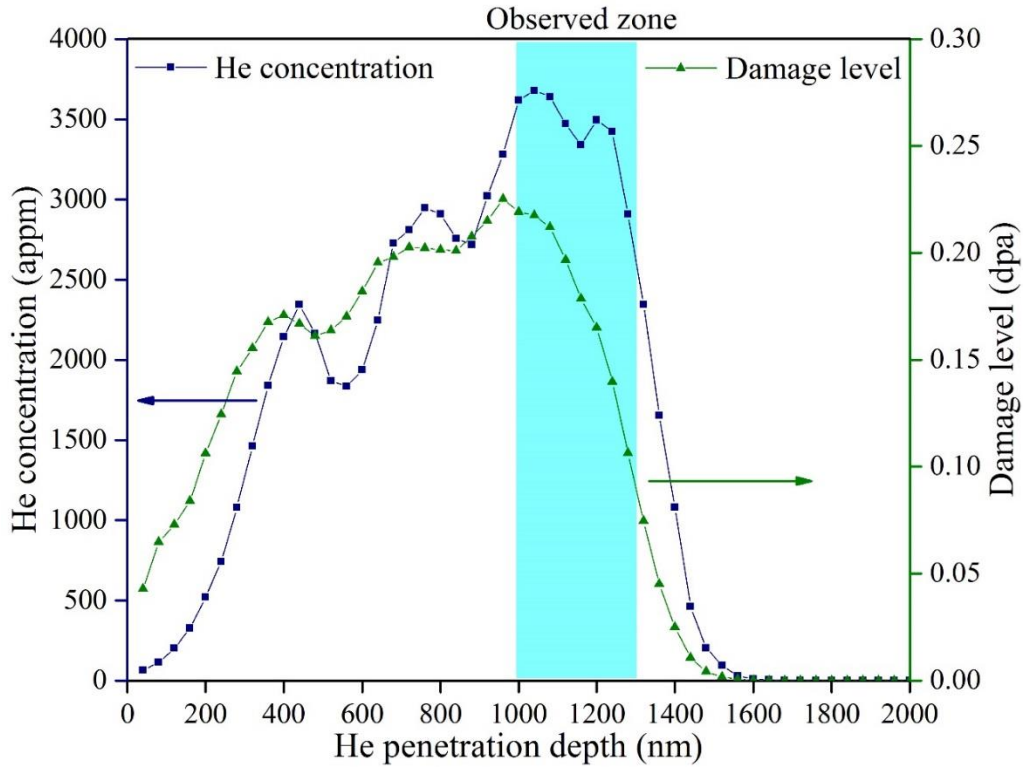


Fig. 4.1 He concentration (appm) and damage level (dpa) of a Fe-14.5Cr alloy as a function of the He-ion penetration depth, as predicted by SRIM simulation (He implanted to a fluence of 4.5×10^{20} He m⁻²).

4.3 Results and discussion

4.3.1 He-ion implantation hardening

The depth profiles of the averaged nanoindentation hardness (H_{NI}) for the as-received and as-implanted specimens are shown in Fig. 4.2(a), indicating that the averaged H_{NI} continuously decreased with increasing the indentation depth (h) from roughly 50 nm to 1500 nm, which is known as the indentation size effect (ISE) [20]. In order to evaluate irradiation hardening, we needed to choose an adequate depth that reflects microstructural changes by ion implantation. The hardness in the near surface depth region, which is shallower than 200 nm, is strongly affected by the depth because of the ISE, whereas in the region deeper than 300 nm, the hardness may already be influenced by un-irradiated region since the depth of the plastic deformation region created by a nanoindent is approximately five times or more of the indentation depth [21–24]. Therefore, we selected the indentation depth of 250 nm as a reference H_{NI} to evaluate He-implantation hardening [23–24]. All the depth profiles in Fig. 4.2(a) show the similar trend. The profiles of He-implanted specimens at 300 and 550 °C are located at the upper side but that at 700 °C is at the lower side of as-received specimen, although the differences are within an error bar.

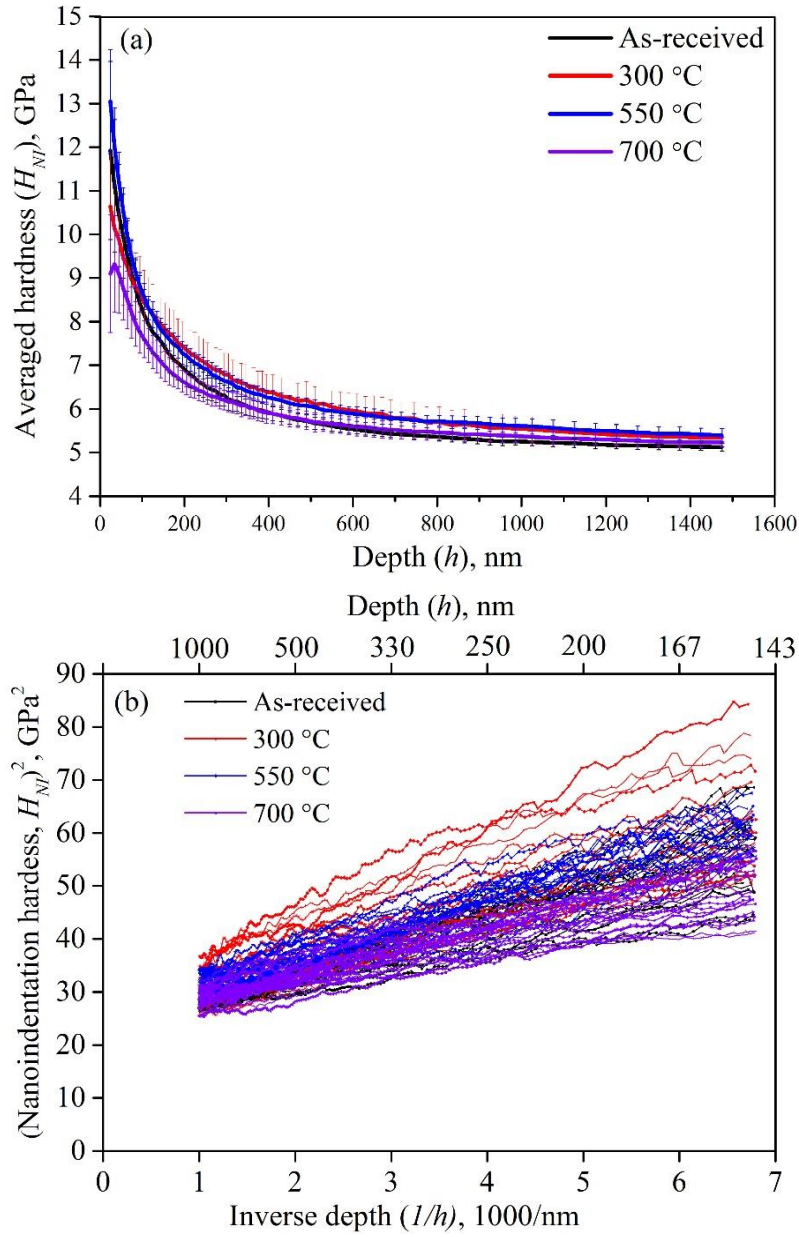


Fig. 4.2 (a) Depth profiles of the average hardness (H_{NI}) for the as-received specimen and as-implanted ones at 300, 550, 700 °C; and (b) plots of square nanoindentation hardness $(H_{NI})^2$ versus the reciprocal indentation depth ($1/h$).

Nix and Gao developed a model to evaluate a bulk relevant macrohardness for a surface thin layer based on the concept of geometrically necessary dislocations [20], which is described in the following equation that explains the depth dependence of hardness:

$$H/H_0 = \sqrt{1+(h^*/h)} \quad (4.1)$$

where H is the hardness at a certain indentation depth, h , and H_0 is the hardness in the limit of infinite depth that is defined to be the bulk relevant hardness. h^* is a characteristic length that depends on the

indenter shape, H_0 and the shear modulus, but is not a constant for a given material and indenter geometry. It is a function of the density of statistically stored dislocations via H_0 . Ideally plotting the square of the hardness against the reciprocal of the indentation depth should deserve a straight line, the intercept and the slope of which are the square of H_0 and h^* , respectively [20]. Fig. 4.2(b) shows the corresponding plots of square nanoindentation hardness $(H_{NI})^2$ versus the reciprocal indentation depth ($1/h$), where all the tangent lines in the indentation depth range of 150–1000 nm and 150–250 nm were used to evaluate the H_{NI} for the as-received and the as-implanted specimen, respectively. Thus, the averaged H_0 values were obtained, being the bulk relevant hardness of an un-implanted layer or a He-implanted layer.

All the measured hardness values and the hardness changes are shown in Fig. 4.3 and the numerical values are presented in Table 4.2. The hardness changes were generally similar for those obtained by the two methods. Fig. 4.3(a) and 4.3(c) showed that a small hardening was induced by He-ion implantation and gradually declined with increasing the implantation temperature. At 300 °C, the hardness changes at approximately 250 nm and obtained by the Nix-Gao model were 514 ± 582 MPa and 544 ± 417 MPa, respectively. Such rather large errors in the hardness changes come from the errors in the obtained hardness values before and after implantation where the latter were less than 8%. In this study, the effect of He-ion implantation on hardness was small, which made errors appear to be large. Therefore, we think the current experimental results are still meaningful for a discussion of the implantation effect.

Temperature dependent microstructural evolution under the He-ion implantations has been discussed in detail in the Chapter 3, which revealed that He bubbles grew up with decreasing number density as the temperature went up from 300 °C to 700 °C.

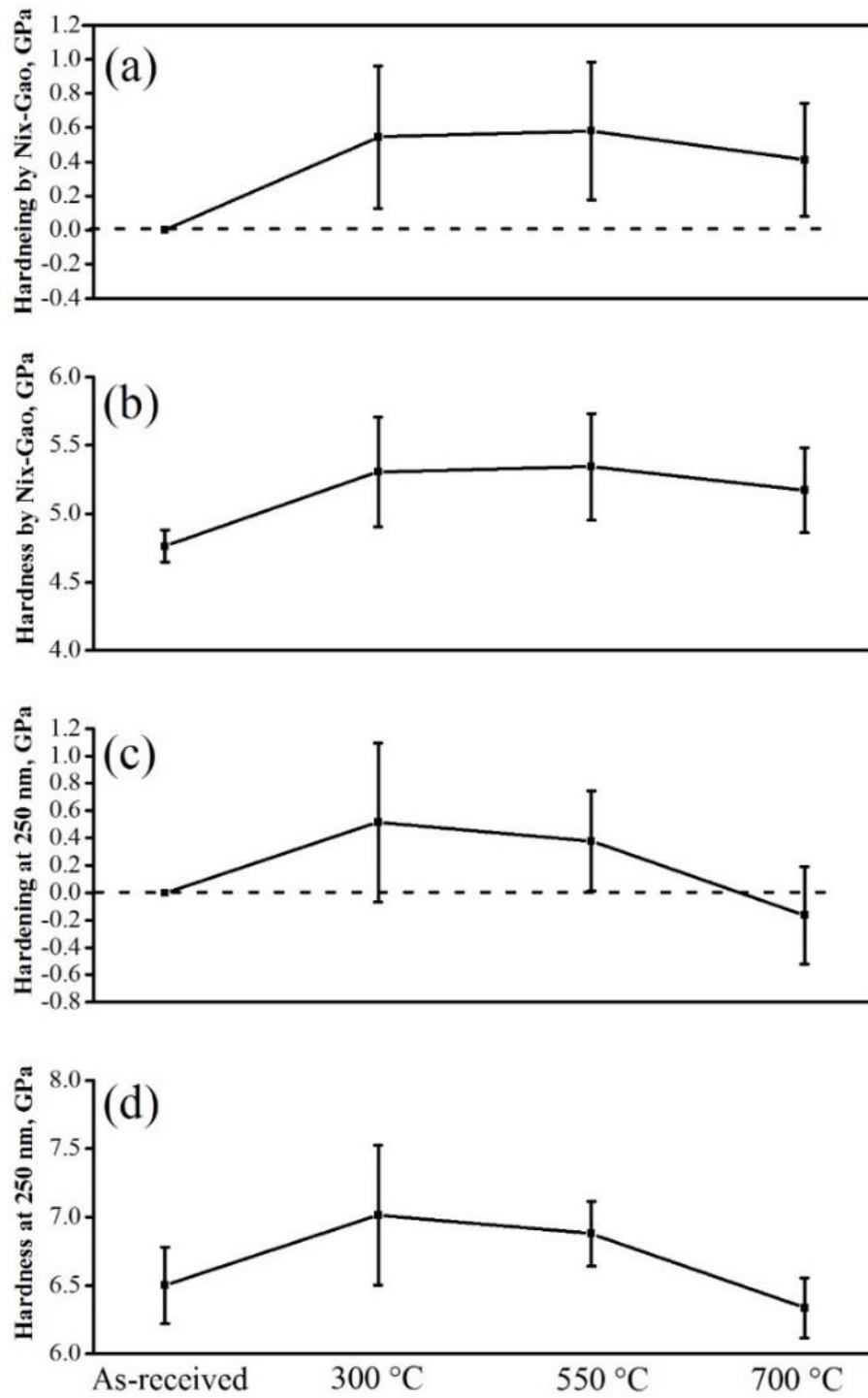


Fig. 4.3 Nanoindentation (NI) hardness (b, d), hardening (a, c) at an indentation depth of 250 nm and obtained by the Nix-Gao plotting for the as-received and as-implanted specimens at 300, 550 and 700 °C.

Table 4.2 Summary of the measured hardness (ΔH_{NI} , MPa) for each implantation condition and the estimated barrier strength factors of cavities (α_c) based on the TEM examinations.

		As-implanted at 300 °C	As-implanted at 550 °C	As-implanted at 700 °C	PIA at 800 °C/100 h
At 250 nm	ΔH_{NI}	514 ± 582	377 ± 365	-164 ± 355	4 ± 410
	α_c	0.085	0.0912	–	0.00085
Nix-Gao model	ΔH_{NI}	544 ± 417	580 ± 405	410 ± 331	-116 ± 294
	α_c	0.09	0.14	0.083	–

“–” means no valid estimated α_c values.

4.3.2 Cavity evolution during PIA treatment

After the implantation at 300 °C, up to 3500 appm He/0.2 dpa (about 1000–1300 nm), almost no dislocation loops were observed, except for spherical tiny He bubbles with the mean diameter and the number density of 2.5 ± 0.4 nm and $(22.2 \pm 1.6) \times 10^{22} \text{ m}^{-3}$, respectively, which are shown in Fig. 4.4. After the PIA at 800 °C/100 h, a similar microstructure in the end of He implantation range was observed as shown in Fig. 4.5, where the cavities were imaged at under-focus (left) and over-focus (right) conditions. The He ion implantation direction is from top to bottom. The spots, changing from white at under-focus to dark at over-focus due to the Fresnel contrast, were considered to be He-cavities. What's more, the cavities became sparser and smaller with increasing depth, in accordance with the He concentration profile predicted by SRIM simulation. Fig. 4.6(a) depicts an inhomogeneous distribution of cavities in the depth range of ~1000–1300 nm in the PIA specimen. The dashed rectangle region is enlarged in Fig. 4.6(b), where round, irregular and “crescent moon” shaped cavities existed. The “crescent moon” cavities, pointed out with black arrows but not observed before annealing, were probably attached with the surface of large oxides in the ODS steel, also being observed in another research [25]. After PIA, the number density and the average diameter of cavities were 5.0 ± 1.7 nm and $(6.7 \pm 0.5) \times 10^{22} \text{ m}^{-3}$, respectively. The other parameters of cavities are presented in Table 4.3.

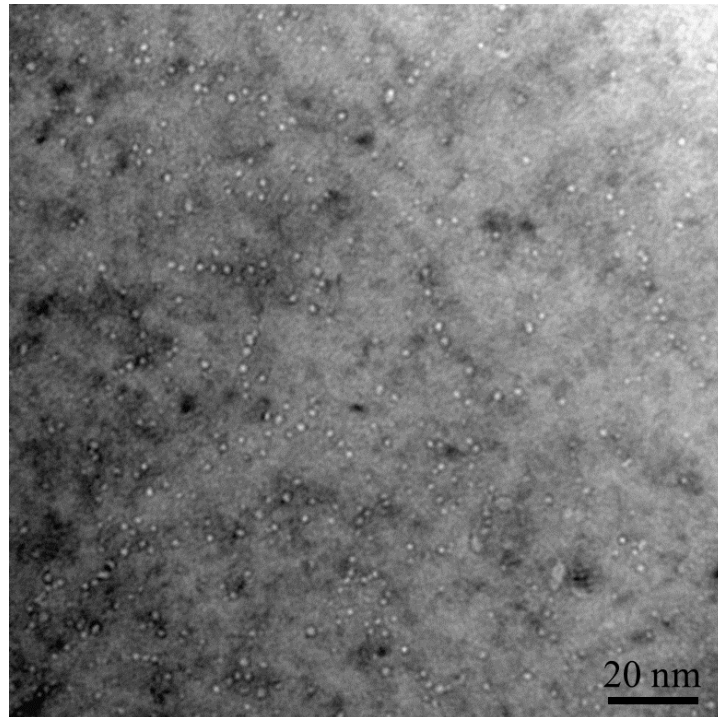


Fig. 4.4 He bubble distribution morphology in Y-Al-Zr-ODS after the He implantation at 300 °C, prior to the annealing.

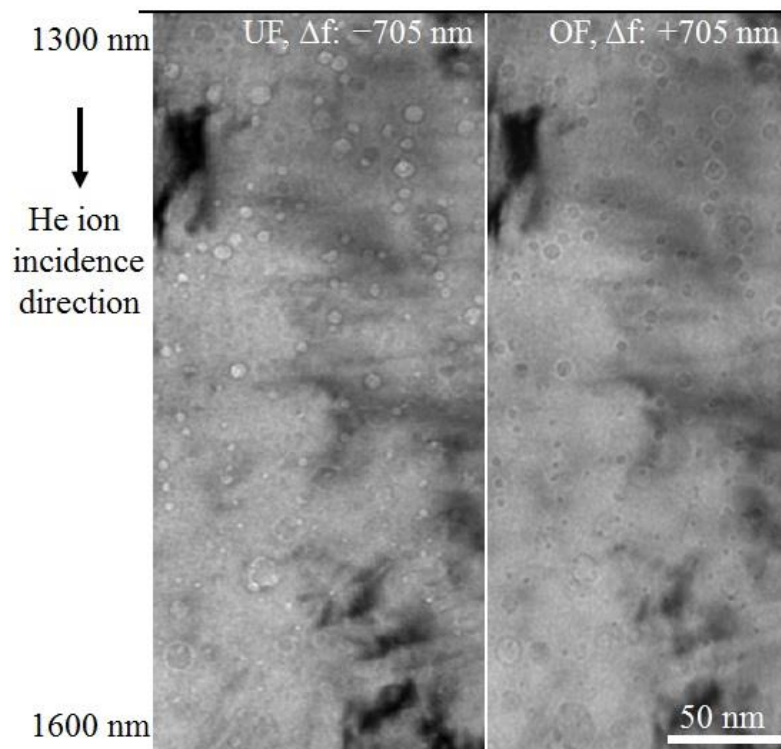


Fig. 4.5 Cavities in the depth range of approximately 1300–1600 nm from the implanted surface imaged at under-focus (UF) (left) and over-focus (OF) (right) conditions after PIA at 800 °C/100 h.

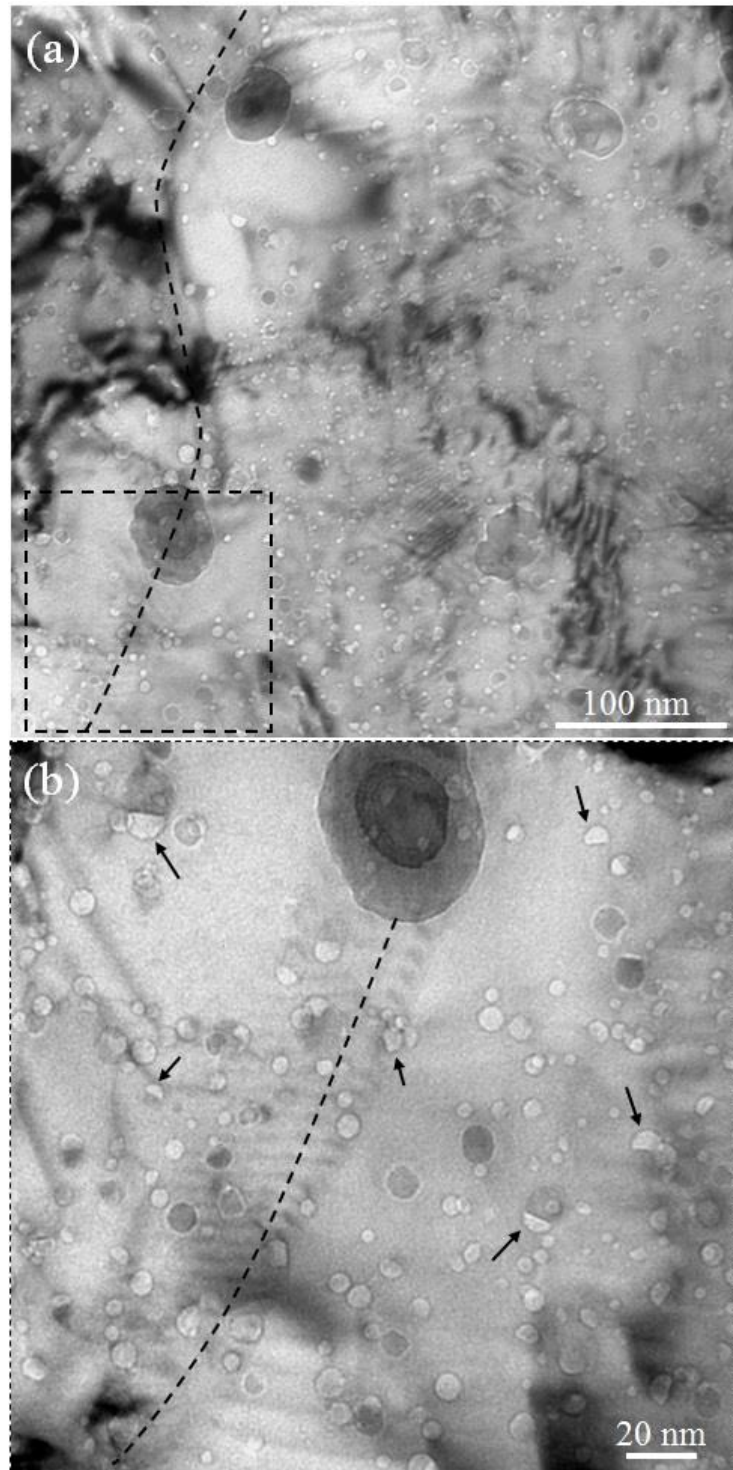


Fig. 4.6 (a) Cavities in the depth range of about 1000–1300 nm from the implanted surface after PIA at 800 °C/100 h. (b) Enlarged image of dashed rectangle in Fig. 4.6(a). Arrows mark “crescent moon” resembling cavities.

Fig. 4.7 shows the statistical size distribution for all the cavities (Fig. 4.7(a)), cavities in ferrite matrix (Fig. 4.7(b)), cavities at grain boundaries (GBs) and sub-GBs (Fig. 4.7(c)) before and after the PIA. For the as-implanted at 300 °C, the size distribution of spheroidal He bubbles was narrow irrespective of their nucleation sites. Following the PIA at 800 °C/100 h, all the cavity size distributions became much broader. Additionally, the minimum and maximum cavity sizes were 1.85 and 10.95 nm, respectively, while the minimum size in the ferrite matrix was close to the corresponding value of 1.68 nm in the as-implanted case before the thermal aging. P. D. Edmondson et al. ascribed the cavity coarsening to the punching out of self-interstitial and dislocation loops, Brownian motion and coalescence and Ostwald ripening [15]. Actually, in this study He bubbles grew up to large cavities under the thermal aging at 800 °C/100 h, where the large cavities might be agglomerations of vacancies, of which the internal gas pressure should be far smaller than the surface tension. Despite that, it is difficult to define the characteristics of cavities during PIA by the hard sphere equation of state (HSEOS) [26] without He atom concentration in the cavities.

Table 4.3 The average diameter (d_c , nm), standard deviation (St. Dev., nm), minimum (Min., nm) and maximum diameters (Max., nm), number density (N_c , $\times 10^{22} \text{ m}^{-3}$), number (T) of cavities counted in the specimens implanted with He at 300 °C before and after PIA.

	As-implanted at 300 °C			PIA at 800 °C/100 h		
	All cavities	Matrix	GBs	All cavities	Matrix	GBs
d_c	2.51	2.53	2.44	5.03	4.89	6.23
St. Dev.	0.38	0.37	0.40	1.66	1.57	1.94
Min.	1.68	1.68	1.71	1.85	1.85	3.08
Max.	3.79	3.79	3.23	10.95	9.34	10.95
N_c	$22.2 \pm 1.6^{[12]}$			6.7 ± 0.5		
T	379	325	54	306	274	32

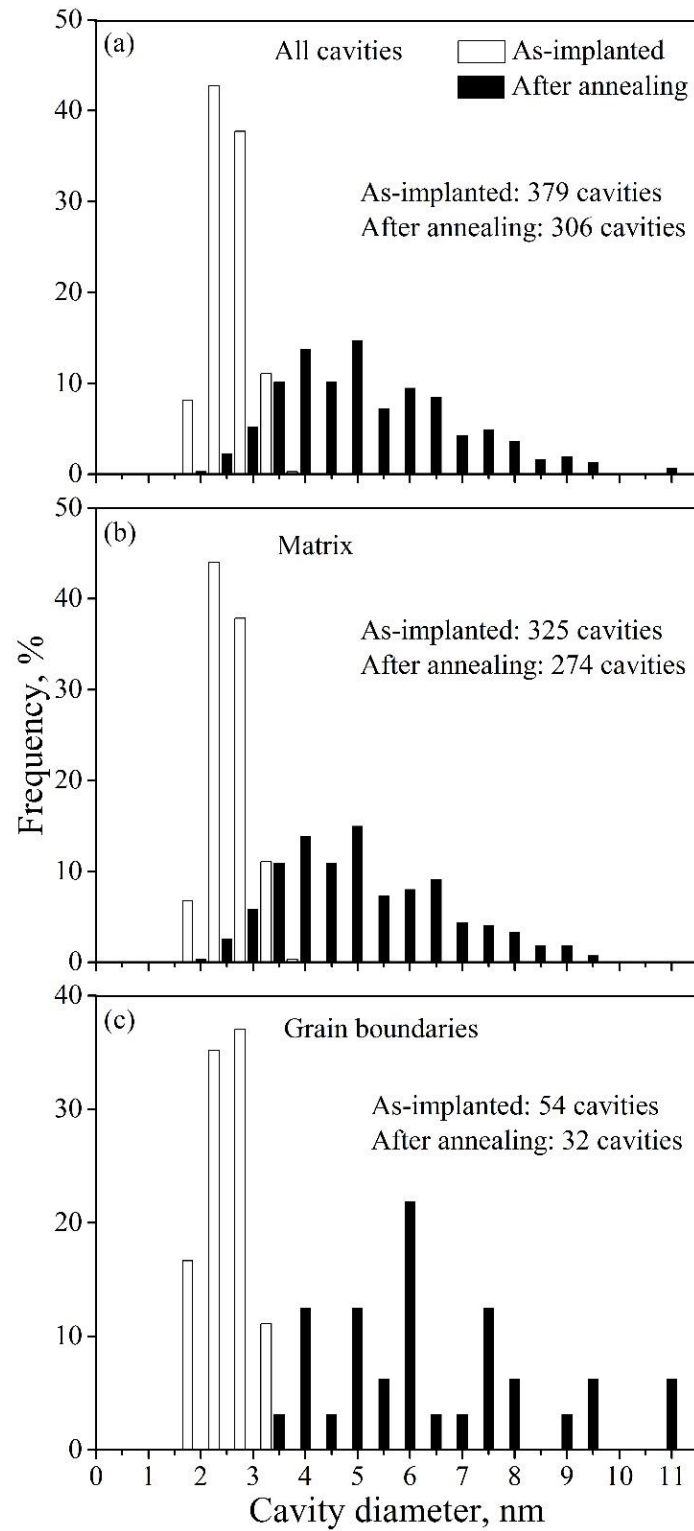


Fig. 4.7 Size distributions for all the cavities (a), cavities in the ferrite matrix (b) and cavities at the grain boundaries (c) in the specimens implanted with He at 300 °C before and after thermally aging at 800 °C/100 h in the depth range of roughly 1000–1300 nm (3500 appm He/0.2 dpa).

The nucleation sites of cavities were examined. In the depth range of 1000–1300 nm, microstructures were observed by using $\mathbf{g} = [1\bar{1}0]$ close to zone $[111]$ with $\mathbf{s}_g \neq 0$ under kinematical bright field (KBF) imaging conditions, as shown in Fig. 4.8. At an in-focus condition, oxide particles and precipitates were imaged as dark spots of the strain contrast as shown in Fig. 4.8(b), while at defocusing conditions of under-focus or over-focus, cavities were imaged as bright dots (see Fig. 4.8(a)) or dark dots (see Fig. 4.8(c)) of the Fresnel contrast as mentioned before. It appears that numerous cavities were attached to dislocations, oxide particles and precipitates, as shown in the two magnified pictures on the left end of Fig. 4.8. However, it is difficult to accurately figure out the corresponding cavity fractions trapped at dislocations on the basis of $\mathbf{g} \cdot \mathbf{b}$ invisibility criterion of dislocations with the two-dimensional observations. In the 14Cr-YWT nanostructured ferritic alloy [16], atom probe tomography results showed that 44% of nano-oxide clusters had He bubbles associated with them after the PIA at 750 °C/100 h. Besides, as marked by the dashed curves in Fig. 4.6(a), few cavities were detected along GBs and sub-GBs, probably owing to the weaker vacancy/helium sink strength of GBs and sub-GBs than the sum of dislocations, oxide particles and precipitates in the ferrite matrix [2], suggesting a good resistance to He induced GB embrittlement in the studied ODS ferritic steel.

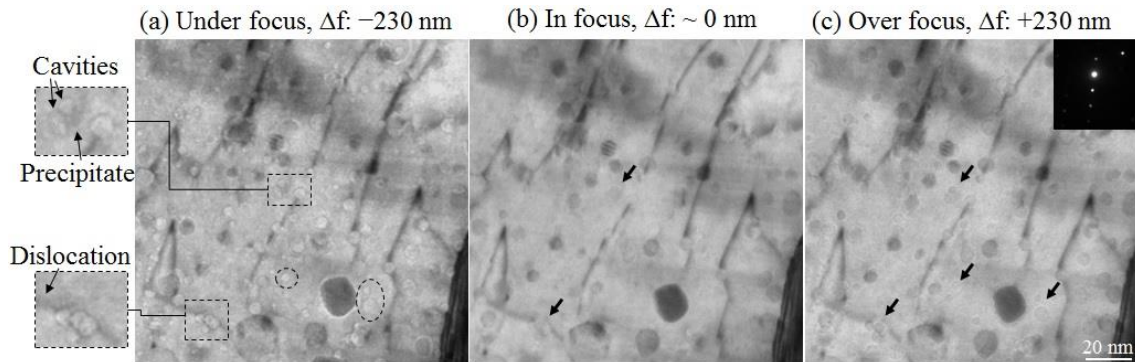


Fig. 4.8 Microstructures in the specimen after PIA imaged at under-focus (a); in-focus (b); over-focus (c) by using $\mathbf{g} = [1\bar{1}0]$ close to zone $[111]$ with $\mathbf{s}_g \neq 0$. Two enlarged pictures on the left end show typical nucleation sites of cavities at precipitates and dislocation. Cavities marked by dashed circles in Fig. 6(a) may be isolated. Positions for comparison were shown by arrows. The depth range: ~1000–1300 nm.

4.3.3 Hardness change by PIA treatment

After the PIA treatment at 800 °C/100 h, the averaged hardness (H_{NI}) versus the indentation depth (h) profile was almost identical to those of the un-implanted specimens before and after the thermal aging. Comparing the PIA treated specimen with the un-implanted being thermally aged, the hardness changes were estimated to be 4 ± 410 MPa and -116 ± 294 MPa based on the nanoindentation

hardness values at around 250 nm and those obtained by the Nix-Gao model, respectively (see Table 4.2). No matter how much hardening contributed by He-Vacancy clusters, the pure hardening produced by cavities should be negligible for the PIA case. Changes of the hardness between the as-implanted at 300 °C and the PIA treated are compared as shown in Fig. 4.9. It turned out that the limited hardening produced by He-implantation was further eliminated by the PIA.

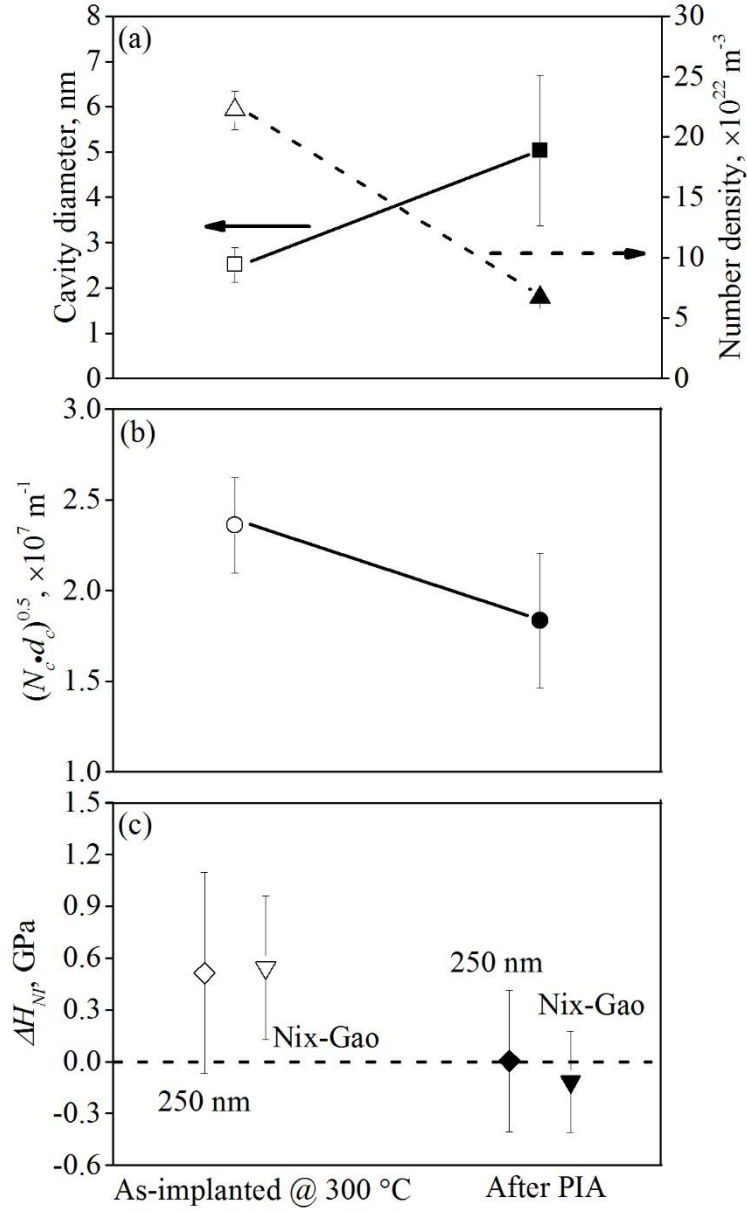


Fig. 4.9 (a) Diameter, d_c , number density, N_c of cavities; and (b) $(d_c \times N_c)^{0.5}$ for the as-implanted at 300 °C and the PIA; (c) The hardening before and after He-implantation at 300 °C and the hardness difference between the specimens after PIA and the un-implanted, which was thermally aged at 800 °C/100 h.

4.3.4 Temperature dependent hardening mechanisms

In general, the He ion implantation hardening was observed at low temperatures below 250 °C in the F/M steels [5–6] and ODS F/M steels with a displacement damage less than 1.0 dpa [11, 13–14]. The possible hardness contributor might be small He bubbles and small dislocation loops, although no clear examination was performed. It was shown that the F/M steels thermally aged at 600 °C [10] still maintained a hardening which was considered to be mainly due to He bubbles. To be noted, solute segregation and associated precipitation as well as clusters and dislocation loops induced by neutron irradiation might contribute to the hardening in a wide temperature range of 400–550 °C [27]. Below 250 °C, except for the direct contribution by high number density tiny He bubbles and He-vacancy complexes, additional hardenings could be induced by interstitial clusters or dislocation loops produced by punching from over-pressurized bubbles [28]. Furthermore, the dislocation loops survived during collision cascades could lead to an enhanced hardening by He-implantation, which was found in a reduced-activation martensitic steel with the He-ion implantation (580 appm/0.226 dpa) at 80–150 °C [29].

The amount of hardening was estimated by the following Orowan equation applied to expressing the short-range interaction between cavities and dislocations:

$$\Delta\sigma_c = M\alpha_c\mu b(N_c d_c)^{0.5} \quad (4.2)$$

where $\Delta\sigma_c$ is the change in the tensile yield stress; M is the Taylor factor (3.06); α_c is the barrier strength factor of cavities; μ is the shear modulus (80 GPa for alpha iron); b is the Burgers vector (0.248 nm for 1/2<111> dislocations in alpha iron); N_c and d_c are the number density and mean diameter of cavities, respectively. Since the number density and the diameter of He cavities decreased and increased, respectively, after the PIA treatment, the hardness change was estimated by comparing the value, $(N_c d_c)^{0.5}$, which was reduced by the PIA. In short, the softening was induced by the PIA, as shown in Fig. 8. The increase of nanoindentation hardness can be calculated following the relationship between nanoindentation hardness H_{NI} and yield stress σ_y : H_{NI} (Mpa) = $9.8\sigma_y / (3.06 \times 0.76)$ (Mpa) [21]. With the obtained values of N_c and d_c of the specimens before and after He-implantation, most of the barrier strength factors were estimated to be less than 0.1, as shown in Table 1, which was almost in agreement with the value of about 0.1 for He bubbles of sizes 1–1.5 nm in neutron irradiated F/M steels [10].

4.4 Conclusions

14.5Cr-ODS ferritic steel (Y-Al-Zr-ODS) was implanted with 3500 appm He (0.2 dpa) at 300, 550 and 700 °C. Post-implantation annealing (PIA) at 800 °C/100 h was conducted on the specimen implanted at 300 °C. Nanoindentation (NI) tests were carried out to investigate the temperature dependent hardening, and transmission electron microscopy (TEM) was performed to characterize the cavity evolution. The following main results were obtained:

- 1) A limited hardening was observed for the as-implanted ODS specimens at all implantation temperatures, which tended to reduce with increasing the temperature. The PIA caused no further hardening.
- 2) There was an evident change in the cavity distribution morphology by the PIA. The cavity diameter increased from 2.5 ± 0.4 nm to 5.0 ± 1.7 nm and the corresponding number density decreased from $(22.2 \pm 1.6) \times 10^{22} \text{ m}^{-3}$ to $(6.7 \pm 0.5) \times 10^{22} \text{ m}^{-3}$ before and after the PIA.
- 3) The negligible hardening accompanied by the change in the cavity morphology in the PIA treated specimen demonstrated that cavities were the weak barriers to the dislocation motion in the present ODS ferritic steel, allowing the corresponding barrier strength factor to be less than 0.1.

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Chapter 5

**Comparison in swelling, hardening resistance of three
ODS steels strengthened by different oxide particles**

5.1 Introduction

Oxide dispersion strengthened (ODS) steels owe their high performance to the ultrahigh density of nanoscale oxides and fine grains. Because of their superior tensile, creep and fatigue strength at elevated temperatures [1, 2] and excellent neutron radiation tolerance [3], ODS steels can be used as a fusion blanket structural material to elevate the operating temperature and the overall thermal efficiency of fusion plants [4]. In addition, ODS ferritic steels with Al addition, which possess high corrosion/oxidation resistance, have been considered as a candidate fuel cladding for the next generation fission reactors [1, 5] and light water reactors with accident tolerant fuel [6]. In harsh nuclear service environments, especially in fusion components, helium atoms generated through (n, α) nuclear reactions or directly from in-core plasma lead to the formation of interstitial helium atoms and helium-vacancy clusters, such as, helium bubbles or voids in structural materials, which may result in the degradation of mechanical properties, such as hardening and embrittlement, as well as swelling [7].

Concerning ODS steels, it is commonly accepted that helium effects are mitigated by numerous dispersed oxide particles, acting as effective sinks providing sites for defect accumulation, combination or annihilation [3, 4]. Previous studies confirmed the trapping effects of oxide particles on nanometer-sized cavities by means of transmission electron microscopy (TEM) [8], scanning TEM [9, 10] and atom probe tomography (APT) [11] after various types of irradiations and post-irradiation annealing treatments in the temperature range of 400–750 °C. Meanwhile, two dominating nucleation styles of cavities in association with oxides were suggested by G.R. Odette [12]: one is the oxide particle that contains cavities and the other is the oxide particle attached with cavities in a side to side way. To our knowledge, the former was only found in amorphous Y-Al-O particles [13]. The previous experimental results revealed that not only oxide/matrix interfaces could provide preferential nucleation sites for cavities, but also the oxides themselves might have some solubility for helium or helium bubbles. The effect of oxide type on the helium solubility was investigated by related simulation studies on various oxides (e.g. Y-Ti-O, Y-Al-O oxides) [14, 15]. Finally, as expected, He-induced swelling was effectively suppressed by oxide particles and was well demonstrated by comparing ODS steels and non-ODS steels [16, 17]. Ion-irradiation experiments of ODS steels with different oxide particle types, sizes and number densities were mainly studied by single He ion irradiations at relatively low displacement damages, indicating that finer oxide particles with a higher number density contributed to a smaller swelling [18, 19]. Regarding the effect of simultaneous dual beam (Fe and He ions) irradiation, the amount of research is limited.

As for the peak swelling temperature, several previous studies indicated that the swelling in ferritic/martensitic (F/M) alloys was peaking at around 420–470 °C in ion irradiations [20] and neutron irradiations [21] being affected by the damage rate. Since helium may reduce the mobility of vacancy and increase the stability of voids, helium effects are expected to be enhanced at a higher temperature

than 470 °C. In the previous research on helium effects in ODS ferritic steels, the targeted irradiation temperatures were ranging up to 700 °C and the maximum swelling rate was at 500–600 °C [22] because the mobility of helium might also become larger at these high temperatures [23]. It is considered that the peak swelling is determined as a result of a balance between the mobility of vacancies and thermal stability of voids.

Helium-induced hardening is another key concern for the structural materials in fusion systems. At room temperature, the implantation of about 750 appm He to an ODS ferritic steel gave rise to an obvious hardening of 21% with homogeneously distributed helium nanobubbles [24]. Likewise, hardening became larger with increasing helium concentration obeying a 1/2-power law [25]. But in another ODS ferritic steel implanted with about 3400 appm He, as the temperature increased from 100 to 500 °C, hardening decreased continuously from ~15% to ~3.5% [22]. These results elucidated that the hardening behavior was affected by implantation temperature and even materials. Furthermore, the difference in hardening between single Fe ion and dual (Fe and He) ion beam irradiations was significantly influenced by irradiation temperature: at 300 °C, the hardening caused by dual beam irradiation was evidently larger than that by single Fe ion irradiation [26], while at 500 °C, the hardening was almost the same between the two [27]. A simulation study indicated that helium bubbles of 2 nm in diameter with more than 5 helium atoms per vacancy were strong obstacles to the glide motion of an edge dislocation in iron [28], and significant hardening has been observed in reduced-activation ferritic/martensitic (RAFM) steels irradiated up to 11.3 dpa/1175 appm He in the Swiss Spallation Neutron Source (SINQ) [29]. In contrast to these hardening effect of helium, Kasada et al. reported that the hardening induced by helium ion irradiation (580 at. Ppm He/0.226 dpa at below 423 K) in a reduced-activation martensitic steel was interpreted simply in terms of displacement damage, suggesting that there is no significant effect of helium on the hardening [30]. Therefore, in fusion relevant temperature region (~400–700 °C for F/M steel) [31], helium effects on irradiation hardening are still uncertain.

Since the material performance of ODS steels depends on the morphology of oxide particle dispersion, dispersion control is essential for development of the steel. The Al-addition to FeCr-ODS steels altered the main particles from $Y_2Ti_2O_7$ pyrochlore to YAH and YAP [32], and a small addition of Zr to FeCrAl ODS steels altered the majority of oxide particles from (Y, Al, O) dispersoids to (Y, Zr, O) dispersoids [33], resulting in an enhanced high-temperature strength of the steel [1].

In this chapter, we investigated the radiation responses of three sorts of ODS ferritic steels mostly strengthened by (Y, Ti, O), (Y, Al, O) and (Y, Zr, O) nanoparticles, respectively, focusing on the roles of helium implantation in the hardness change and swelling under dual beam irradiation at 550 °C.

5.2 Experimental

5.2.1 Materials

The materials used in this chapter were three sorts of ODS ferritic steels, Fe-13.6Cr-1.9W-0.16Ti-0.33Y₂O₃ (Y-Ti-ODS), Fe-15.42Cr-3.8Al-1.85W-0.1Ti-0.36Y₂O₃ (Y-Al-ODS) and Fe-14.59Cr-3.46Al-1.84W-0.14Ti-0.27Zr-0.33Y₂O₃ (Y-Al-Zr-ODS), which were produced by mechanical alloy processing. After hot extrusion and forging were performed at 1150 °C, the materials were finally annealed at 1150 °C for 1 h and followed by air-cooling. More details of the material conditions and processing were described in Chapter 2 and also in Ref. [34].

Specimens were sampled so that the specimen surface was perpendicular to the extrusion direction. Specimen surface was mechanically ground with SiC papers, and subsequently polished with successive grades of diamond spray down to 0.25 μm. Finally, electrolytic polishing was conducted in a solution of 10% (vol.) HClO₄ and 90% (vol.) CH₃COOH at room temperature except for Y-Al-ODS.

5.2.2 Irradiation conditions

Specimens were simultaneously irradiated with 6.4 MeV Fe³⁺ and 1 MeV He⁺ at the DuET facility in Kyoto University [35]. Single Fe³⁺ irradiation was also carried out for comparison. The beams were raster scanned at a frequency of 1000 Hz in a horizontal direction and 300 Hz in a vertical direction. In the dual beam irradiation, the He⁺ beam was declined with 45 degrees to the normal of the specimen surface and maintained a simultaneous injection with Fe³⁺ beam. A rotating energy degrader foil was applied for obtaining a rather homogenous distribution of helium atoms in specimens. The fluxes of He⁺ and Fe³⁺ ion beams were approximately 1.5×10^{16} ions m⁻² s⁻¹, 1.7×10^{16} ions m⁻² s⁻¹, respectively. The irradiation temperature was measured by an infrared thermography to be 550 °C within a fluctuation of ±10 °C. All three sorts of ODS steels were irradiated together for about 8 hours. Main parameters are presented in Table 5.1.

The injected helium concentration and displacement damage (displacements per atom, dpa) were obtained by SRIM [36] simulation, and shown in Fig. 5.1. The nominal displacement damage at 600 nm depth was 15 dpa, and in the depth range from 1000 to 1300 nm, the local damage level and helium concentration were approximately 30 dpa and 3500 appm, respectively.

Table 5.1 Parameters of dual-beam (Fe³⁺ & He) and single-beam (Fe³⁺) irradiations at 550 °C.

Materials	Dose of Fe beam, ions m ⁻²	Dose of He beam, ions m ⁻²	Local He content, appm	Local damage level, dpa
Y-Ti-ODS, Y-Al-ODS, Y-Al-Zr-ODS	$\sim 4.8 \times 10^{20}$	$\sim 4.5 \times 10^{20}$	~ 3500	~ 30

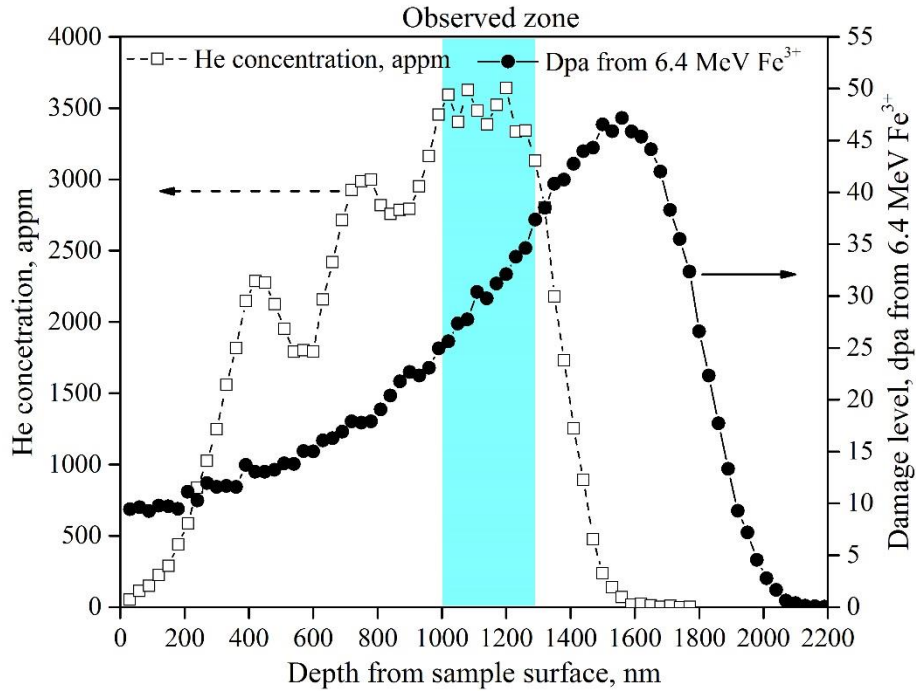


Fig. 5.1 SRIM simulation results of damage level, dpa and He concentration, appm.

5.2.3 Transmission electron microscopy (TEM)

Cross-sectional TEM specimens were prepared by using the FIB lift-out technique, followed by the flash polishing with 5% (vol.) HClO_4 and 95% (vol.) CH_3OH around -35°C to remove a FIB damage layer. Dislocations and oxide particles were imaged under kinematical bright field (KBF) image conditions ($\mathbf{g} = \langle 110 \rangle$, $\mathbf{s}_g \neq 0$) by using a conventional 200 kV JEOL JEM 2010 microscope. Meanwhile, helium bubbles were imaged by Fresnel contrast at both under- and over-focused conditions. The thickness of the observation area in TEM foil was obtained by measuring the fringe spacing in Convergent Beam Electron Diffraction (CBED) patterns.

5.2.4 Hardness measurements

Vickers hardness was measured for as-received ODS bulk samples using a diamond indenter with a Vickers hardness tester (HVM-G21, Shimadzu). The sample surface tested was perpendicular to the extrusion direction. The load and dwell time were 1 kg and 10 s, respectively. 10 tests were done for each sample and the averaged values were obtained.

Nanoindentation testing was performed on as-received and irradiated samples by using a nanoindenter (Agilent G200) equipped with a Berkovich tip. A continuous stiffness measurement (CSM) was adopted to obtain continuous hardness and elastic modulus as a function of indentation depth. Before testing, the indenter tip geometry was calibrated by indenting a fused silica reference sample with known mechanical properties. Other main testing parameters were depicted as follows:

the maximum indentation depth was 2000 nm, the strain rate was 0.05 s^{-1} , the harmonic displacement was 1 nm, and the Poisson's ratio was 0.3. For each specimen, 24 testing points (60 μm between two adjacent points) were chosen and the averaged hardness was acquired by calculating the measured hardness data of roughly 20 tests after several test results were omitted because of the significance in the data scattering.

5.3 Results and discussion

5.3.1 TEM examinations

5.3.1.1 Microstructure before irradiation

Prior to irradiation, oxide particles and dislocation structures of Y-Al-ODS were observed under KBF image contrast by using $\mathbf{g} = [1\bar{1}0]$ close to zone $[111]$, and shown in Fig. 5.2(a) with the corresponding particle size distribution in Fig. 5.2(b). The related dispersion parameters of oxide particles for the three ODS ferritic steels were summarized in Table 5.2. The average particle spacing distance (λ_o) was calculated as $[(N_o)^{-1/3} - d_o]$, where N_o and d_o were the particle number density and the mean diameter, respectively [37]. The dislocation densities in as-received ODS ferritic steels are presented in Table 5.3. Grains were found to be elongated parallel to the extrusion direction and the grain size of Y-Al-ODS was measured to be about 0.46 μm in width based on the STEM bright-field image (shown in Chapter 2).

Table 5.2 Mean diameter (d_o), number density (N_o), volume fraction (f_o) and averaged distance (λ_o) of oxide particles in the three as-received ODS ferritic steels.

	Y-Ti-ODS ^[19]	Y-Al-ODS	Y-Al-Zr-ODS ^[19]
d_o , nm	3.0 ± 0.1	6.3 ± 0.2	6.2 ± 0.1
N_o , m^{-3}	$(1.1 \pm 0.1) \times 10^{23}$	$(1.9 \pm 0.1) \times 10^{22}$	$(3.5 \pm 0.6) \times 10^{22}$
f_o , %	0.18 ± 0.02	0.32 ± 0.03	0.52 ± 0.08
λ_o , nm	17.6 ± 0.1	31.2 ± 0.2	24.3 ± 0.1

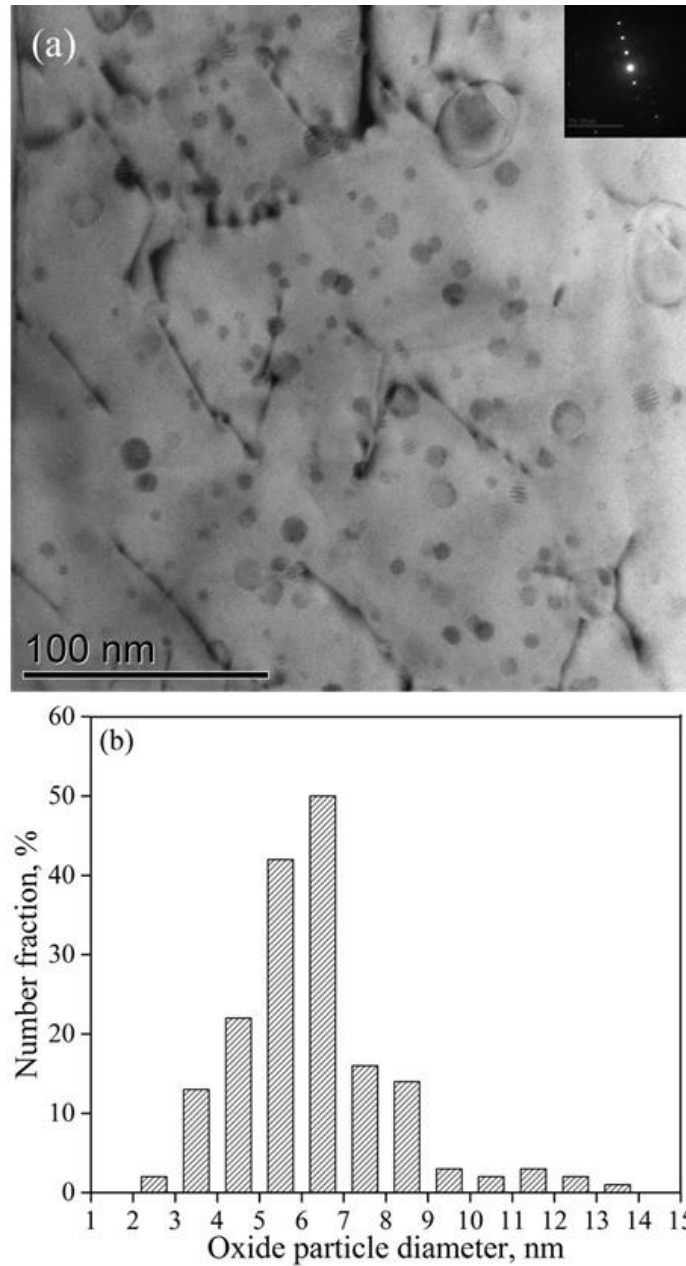


Fig. 5.2 (a) oxide particles and dislocations in as-received Y-Al-ODS steel and (b) the corresponding particle size distribution.

Table 5.3 Dislocation density (ρ) in the depth range of 1000–1300 nm (~30 dpa) in the three ODS steels before and after ion irradiation.

$\rho, \times 10^{14} \text{ m}^{-2}$	Y-Ti-ODS	Y-Al-ODS	Y-Al-Zr-ODS
As-received	1.2 ^[19]	1.2	1.4 ^[19]
Single beam	1.1	0.7	2.1
Dual beam	0.3	1.1	2.8

5.3.1.2 Ion-irradiation induced He bubbles and dislocations

Fig. 5.3 shows a TEM cross-sectional micrograph of whole range of the damage layer in Y-Al-ODS irradiated with dual ion beams where numerous tiny bubbles were mainly distributed in the depth region of 600 to 1600 nm. The distribution of helium bubbles after dual ion beam irradiation was well consistent with the SRIM simulation results, while in the case of single ion beam irradiation, tiny voids with negligible number densities were observed.

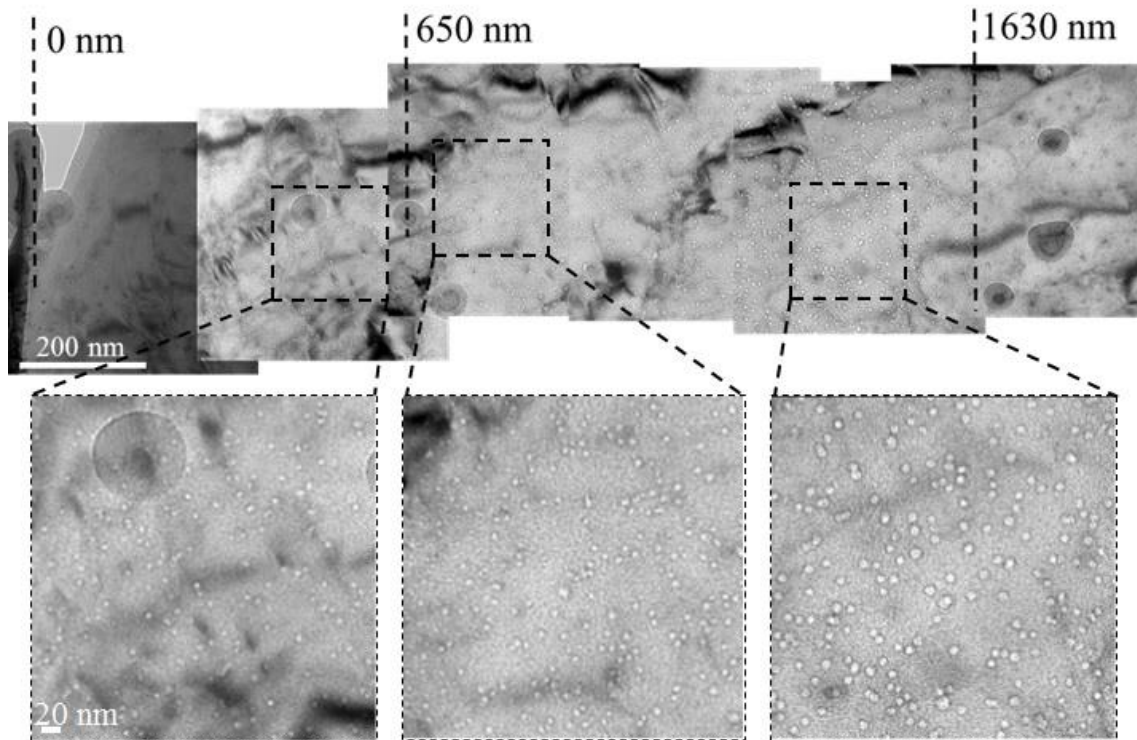


Fig. 5.3 He bubble distribution in Y-Al-ODS steel after dual-beam irradiation.

In order to distinguish between the contrasts of helium bubbles and oxide particles to accurately investigate the positional relationship between the two, helium bubbles were observed with Fresnel contrast technique at under to over focused conditions with KBF imaging using $g = \langle 110 \rangle$. The distribution of both helium bubbles and oxide particles after the dual ion irradiation are shown in Fig. 5.4(a) to 5.4(c) for Y-Ti-ODS, Fig. 5.4(d) to 5.4(f) for Y-Al-ODS and Fig. 5.4(g) to 5.4(i) for Y-Al-Zr-ODS steel in the region from 1000 to 1300 nm depth with approximately 30 dpa and 3500 appm He concentration. Helium bubbles, oxide particles as well as dislocations were characterized for each ODS steel. The bright spots in the under focused images (Fig. 5.4(a), 5.4(d) and 5.4(g)) became dark spots in the over-focused images (Fig. 5.4(c), 5.4(f) and 5.4(i)), from which it could be judged that the spots corresponded to helium bubbles. The black spots in in-focused images (Fig. 5.4(b), 5.4(e) and 5.4(h)) were mostly oxide particles and the other precipitates. Precise TEM observations revealed that

most of the imaged helium bubbles nucleated as attached to oxide particles by side to side, which was further verified in this research with the use of high resolution STEM BF imaging conditions for dual beam irradiated Y-Al-ODS. The numerical data of the mean diameter and the number density of helium bubbles were obtained by counting 610 helium bubbles in TEM photos and given in Table 5.4. Size distribution of He bubbles are shown in Fig. 5.5, indicating that the bubble size of the studied three ODS steels increases in the order of Y-Ti-ODS (2.8 ± 0.1 nm) < Y-Al-Zr-ODS (4.5 ± 0.2 nm) < Y-Al-ODS (6.6 ± 1.0 nm). Smaller the helium bubbles tended to larger the number density. The reason for the distribution difference of helium bubbles among the three ODS steels is discussed in the next section. The fraction of helium bubbles affiliated with oxide particles were estimated to be 73.7%, 81.4% and 82.2% for Y-Ti-ODS, Y-Al-ODS and Y-Al-Zr-ODS, respectively (see Table 5.4). These values might be overestimated essentially due to invisible dislocations, oversight of helium bubbles formed at grain boundaries and unavoidable overlay in a two-dimensional micrograph. C.M. Parish et al. estimated the fraction of bubbles associated with precipitates to be roughly 40% by virtue of STEM chemical analysis after dual ion (Fe, He) beam irradiation up to ~20 dpa and ~450–750 appm He implantation at 650 °C [10]. Although the trapping capacity appears to depend on the oxide particles and/or precipitates, it is clear that the oxide/matrix interfaces can effectively trap helium atoms, accelerating the formation of more stable helium bubbles adjacent to oxide particles [38].

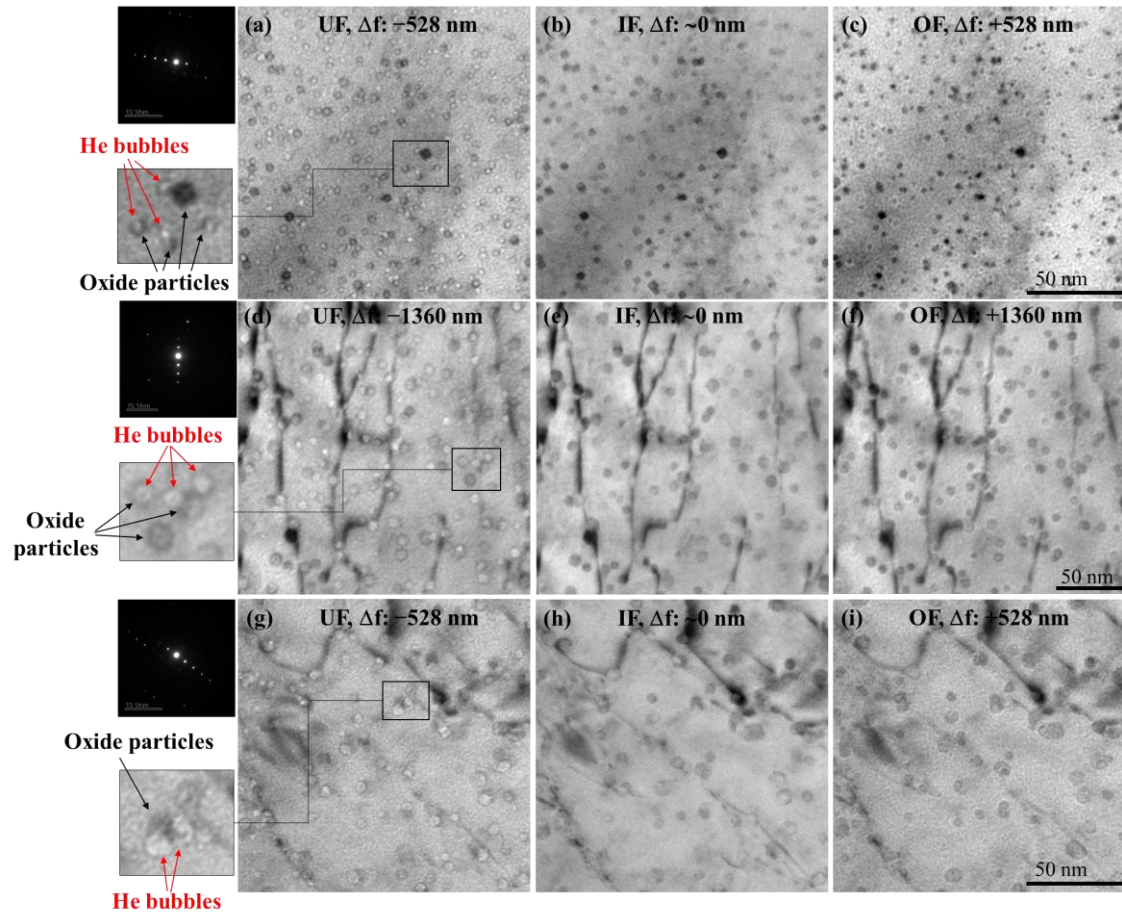


Fig. 5.4 TEM observations of He bubbles, oxide particles and dislocation lines in Y-Ti-ODS (a–c), Y-Al-ODS (d–f), Y-Al-Zr-ODS (g–i) with changing focus conditions from under-focus to over-focus; a nominal damage of approximately 30 dpa and He concentration of 3500 appm. The farthest left magnified images show He bubbles attached to oxide particles. All images were taken by using $g = [110]$ close to pole $[001]$; the diffraction pattern for the TEM images located in the same column. UF: under focus, IF: in focus, OF: over focus.

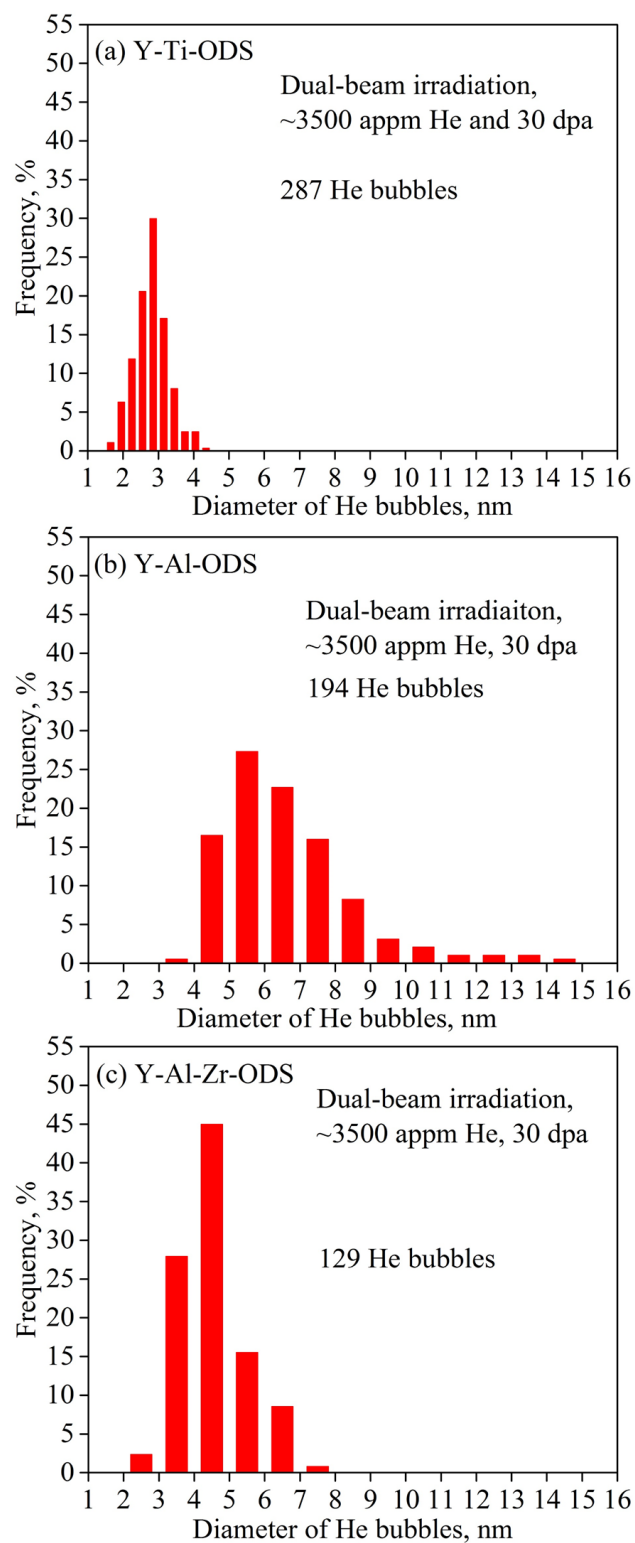


Fig. 5.5 Size distribution of He bubbles formed in the three ODS steels after dual-beam irradiations at ~30 dpa and 3500 appm He.

Table 5.4 Mean diameter (d_b), number density (N_b) of He bubbles, swelling ($\Delta V/V$), the number (T) of counted bubbles and the fraction (F) of bubbles adjacent to oxide particles in the depth range of 1000–1300 nm under dual beam irradiation.

	Y-Ti-ODS	Y-Al-ODS	Y-Al-Zr-ODS
d_b , nm	2.8 ± 0.1	6.6 ± 1.0	4.5 ± 0.2
N_b , m ⁻³	$(1.1 \pm 0.1) \times 10^{23}$	$(2.7 \pm 0.2) \times 10^{22}$	$(3.6 \pm 0.6) \times 10^{22}$
$\Delta V/V$, %	0.13 ± 0.02	0.53 ± 0.19	0.20 ± 0.04
T ; F , %	287; 73.7	194; 81.4	129; 82.2

In our previous research, single He⁺ implantation to ~3500 appm He/0.2 dpa at 550 °C [19] resulted in a similar helium bubbles distribution with a mean diameter and number density of 2.5 ± 0.1 nm, $(1.6 \pm 0.4) \times 10^{23}$ m⁻³ and 5.0 ± 0.5 nm, $(5.2 \pm 0.2) \times 10^{22}$ m⁻³ for Y-Ti-ODS and Y-Al-Zr-ODS, respectively, which suggests that the two orders of magnitude of difference in the He/dpa ratio never causes a significant effect on the He bubble formation. At high temperatures between $0.2T_m$ and $0.5T_m$ (T_m : the melting temperature), not the damage rate but the flux of He⁺ implantation can effectively control to stabilize helium-vacancy clusters above some critical sizes [39]. As a result, bubble embryos were nucleated at a higher number density irrespective of damage rate.

Dislocations were observed using $\mathbf{g} = \langle 110 \rangle$ for three ODS steels irradiated with dual (Fe³⁺ and He⁺) beam and single Fe³⁺ beam irradiation. The measured line dislocation densities in the three steels are shown in Table 5.3, and an example of dislocation segments is shown in Fig. 5.6 for the single Fe³⁺ beam irradiated Y-Ti-ODS. After irradiation, the line dislocation density appeared to decrease in Y-Ti-ODS and Y-Al-ODS, although some dislocations were invisible due to the $\mathbf{g} \cdot \mathbf{b} = 0$ condition. No dislocation loops were found at this irradiation temperature (550 °C). This result was consistent with the other ODS steels irradiated with single Fe ion beam at 500 °C [40] and dual (Fe-ion and He-ion) beam at 650 °C [41], while in the neutron irradiated ODS ferritic alloy at 500 °C, dislocation loops with two sorts of Burgers vectors, $a/2\langle 111 \rangle$ and $a\langle 100 \rangle$, were observed [13]. This difference is considered to be attributed to high dpa rate in heavy-ion irradiations ($\sim 1.0 \times 10^{-3}$ dpa/s in this research), providing effective spatial overlap of cascades above about 0.01 dpa [42]. Consequently, the majority of radiation induced defects can be annihilated by mutual recombination of one vacancy/vacancies and one interstitial/interstitials especially at elevated temperatures.

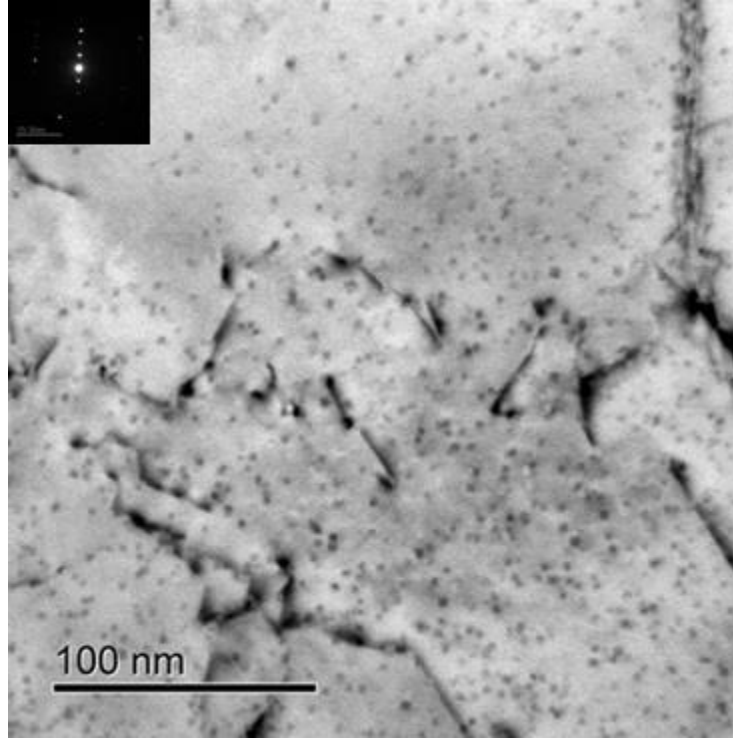


Fig. 5.6 Microstructures in single (Fe^{3+}) beam irradiated Y-Ti-ODS with a nominal damage of 30 dpa, imaged by using $g = [1\bar{1}0]$ close to pole $[110]$ under KBF.

5.3.1.3 Swelling

The void swelling calculated on the basis of bubble size distribution [43] was estimated to be 0.13%, 0.53% and 0.20% in Y-Ti-ODS, Y-Al-ODS and Y-Al-Zr-ODS, respectively. The difference in swelling can be explained in terms of trapping capacity at oxide particles, dislocations and grain boundaries. According to the previous study [3], the sink strength is described by the number of trapping sites per unit area, where the sink strength of dislocations, Z_d , is denoted by the dislocation density, while the sink strength of oxide particles, Z_o , is expressed by $2\pi N_o d_o$, where N_o and d_o are the mean diameter and the number density of oxide particles, respectively. And the sink strength of grain boundaries, Z_{gb} , is given by $15/h^2$, where h is the average grain size [44]. Here, the average grain sizes of Y-Ti-ODS and Y-Al-Zr-ODS were around 370 nm [19] and that of Y-Al-ODS was roughly 460 nm. The calculated sink strength values are summarized in Table 5.5. It turns out that the oxide particles act as dominant sinks for defect recombination and/or bubble nucleation when compared to dislocations and grain boundaries. Nevertheless, the heterogeneous distribution of helium bubbles may be caused by the sparse distribution of oxide particles and dislocations in grains. Under these circumstances, numerous intergranular bubbles were formed (see Fig. 5.7), demonstrating the strong sinking effects of grain boundaries.

Table 5.5 Estimated sink strengths of oxide particles (Z_o), line dislocations (Z_d) and grain boundaries (Z_{gb}) on the assumption that a lattice site provides a trapping site.

($\times 10^{14} \text{ m}^{-2}$)	Y-Ti-ODS ^[19]	Y-Al-ODS	Y-Al-Zr-ODS ^[19]
Z_o	20.7	7.5	13.6
$^a Z_d$	0.3	1.1	2.8
Z_{gb}	1.1	0.7	1.1

^aSink strengths of line dislocation come from that of the ODS specimens after dual beam irradiation

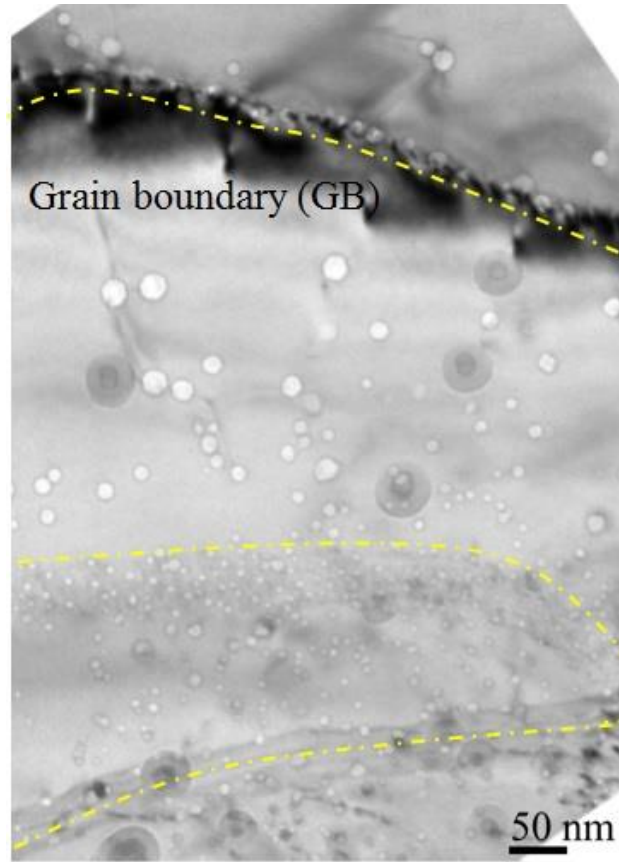


Fig. 5.7 Inhomogeneous He bubble distribution in dual beam irradiated Y-Al-ODS steel. GB is marked by three dash lines.

Actually, $\text{He}_n\text{-V}_m$ ($n=1, 2, 3$ and $m=0, 1$) clusters have much lower formation energies at the ferrite/ $\text{Y}_2\text{Ti}_2\text{O}_7$ interfaces than in the ferrite matrix [45], implying the preferential nucleation of a helium bubble nucleus at oxide/matrix interfaces. A short distance between neighboring oxide particles can enhance the trapping probability of helium, point defects and their clusters, which leads to the formation of helium bubbles in a high number density at the oxide particles. Once a helium bubble is formed, the bubble does immediately behave as an excellent sink for point defects [3] and further

improves the swelling resistance of ODS steels. An increased number density of bubbles in Y-Ti-ODS compared to the Y-Al-ODS and Y-Al-Zr-ODS alloys was mainly attributed to the higher number density of oxide particles in Y-Ti-ODS.

As discussed before in this section, the sink strength is a measure of the number of trapping site per unit area, and the difference in the swelling among the three ODS steels was well explained by the sink strength estimated from the TEM examinations. Indeed, void swelling was inversely proportional to the sink strength of oxide particles in this work, as shown in Fig. 5.8. A similar trend was also observed in other research on ODS steels containing one type of oxide particle [18, 44]. However, at a very high He concentration, trapping efficiency, which is the number of helium atoms trapped at a site, should be taken into account and it can be changed among different types of oxide particles since it might be determined by the binding energy between the helium atom and the trapping site. A simulation study is effective to discuss this issue and to clarify the effect of type of oxide particles which have different crystal structures as observed in Y-Ti-ODS [46], Y-Al-ODS [32] and Y-Al-Zr-ODS [33].

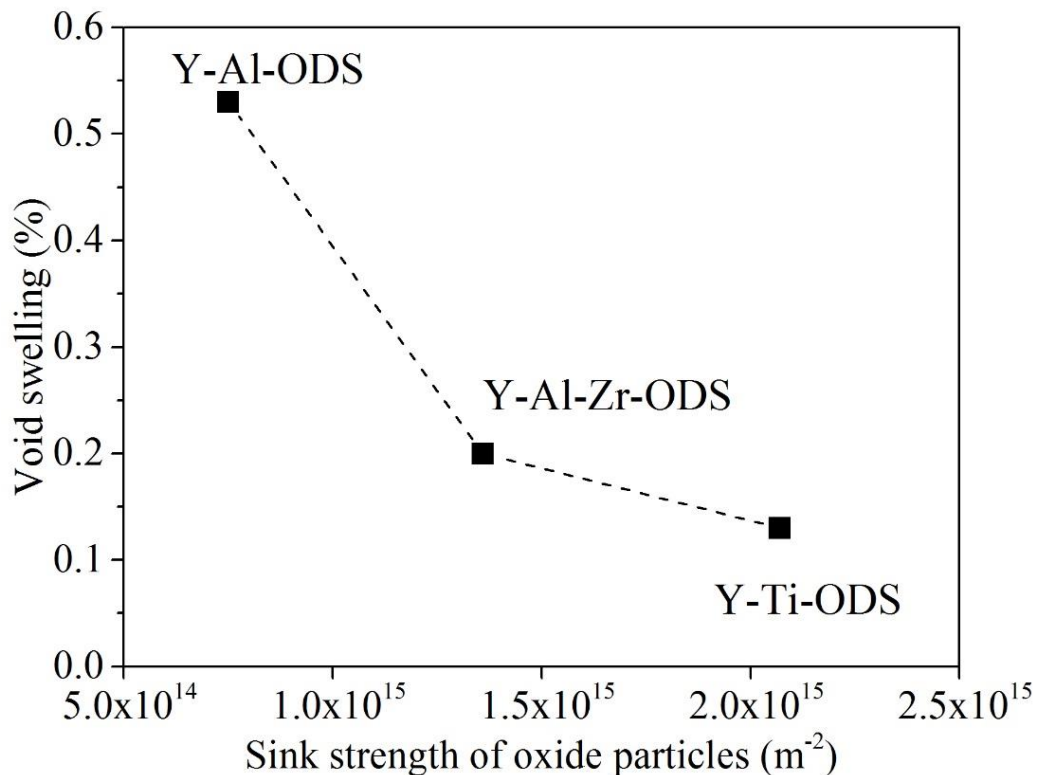


Fig. 5.8 Void swelling in the three studied ODS steels after the dual-beam irradiation (~ 30 dpa, 3500 appm) as a function of the corresponding sink strength of oxide particles.

5.3.2 Hardness measurements

5.3.2.1 Hardness before irradiation

Fig. 5.9 shows the relationship between Vickers hardness (HV) and nanoindentation (NI) hardness of as-received ODS steels. The NI hardness was obtained by two methods: one is by obtaining the values at each indentation depths of 200, 250, 300, 500, 1000 and 2000 nm in the depth profile of NI (see the averaged black lines in Fig. 5.10(a), 5.10(b) and 5.10(c)), and the other is by applying the Nix-Gao model to all of the measured data of the indentation depth from 200 to 1000 nm (see black lines in Fig. 5.11(a), 5.11(b) and 5.11(c)) [47].

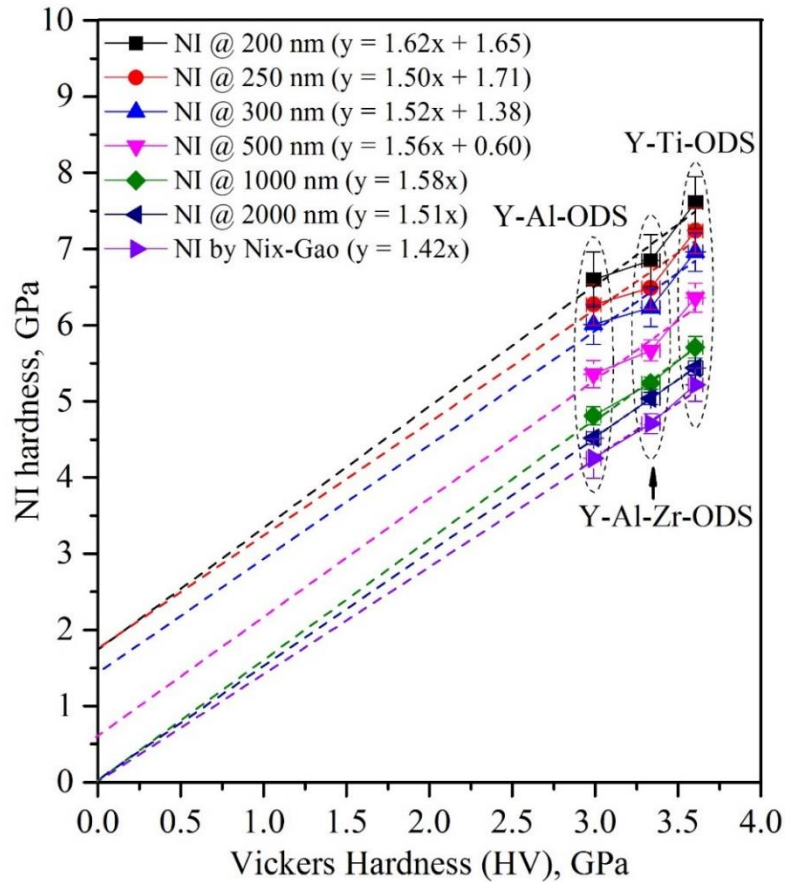


Fig. 5.9 Nanoindentation (NI) hardness at different indentation depths and obtained by the Nix-Gao model as a function of Vickers hardness (HV) for the three as-received ODS steels.

As shown in Fig. 5.10, in the near surface region, below the depth of 50 nm, NI hardness increased abruptly with increasing depth, which is known as the reverse indentation size effect (ISE) and is often ascribed to testing artifacts [48]. In the depth range of deeper than 50 nm, a normal ISE was observed where the hardness decreased with increasing indentation depth, which is considered to be due to so called geometrically necessary dislocations (GND) that mathematically decreases dislocation density with increasing indentation depth [48].

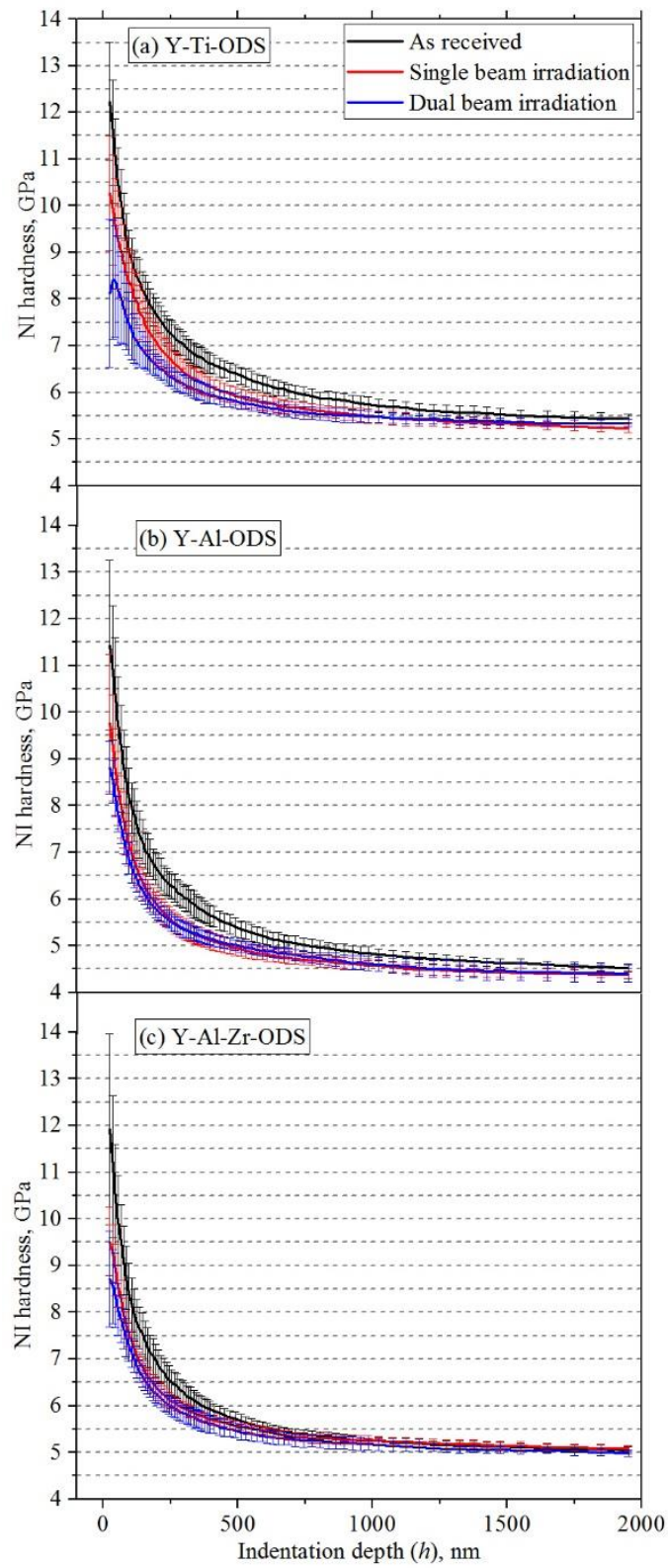


Fig. 5.10 Averaged depth profiles of nanoindentation (NI) hardness of (a) Y-Ti-ODS, (b) Y-Al-ODS and (c) Y-Al-Zr-ODS: black/unirradiated, red/single ion irradiated, blue/dual ion irradiated.

Fig. 5.9 shows that there is a proportional relationship between the Vickers hardness and the NI hardness obtained by the Nix-Gao model and the NI hardness obtained at 1000 and 2000 nm, in both of which the indentation size effect (ISE) can be neglected. Meanwhile a linear relationship can be seen for the NI hardness obtained at 200, 250, 300 and 500 nm, where the ISE became significant. It is considered that the intercept values of the lines of the linear equations reflect the amount of GND of ISE.

Generally, it can be said that the NI hardness is expressed as $H_{NI} = 1.5HV$. The mismatch between HV and H_{NI} is considered to be due to the difference in the hardness measurement technique between the two methods. As for the NI hardness value obtained at each indentation depth, it becomes larger with smaller indentation depth, which is known as ISE. Although the NI hardness was roughly 1.5 times larger than the Vickers hardness, there was a good correlation in the order of the hardness: Y-Ti-ODS > Y-Al-Zr-ODS > Y-Al-ODS. The strengthening mechanisms were discussed in Ref. [49].

5.3.2.2 Irradiation induced hardness changes

As explained in the previous section, the NI hardness after ion-irradiation was analyzed by two methods: one is the conventional method to measure the NI hardness at a constant indentation depth and the other is to measure the hardness following the Nix-Gao model. In the former, the hardness at the indentation depth of 250 nm was measured for three ODS ferritic steels before and after irradiation. In fact, the plastic zone at the 250 nm indentation depth was reported to be able to reflect the hardness of the peak damage region (approximately 1600 nm) at the present ion-irradiation experimental conditions [50]. In the latter, NI hardness was extrapolated by applying the Nix-Gao model to each H^2 versus $1/h$ plot of the irradiated specimens in the indentation depth range from around 200 to 250 nm, as shown in Fig. 5.11(a), 5.11(b) and 5.11(c). All hardness values obtained by the above two methods were shown in Fig. 5.12 and the numerical values are summarized in Table 5.6.

The NI hardness derived by the former indicated that the three ODS ferritic steels were softened by both single Fe^{3+} and dual (Fe^{3+} and He^+) beam irradiation. The softening was rather evident in dual beam irradiated Y-Ti-ODS (-0.91 ± 0.36 GPa at 250 nm) and Y-Al-ODS (-0.77 ± 0.32 GPa at 250 nm). Such phenomenon was also found in reduced activation martensitic steels under neutron irradiation at temperatures above 423 °C which is much lower than the threshold temperature of 600 °C beyond which the martensite phase became unstable [51, 52]. The softening behavior might be owing to the radiation enhanced recovery of dislocation structures. However, a different trend showing no significant ion irradiation hardening was found in the NI hardness measured by the Nix-Gao model. This result is consistent with a hardness decreasing significantly as the irradiation temperature increases to 500 °C in single He^+ or Fe^{3+} irradiated ODS steels [22, 40].

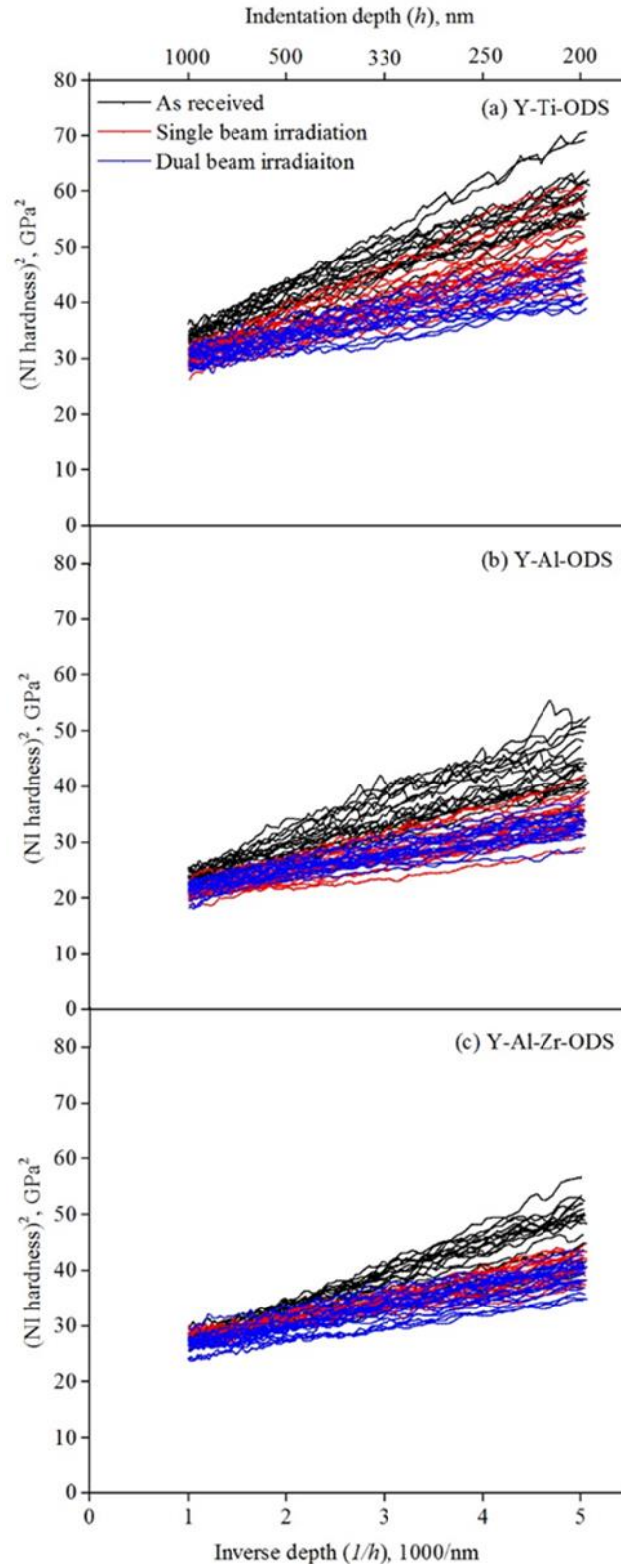


Fig. 5.11 H^2 versus $1/h$ plots of all nanoindentation (NI) hardness data based on the Nix-Gao model for (a) Y-Ti-ODS, (b) Y-Al-ODS and (c) Y-Al-Zr-ODS: black/unirradiated, red/single ion irradiated, blue/dual ion irradiated.

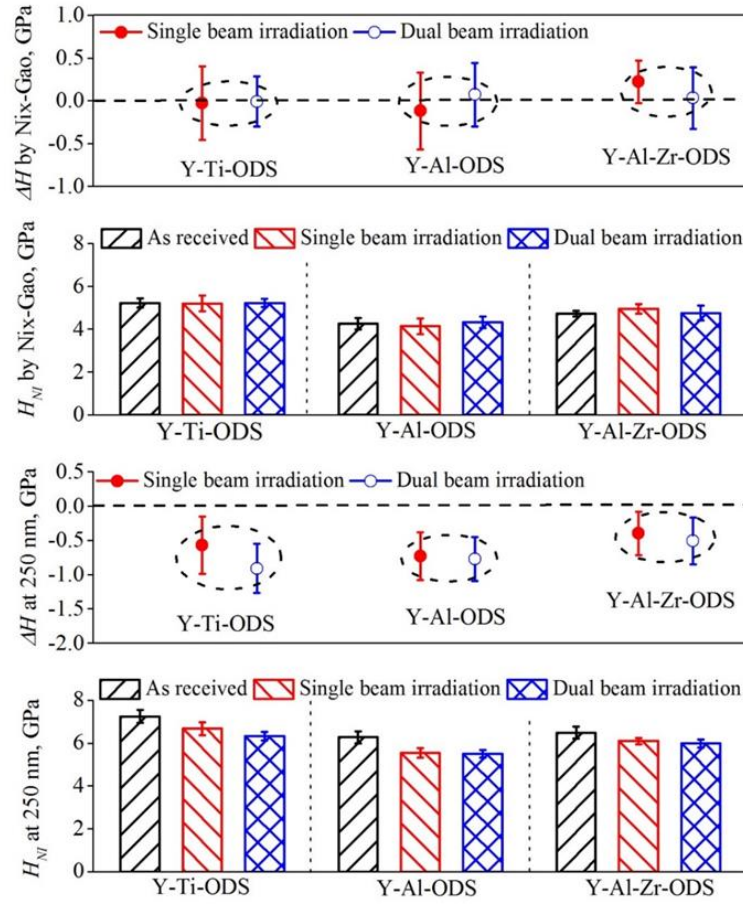


Fig. 5.12 Nanoindentation (NI) hardness (H_{NI}) and the corresponding hardness changes (ΔH_{NI}) at the indentation depth of around 250 nm and that obtained by applying the Nix-Gao model to each H^2 versus $1/h$ plot.

Table 5.6 Nanoindentation (NI) hardness at the indentation depth of around 250 nm and obtained by the application of the Nix-Gao model before and after ion-irradiation.

(GPa)	Y-Ti-ODS			Y-Al-ODS			Y-Al-Zr-ODS		
	As received	Single	Dual	As received	Single	Dual	As received	Single	Dual
NI hardness @ 250 nm	7.24 ± 0.30	6.67 ± 0.30	6.33 ± 0.20	6.27 ± 0.27	5.54 ± 0.22	5.50 ± 0.18	6.49 ± 0.28	6.09 ± 0.15	5.98 ± 0.19
NI hardness by Nix-Gao	5.22 ± 0.22	5.19 ± 0.37	5.21 ± 0.19	4.25 ± 0.26	4.13 ± 0.37	4.32 ± 0.26	4.72 ± 0.13	4.94 ± 0.22	4.75 ± 0.34

5.3.3 Correlation between microstructure and hardness

In this study, ion-irradiation induced the changes in dislocation density and in the distribution morphology of vacancy clusters. The contribution of dislocations to hardness is estimated by the following equation [43]:

$$\Delta\sigma_d = M\alpha_d\mu\Delta\rho^{0.5} \quad (5.1)$$

where $\Delta\sigma_d$ is the change in the tensile yield stress; M is the Taylor factor (3.06); α_d is the strength factor of line dislocations, equal to 0.212 [50]; μ is the shear modulus (80 GPa for alpha iron); b is the Burgers vector (0.248 nm for $1/2\langle 111 \rangle$ dislocations in alpha iron); $\Delta\rho^{0.5}$ is the change in the square root of dislocation density obtained by TEM measurements. Meanwhile, the tensile yield stress can be converted to Vickers hardness following the relationship, $\Delta\sigma$ (MPa) = 0.3 ΔHV (MPa) [53]. Softening induced by the reduction of the dislocation density only occurred in dual beam irradiated Y-Ti-ODS and Fe beam irradiated Y-Al-ODS, estimated as $\Delta H = -0.35$ GPa (−348 MPa) and -0.16 GPa (−162 MPa), respectively, smaller than the corresponding values $\Delta H_{NI} = -0.91 \pm 0.36$ GPa and -0.73 ± 0.35 GPa measured by the conventional method (at 250 nm) in NI tests. It is possible that the reduction of the dislocation density after ion irradiations can be underestimated due to the inhomogeneous distribution of dislocations in ODS steels and the $\mathbf{g} \cdot \mathbf{b} = 0$ invisibility criteria, but it can be still concluded that the contribution of the difference in the density of line dislocations to hardness is negligible. Taking the NI hardness results into account, we can conclude that no hardening was induced by ion irradiation at 550 °C in the studied ODS steels irradiated with single ion or dual ions.

According to the TEM observation results, another possible contribution to hardening might be He bubbles, which is calculated by the Orowan hardening model $\Delta\sigma_b = M\alpha_b\mu b(N_b d_b)^{0.5}$, where N_b and d_b are the number density and mean diameter of He bubbles, respectively [43]. In the present study, the hardening by voids or bubbles can be ignored regarding the NI hardness results and no significant dislocation recovery, although there are several studies showing a rather large contribution of voids or bubbles to irradiation hardening with a strength factor α_b of 0.3–0.6 estimated from experimental results [54, 55] and 0.2–0.4 obtained through molecular dynamics (MD) simulations on cavities in the diameter range of 1–4 nm [7].

It is considered that voids and helium bubbles with high He content may be short-range obstacles for dislocation motion [43, 56] and helium bubbles at grain boundaries (GB) cause intergranular embrittlement [39, 43, 57]. Therefore helium may degrade fracture toughness by different mechanisms: hardening mechanism, non-hardening (GB embrittlement) mechanism and their synergistic effect. Previous research on helium effects showed that a significant amount of irradiation hardening remained after post-irradiation annealing at temperatures between 550–600°C in neutron irradiated RAFM steels up to 11.3 dpa/1175 appm He [29] and in helium implanted reduced activation martensitic steel up to 0.2 dpa/580 appm He [23]. The residual hardening was attributed to helium bubbles which still survived the annealing process. Detailed TEM examinations, however, are

necessary to prove the annealing effects on the hardness.

In this research, the insignificant bubble hardening may be relevant to the great fractions of helium bubbles adjacent to oxide particles (from about 74% to 82%). Because of the identical position of helium bubbles and oxide particles, the number density of obstacles to dislocation motion doesn't change by the formation of helium bubbles, known as "strength superposition effect". Based on this effect, the negligible contribution of isolated He bubbles (around 20%) from oxide particles to hardening allows their strength factor to be 0.1–0.2. Besides, it is expected that there is a critical helium concentration that exceeds the upper limit of helium trapping capacity in ODS steels as also proposed for conventional ferritic/martensitic steels [39].

5.4 Conclusions

Helium bubble formation behavior, swelling and hardness changes were investigated for three ion irradiated ODS ferritic steels (Y-Ti-ODS, Y-Al-ODS and Y-Al-Zr-ODS), which were strengthened by different types of oxide particles. Single Fe^{3+} and dual (Fe^{3+} and He^+) beam irradiations were performed at 550 °C with a damage of around 30 dpa and helium concentration of 3500 appm in the depth range of 1000–1300 nm. The main results are as follows:

- 1). Three ODS steels possessed similar grain sizes (370 nm for Y-Ti-ODS and Y-Al-Zr-ODS, 460 nm for Y-Al-ODS) and dislocation densities ($\sim 10^{14} \text{ m}^{-2}$). The mean diameters and number densities of oxide particles were 3.0 nm/ $1.1 \times 10^{23} \text{ m}^{-3}$, 6.3 nm/ $1.9 \times 10^{22} \text{ m}^{-3}$ and 6.2 nm/ $3.5 \times 10^{22} \text{ m}^{-3}$ for Y-Ti-ODS, Y-Al-ODS and Y-Al-Zr-ODS, respectively.
- 2). After dual-beam irradiation, nano-sized helium bubbles were observed. The mean diameter and the number density of helium bubbles were 2.8 nm/ $1.1 \times 10^{23} \text{ m}^{-3}$, 6.6 nm/ $2.7 \times 10^{22} \text{ m}^{-3}$ and 4.5 nm/ $3.6 \times 10^{22} \text{ m}^{-3}$ in Y-Ti-ODS, Y-Al-ODS and Y-Al-Zr-ODS, respectively. About 80% of the intragranular helium bubbles were adjacent to oxide particles in the three ODS ferritic steels.
- 3). Void swelling in Y-Ti-ODS, Y-Al-ODS and Y-Al-Zr-ODS was 0.13%, 0.53% and 0.20%, respectively, in accordance with the total sink strength estimated by counting the number of trapping sites. It is considered that the morphology of oxide particle dispersion not the oxide particle/matrix interface structure was the main contributor for suppressing swelling in despite of different crystal structures of dominant oxide particles in the three ODS steels.
- 4). No dislocation loops were found in the three ODS steels after ion-irradiation at 550 °C irrespective of helium implantation.
- 5). No hardening was observed in the three ODS steels irradiated with both single Fe^{3+} and dual (Fe^{3+} and He^+) ions and the possible softening should be considered to be due to radiation enhanced recovery of dislocations. The comparison between hardness values of the three ODS steels after single and dual beam irradiation provided evidence that a high number density of helium bubbles caused negligible hardening, which should be related to the results that the

majority of helium bubbles formed were adjacent to oxide particles in the three ODS steels.

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Chapter 6

Phase stability and hardening of ODS steels strengthened by different oxide particles after room temperature irradiations

6.1 Introduction

Because of the prominent high-temperature performance, oxide dispersion strengthened (ODS) steels have been developed as the candidate structural materials for the blanket components in fusion reactors [1] and fuel claddings in fast breeder reactors [2]. The oxide particles dispersed in the steel matrix can impede dislocation motion as well as suppress recovery and grain growth to a great extent with maintaining the superior tensile and creep strength of the steels at elevated temperatures [3]. Furthermore, the oxide/matrix (O/M) interfaces provide numerous sinks for point defect recombination and helium trapping, which contribute much to excellent radiation tolerance of ODS steels [4] [5]. Because of the significance in the roles of oxide particles, both the thermal stability and radiation tolerance of dispersed particles are required for ensuring the property integrity of the ODS steels.

Yttria (Y_2O_3) is generally selected as the dispersed oxide particles for strengthening because it is one of the most thermodynamically stable oxides [6]. Meanwhile, the Ti addition to ODS steels effectively refined oxide particles by the formation of ultrafine (Y, Ti) complex oxides, which improved drastically the high temperature strength of steels [7]. Accordingly, a great number of studies were done on oxide particles in various (Y, Ti)-added ODS steels, such as dispersion morphology, crystallographic structure and chemical composition, as well as interface coherency and orientation relationship with the matrix [8–12]. Sakasegawa et al. [8] analyzed the chemical composition of small particles in MA957 ODS alloy by energy dispersive X-ray spectroscopy (EDS), revealing that the ones with diameter ranging from 2 to 15 nm were non-stoichiometric (Y, Ti, O) oxides, while the bigger ones (15–35 nm) were stoichiometric $\text{Y}_2\text{Ti}_2\text{O}_7$. Similar EDS results were reported on oxides smaller than 5 nm in diameter by Hirata et al. [9] that the defective NaCl-type $\text{Ti}(\text{Y}, \text{Fe}, \text{Cr})\text{-O}$ was the most promising structure with low Y/Ti atomic ratios (0.1–0.6). However, Kasada et al. [10] and Wu et al. [11] confirmed the oxides smaller than 5 nm in diameter to be cubic pyrochlore $\text{Y}_2\text{Ti}_2\text{O}_7$ by using X-ray diffraction (XRD) and transmission electron microscopy (TEM), respectively. Moreover, most of the pyrochlore $\text{Y}_2\text{Ti}_2\text{O}_7$ particles (< 3 nm) were found to be well coherent and embedded with a cube-on-cube orientation relationship with the bcc matrix, as well as of low interfacial energy [12]. In addition to the pyrochlore-type clusters, other phases like hexagonal and orthorhombic Y_2TiO_5 might coexist in those ODS steels with (Y, Ti) addition [8]. The Al-addition to FeCr-(Y, Ti)-ODS steels altered the dominated particles from (Y, Ti) oxide particles (mainly $\text{Y}_2\text{Ti}_2\text{O}_7$ pyrochlore) to YAlO_3 (YAH and YAP) [13], and a small addition of Zr to FeCr-(Y, Ti, Al)-ODS steels altered the majority of oxide particles from (Y, Al) oxide particles to (Y, Zr) ones [14].

In the absence of irradiation, Y-Ti-O nano-oxides, particularly pyrochlore $\text{Y}_2\text{Ti}_2\text{O}_7$ could remain fully stable up to 900 °C [15]. Cunningham et al. [15] attributed such outstanding coarsening resistance to be the extremely low matrix solubility and diffusion rate of Y in equilibrium with $\text{Y}_2\text{Ti}_2\text{O}_7$. The former part was directly related to the low interfacial energy of nano-oxides [12]. What's more,

Oono et al. [16] compared the Gibbs free energies of dominant oxides at 1623 K, elucidating the stability order to be $\text{Y}_4\text{Al}_2\text{O}_9$ (YAM) $>$ $\text{Y}_2\text{Ti}_2\text{O}_7$ $>$ Y_2O_3 $>$ YAlO_3 (YAP) $>$ $\text{Y}_4\text{Zr}_3\text{O}_{12}$.

Differing from the thermal aging, energetic particles (electron, proton, neutron and heavy ions) collisions can directly knock solute atoms out of precipitates or clusters, which is independent of temperature, and also enhance the diffusion of solute atoms in the matrix. Therefore, the radiation effect on the stability of complex nano-oxide particles such as pyrochlore $\text{Y}_2\text{Ti}_2\text{O}_7$ has been investigated to characterize their morphology, chemical compositions and crystal structure under a wide variety of irradiation conditions. Unfortunately, the obtained results showed that there were many disagreements among the studies on the irradiation effects on the size and number density of nano-oxide particles as well as the compositions, Y/Ti and (Y+Ti)/O ratios, especially in the irradiation temperature range of 300–700 °C [17–18]. Such disagreement might be due to the variety in the possible mechanisms depending on irradiation conditions: ballistic dissolution by nuclear displacements, Ostwald ripening, irradiation-enhanced diffusion and homogeneous nucleation [17], one or the combination of which may produce a variety of influences on the phase stability of nano-oxide particles under irradiation.

By using TEM techniques, Ribis et al. [19] found that no distinguishable changes in nano-features, such as the size nor number density, were observed for Y-Ti-O nano-oxides after fast neutron irradiation at 412 °C up to 50 dpa and 430 °C up to 75 dpa. Energy-filtered TEM (EFTEM) analysis demonstrated limited change in the size and number density of Y-Ti-O clusters in 14YWT after ion irradiations to 100 dpa at temperatures 300–600 °C [20]. The above different behavior between the neutron and ion irradiations might be interpreted in terms of displacement rate effect. It is shown that after 500 keV Fe ion irradiation at 500 °C up to 150 dpa, the size and number density of nano-oxides of a pyrochlore type were slightly increased and decreased, respectively, similar to the effect of thermal annealing at 1300 °C for 1h [21]. Such a phenomenon was elucidated by the Ostwald ripening where diffusion-driven growth of nanoclusters should be preponderant [21]. In contrast, by using atom probe tomography (APT), Swenson et al. [18] found that with increasing displacement damage, the average size of Y-Ti-O nanoclusters decreased slightly while the number density decreased evidently at the beginning of irradiation, and then increased slightly in a Fe-9%Cr ODS steel after 5 MeV Fe ion irradiation and proton irradiation over 1–100 dpa at 500 °C. In addition, by means of APT, X. Liu et al. [22] revealed that the maximum concentrations of O and Ti in small nanoclusters (1.5–2.0 nm) were apparently reduced by neutron irradiations at 300 °C and 450 °C up to 5 dpa, although the small nanoclusters never shrank or dissolved under the neutron irradiations. The most remarkable is that no significant dissolution of Y-Ti-O oxide particles was found in the irradiation temperature range of 300–700 °C. Radiation effects on the stability of (Y, Al) or (Y, Zr) oxide particles in ODS steels were investigated by few researchers. H. Joon Jung et al. [23] reported that the neutron irradiations at 500 °C up to ~21 dpa led to complete amorphization of the YAlO_3 oxides in PM2000 ODS, but did not

cause significant changes in their dispersion morphology and the Y/Al ratio.

Ion-irradiation effect at lower irradiation temperatures less than room temperature (RT), where the ballistic dissolution became significant, was investigated by several researchers. A nearly complete dissolution of nano-sized Y-Ti-O particles was confirmed in several ODS steels irradiated at 25 °C up to 156 dpa [21], at 150 K up to 100 dpa [24] and at -75 °C up to 100 dpa [20], which were detected by means of APT, glancing-incident angle X-ray diffraction (GIXRD) and APT, as well as EFTEM and APT, respectively. However, no significant changes in the dispersion morphology and chemical compositions of the Y-Ti-O nanoparticles were also observed in a 14YWTi ODS steel irradiated at -80 °C up to 15 dpa [25]. Interesting is that in a 13.5Cr-0.3Ti ODS steel irradiated at RT and 300 °C up to 0.8 dpa, the cluster number density increased by around 3 times and the size distribution shifted towards smaller size, which were characterized by APT and TEM, respectively [26]. Such an effect of displacement damage at RT on the phase stability of Y-Ti-O nanoparticles still needs to be clarified. Further, we are concerning about the irradiation hardening accompanied by the dissolution of oxide particles. Only a few papers reported that ion-irradiation induced a hardening in a 16Cr-0.1Ti ODS steel at -50 °C to 0.8 dpa [27] and at RT up to 18 dpa [28] but without characterization of oxide particles.

The objectives of this study are, firstly to investigate the effect of displacement damage on the phase stability of the different oxide particles in the three ODS steels with different alloy elements addition, secondly to correlate the irradiation hardening with the distribution morphology changes including dissolution of oxide particles in the ODS steels.

6.2 Experimental

6.2.1 Materials

The materials used in this chapter are Y-Ti-ODS, Y-Al-ODS, Y-Al-Zr-ODS ferritic steels, which were produced by mechanical alloy processing. The chemical compositions of these three ODS steels are shown in Table 6.1. After hot extrusion and forging were performed at 1150 °C, the material was finally annealed at 1150 °C for 1 h followed by air-cooling. More details of the material processing were described in Chapter 2. In addition, one Y-Ti-ODS bulk specimen was isothermally annealed at 1350 °C for 1 hour in a vacuum atmosphere for recrystallization, named by Recry. Y-Ti-ODS.

Specimens were sampled so that the specimen surface was perpendicular to the extrusion direction, that is, the ion-irradiation direction is parallel to the extrusion direction. Specimen surface was mechanically ground with SiC papers, and subsequently polished with successive grades of diamond spray down to 0.25 µm. Finally, electrolytic polishing was conducted on ODS specimens except for Y-Al-ODS and Recry. Y-Ti-ODS in a solution of 10% (vol.) HClO₄ and 90% (vol.) CH₃COOH at room temperature for ion-irradiation.

Table 6.1 Chemical compositions (wt.%) of Y-Ti-ODS, Y-Al-ODS, Y-Al-Zr-ODS.

Elements	C	Cr	W	Al	Ti	N	Ar	Y ₂ O ₃	Ex.O
Y-Ti-ODS	0.045	13.6	1.9	0.02	0.16	0.004	0.007	0.33	0.04
Y-Al-ODS	0.03	15.42	1.85	3.8	0.1	0.004	0.0068	0.36	0.084
Y-Al-Zr-ODS	0.03	14.59	1.84	3.46	0.14	0.001	0.005	0.33	0.11

Ex. O: the excess oxygen content.

6.2.2 Irradiation conditions

Specimens were irradiated with 6.4 MeV Fe³⁺ ions using the DuET facility in Kyoto University [29]. The flux of Fe³⁺ ion beam was approximately 2.1×10^{16} ions m⁻² s⁻¹. The specimens for irradiation were set on the copper holder cooled by flowing water inside the holder. The irradiation temperature was measured by a thermocouple and controlled to be 30 °C within a fluctuation of ± 5 °C. Main parameters are shown in Table 6.2.

The displacement damage (displacements per atom, dpa), injected Fe concentration and electronic stopping power of a Fe-14Cr alloy were obtained by SRIM [30] simulation with use of the Kinchin-Pease method, recommended by Stoller et al. [31] and shown in Fig. 6.1. The damaged layer was located in the depth range of 0–2100 nm (see Fig. 6.1(a)). The irradiation periods were about 1 hour, 5 hours and 25 hours for a nominal displacement damages of 2, 10 and 50 dpa, respectively, at the depth of 600 nm. Corresponding to the nominal damage levels of 2, 10 and 50 dpa, the local damage levels were ~ 1.2 –6 dpa, ~ 6 –30 dpa and ~ 30 –150 dpa, respectively for the depth range of 0 to ~ 1600 nm (see Fig. 6.1). The nominal displacement rate was $\sim 6.4 \times 10^{-4}$ dpa/s.

Table 6.2 Main irradiation parameters

Materials	Nominal damage levels			Temperature
Y-Ti-ODS	2 dpa	10 dpa	50 dpa	30 ± 5 °C.
Y-Al-ODS	2 dpa	10 dpa	50 dpa	
Y-Al-Zr-ODS	2 dpa	10 dpa	50 dpa	
Recry. Y-Ti-ODS	2 dpa	none	none	

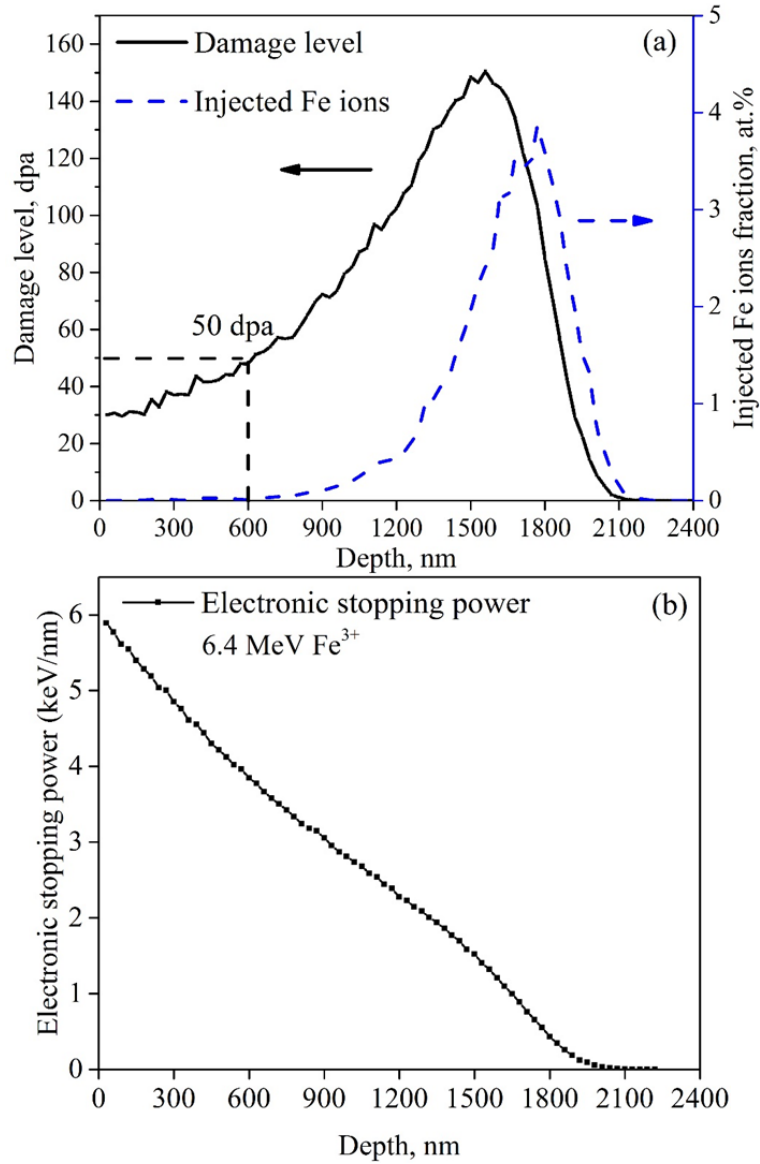


Fig. 6.1 (a) Depth profiles of displacement damage (dpa) and fraction (at.%) of injected Fe ions, and (b) depth file of electronic stopping power (keV nm^{-1}) of 6.4 MeV Fe^{3+} ions into Fe-14Cr alloy.

6.2.3 Transmission electron microscopy (TEM)

Cross-sectional TEM specimens were prepared by the lift-out technique using a Focused Ion Beam (FIB) instrument where the final beam used was 20 keV Ga^+ . Prior to TEM observations, flash polishing was done by using a solution consisting of 5% (vol.) HClO_4 and 95% (vol.) CH_3OH at around -35°C to remove a FIB damage layer. The size and morphology of dislocations loops and oxide particles were analyzed by using a conventional 200 kV JEOL JEM 2010 microscope with a LaB_6 electron emitter. Moreover, kinematical bright field (KBF) image conditions ($s_g \neq 0$) were chosen to image the strain contrasts. The lattice structure and chemical elements were analyzed by using a

200 kV JEM 2200FS field emission microscope, which was equipped with an in-column energy filter (Omega filter). Energy-Filtered TEM (EFTEM) analytical data was obtained by using two-window jump ratio imaging. For the Ti $M_{2,3}$ edge jump ratio image, the pre-edge and post-edge energies were 25 eV and 45 eV, respectively. For the Y $N_{2,3}$ edge jump ratio image, the pre-edge energy was 22 eV while the post-edge energy was 39 eV. The slit width was 10 eV. The thickness of all observation areas in TEM foils was measured using electron energy-loss spectroscopy (EELS) log-ratio technique [32].

6.2.4 Nano-hardness measurements

Nanoindentation testing was performed on as-received and irradiated samples by using a nanoindenter (Agilent G200) equipped with a Berkovich tip. A continuous stiffness measurement (CSM) was adopted to obtain continuous hardness and elastic modulus as a function of indentation depth. Before testing, the indenter tip geometry was calibrated by indenting a fused silica reference sample with known mechanical properties. Other main testing parameters were depicted as follows: the maximum indentation depth was 2000 nm, the strain rate was 0.05 s^{-1} , the harmonic displacement was 1 nm, and the Poisson's ratio was 0.3. For each specimen, 24 testing points (60 μm between two adjacent points) were chosen and the averaged hardness was obtained by calculating the measured hardness data of roughly 20 tests after several test results were omitted because of the significance in the data scattering.

6.3 Results and discussion

6.3.1 Microstructures change

6.3.1.1 Microstructures before irradiation

The oxide particles in as-received Y-Ti-ODS were observed under KBF image contrast condition by using $g = [1\bar{1}0]$ with the incident electron beam direction parallel to the zone $[110]$, as marked with arrows in Fig. 6.2(a). The size distribution was obtained by measuring diameters of 225 oxide particles, and shown in Fig. 6.2(b). The average size and number density of oxide particles were $3.8 \pm 1.0 \text{ nm}$ and $(7.4 \pm 0.8) \times 10^{22} \text{ m}^{-3}$, respectively. The volume fraction of oxide particles was estimated to be 0.234 %. As for the structure of the oxides in this steel, we expect the main oxide particles to be pyrochlore $\text{Y}_2\text{Ti}_2\text{O}_7$, because in our previous XRD measurements of extracted residues of the similar ODS ferritic steel with (Y, Ti) addition, only cubic pyrochlore type $\text{Y}_2\text{Ti}_2\text{O}_7$ oxides were detected [10].

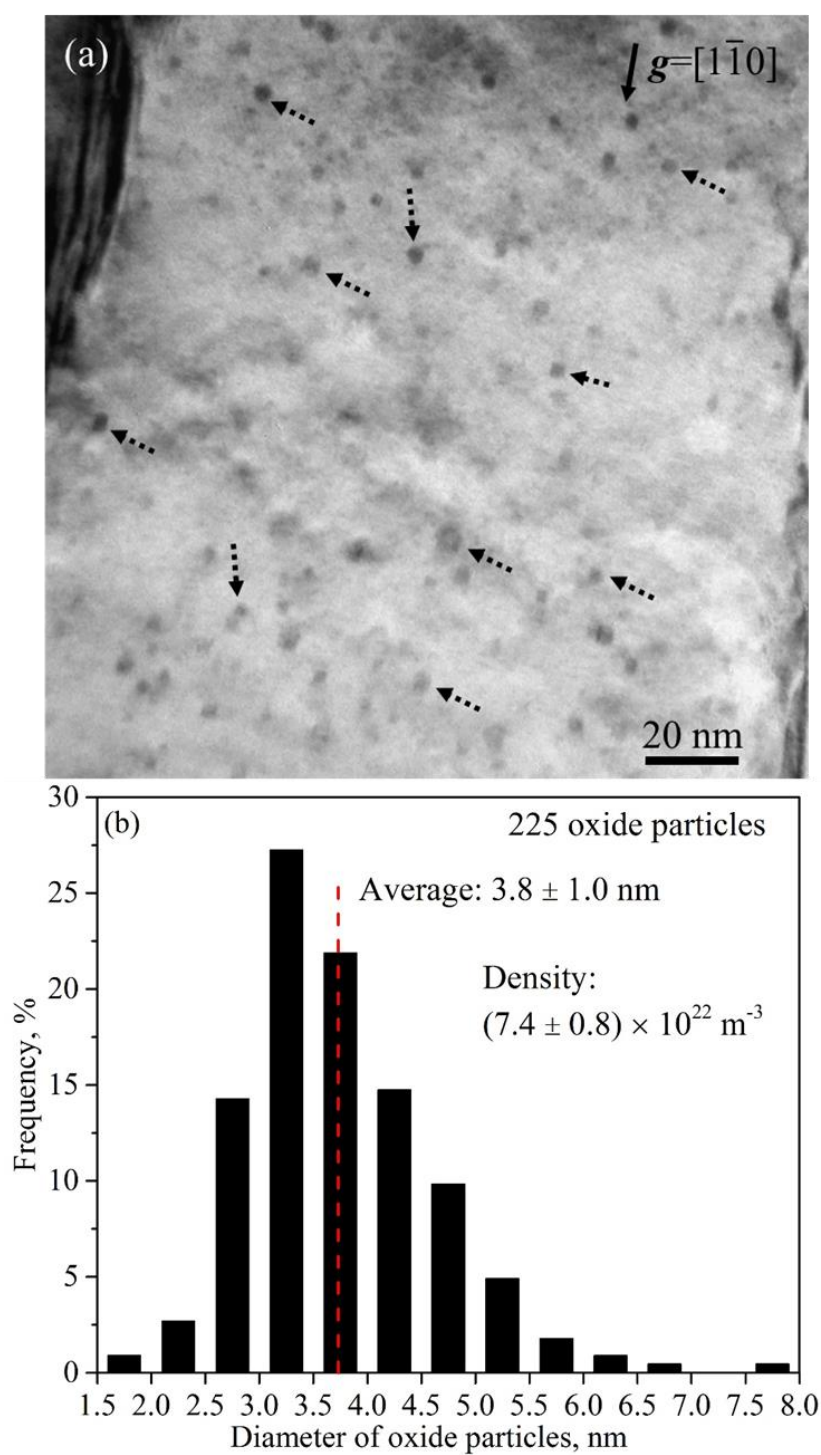


Figure 6.2 (a) Oxide particles imaged by using $g = [1\bar{1}0]$ with the electron beam direction close to the pole $[110]$ and (b) size distribution histogram of oxide particles in the un-irradiated Y-Ti-ODS.

In the Recry. Y-Ti-ODS, the size distribution of oxide particles shifted to larger size with the averaged value of 8.5 ± 2.7 nm. The minimum, maximum diameter were 4.0 and 17.9 nm, respectively.

The number density decreased to be $(1.9 \pm 0.4) \times 10^{22} \text{ m}^{-3}$. One oxide particle in Fig. 6.3(a) was analyzed with regard to its chemical compositions and lattice structure. By Ti-M jump ratio image (Fig. 6.3(b)) and Y-N jump ratio image (Fig. 6.3(c)), this oxide particle should consist of Ti and Y. Fig. 6.3(d)–6.3(e) show its HRTEM lattice image with indexation of the corresponding FFT image and the inverse FFT (IFFT) image. Table 6.3 displays the measured and calculated inter-planar distances and angles, being shown in Fig. 6.3(e). The results were well in accordance with cubic pyrochlore $\text{Y}_2\text{Ti}_2\text{O}_7$, which was indexed with zone $[011]$.

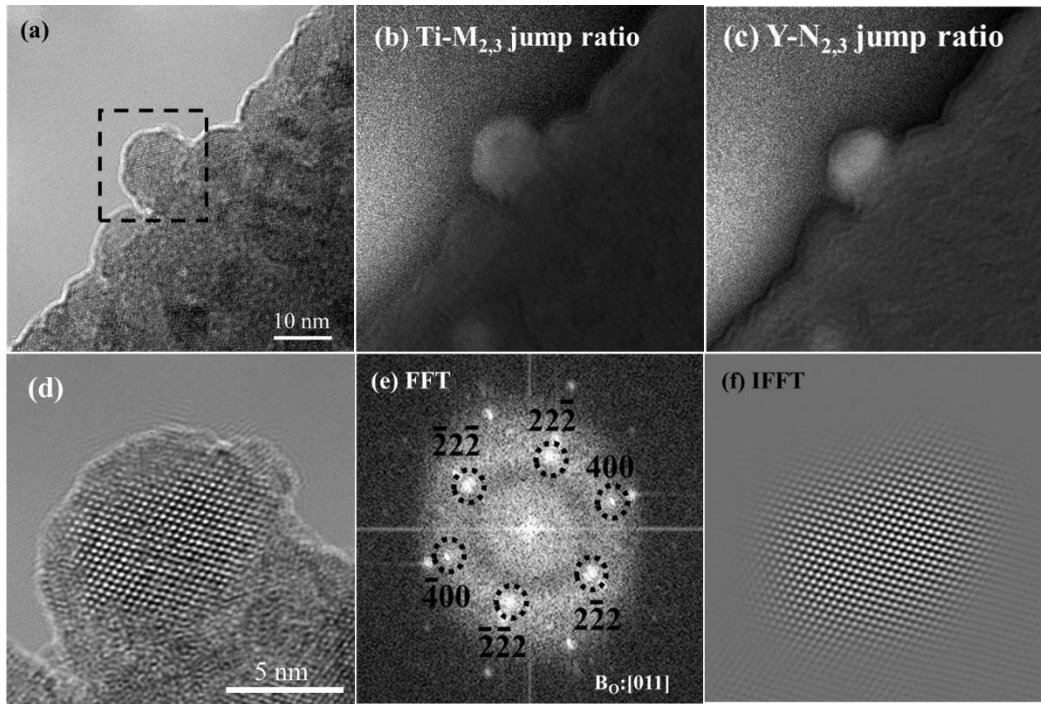


Figure 6.3 (a) a zero-loss filtered image showing nano-sized dispersoids; (b)–(c) corresponding to jump ratio images of Ti-M_{2,3} and Y-N_{2,3}, respectively; (d) HRTEM lattice image of one dispersoid marked in 3(a); (e) FFT pattern of 3(d); (f) inverse FFT (IFFT) image reconstructed by the FFT spots circled in 3(e).

Table 6.3 Calculated and measured inter-planar distance (d) and angle (α).

d (Å), α (°)	d_1 (22–2)	d_2 (2–22)	d_3 (400)	α_{12}	α_{13}	α_{23}
Calculated ^[33]	2.94	2.94	2.55	109.4	54.7	54.7
Measured	2.95	2.92	2.52	109	55	55

6.3.1.2 Microstructure evolution of Y-Ti-ODS after irradiations to 2 and 10 dpa

After the irradiations up to nominal damages of 2 and 10 dpa, the TEM microstructure of Y-Ti-ODS in the region ~ 400 – 1300 nm away from the specimen surface was observed using $g = \langle 110 \rangle$

under KBF ($s_g \neq 0$). Fig. 6.4 shows that there are three types of defect structures, which were oxide particles, line shaped dislocations and black dot type defects. As for the black dots, Yao et al. [34] observed them of about 1–4 nm in size in bright-field (BF) imaging condition in Fe-(8~11)Cr alloys irradiated with 100 keV or 150 keV Fe^+ , or with 30 keV Ga^+ in the FIB at RT, and they denoted the black dots as fine dislocation loops. Since it was very difficult to distinguish nano-sized oxide particles (~3 nm) from the black dots, the size histograms were obtained for both nano-features, namely, nano-sized oxide particles and black dots and shown in Fig. 6.5. As the displacement damage increased, the size histogram indicates an increasing fraction of finer nano-sized particles and black dots, which also became sparse and tended to disappear at ~21 dpa. This can be interpreted in terms of the refining of the oxide particles caused by dissolution and/or the formation of small dislocation loops. Fig. 6.6 shows the averaged diameter and number density of nano-features as a function of dpa, where each data point was obtained for the grain located at each displacement damage. Due to the detection limit of the TEM, nano-features including oxide particles and black dots smaller than 1.5 nm might be indistinguishable in this study. However, about 800 nano-features in total were taken into account for estimating all the averaged diameters and number densities in each region. Above ~20 dpa, since only several nano-features were observed in a view (see Fig. 6.4(d)), no averaged value was obtained. Finally, it can be said that with increasing displacement damage, the averaged diameter of oxide particles slightly decreased, while the corresponding number density was evidently reduced by almost two orders of magnitude at above 20 dpa compared to that before irradiation.

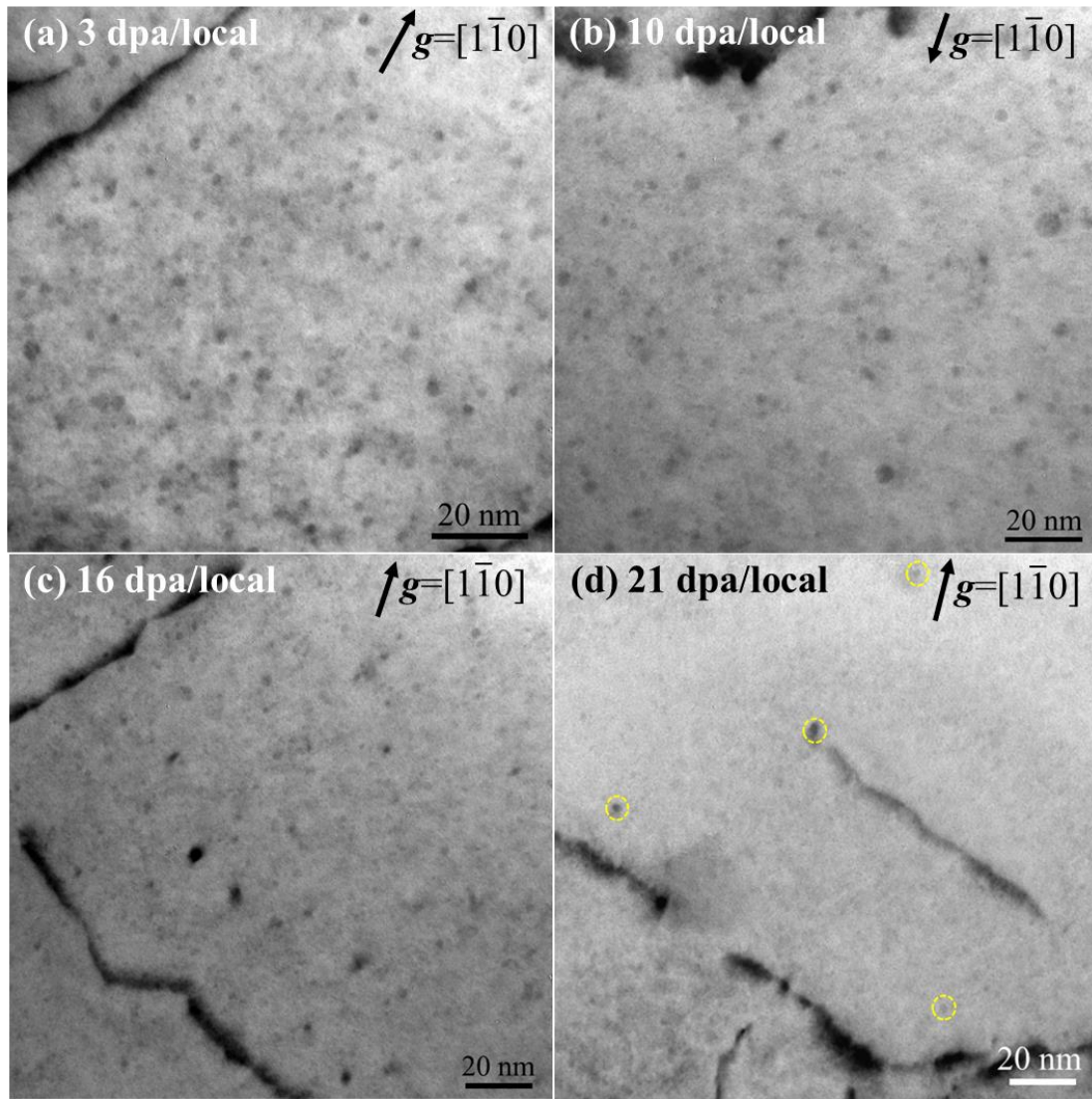


Fig. 6.4 Oxide particles and black dots imaged by using $g = [1\bar{1}0]$ under KBF ($s_g \neq 0$) for the irradiated grains at (a) 3 dpa/local: the dpa value is at the depth of 900 nm in the specimen irradiated to 2 dpa/nominal, (b) 10 dpa/local: at 650 nm in 10 dpa/nominal, (c) 16 dpa/local: at 1000 nm in 10 dpa/nominal, (d) 21 dpa/local: at 1200 nm in 10 dpa/nominal. Nano-features are marked with cycles.

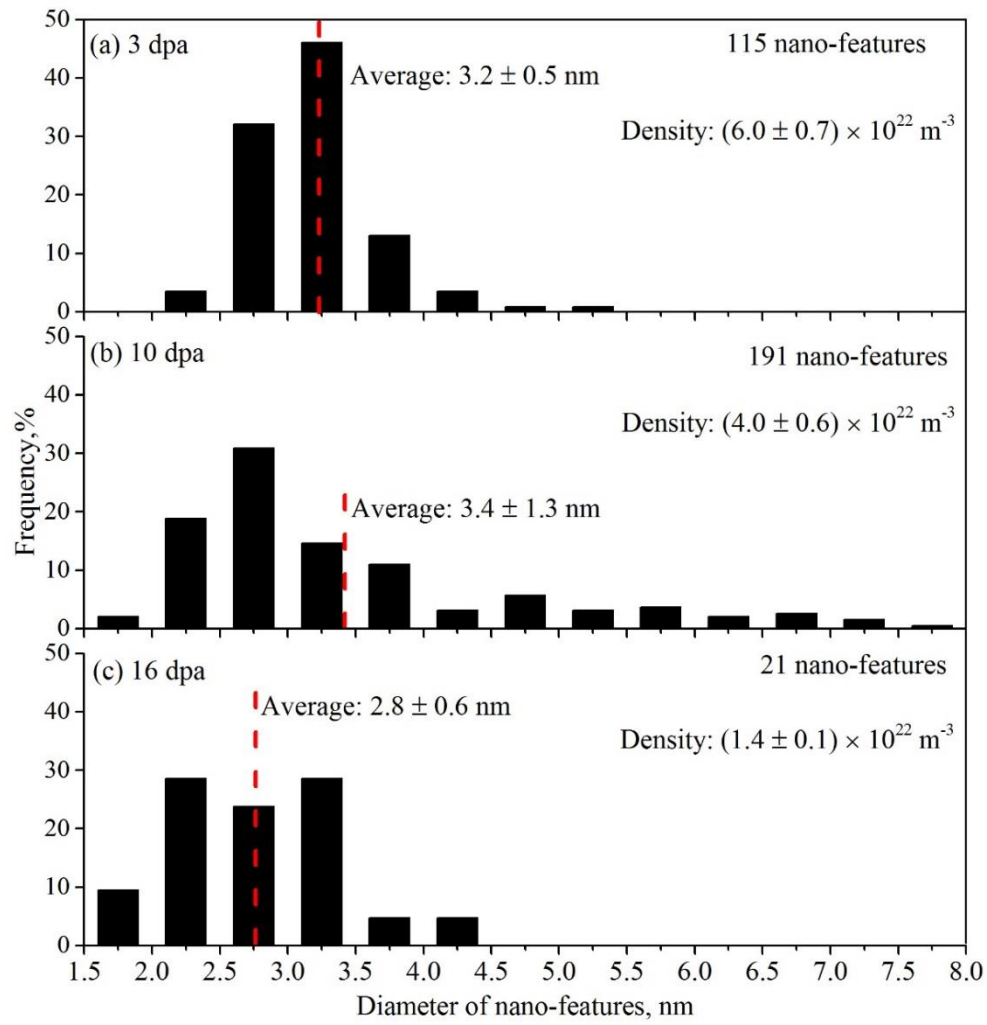


Fig. 6.5 Size distribution histograms of oxide particles and black dots (nano-features) formed at the local regions in Y-Ti-ODS irradiated to approximately 3, 10, 16 dpa.

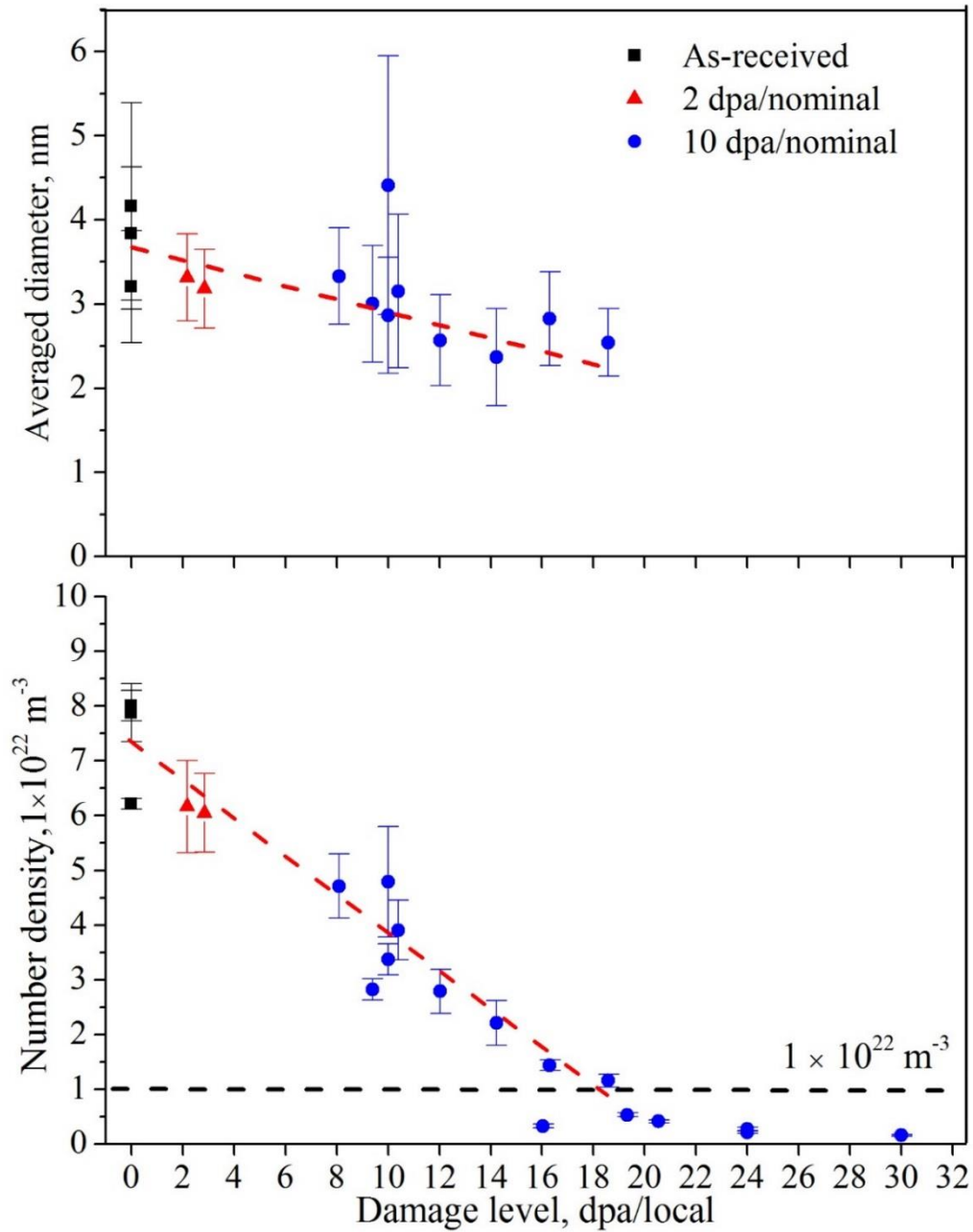


Fig. 6.6 (a) Averaged diameter and (b) number density of oxide particles in the as-received (squares), as well as nano-features as a function of dpa in (Y, Ti)-ODS irradiated to nominal displacement damages of 2 (triangles) and 10 (circles) dpa/nominal. The damage level corresponds to the calculated value at each local depth position on the damage profile obtained by SRIM calculation. Most of data between 2 to 24 dpa/local correspond to the local depth position between ~600 to 1300 nm.

6.3.1.3 Microstructure evolution in Y-Ti-ODS after irradiation to 50 dpa

At a nominal displacement damage of 50 dpa, the majority of oxide particles in Y-Ti-ODS dissolved into the matrix in the whole irradiated region (30–150 dpa) as can be expected from the results of the previous section (3.1.2). Fig. 6.7 shows an evident transition of microstructure between the irradiated and unirradiated region, which proved an effective removal of FIB damages by the flash polishing during the TEM cross-sectional specimen preparation. An evident damage peak in Fig. 6.7(a) was recognized in a depth range of 1500–2000 nm, which consisted of dislocation networks and dislocation loops shown in Fig. 6.7(b). The dislocation networks and loops were produced by the synergistic effect of displacement damages and injected iron ions. In the weak beam dark field (WBDF) image, dislocation loops were observed as “white spots” by using $\mathbf{g} = [1\bar{1}0]$ (see Fig. 6.8(a) and 6.8(c)) and $\mathbf{g} = [002]$ (see Fig. 6.8(b) and 6.8(d)). In addition, some slightly weak contrasts were also observed as shown in Fig. 6.8(d), which were possibly surface contaminations or oxides. In this study, only the white spots circled were counted for estimating the number density of the dislocation loops. Previous literatures [34–35] revealed that the primary loops formed in Fe-Cr alloys after ion irradiations consisted of the $1/2\langle 111 \rangle$ and $\langle 100 \rangle$ dislocation loops, with no visible $1/2\langle 110 \rangle$ loops. According to the $\mathbf{g} \cdot \mathbf{b} = 0$ invisibility criteria, a half of the $1/2\langle 111 \rangle$ loops and two thirds of the $\langle 100 \rangle$ loops are visible with $\mathbf{g} = [1\bar{1}0]$, while all of the $1/2\langle 111 \rangle$ loops and one third of the $\langle 100 \rangle$ loops are visible with $\mathbf{g} = [002]$. Defining $N_{[1\bar{1}0]}$ and $N_{[002]}$ to be the number density of loops observed by using $\mathbf{g} = [1\bar{1}0]$ and $\mathbf{g} = [002]$, respectively, we can obtain the number density of the $1/2\langle 111 \rangle$ loops (ρ_{111}) and the $\langle 100 \rangle$ loops (ρ_{100}) by the following equations:

$$\rho_{111} = 2/3 (2N_{[002]} - N_{[1\bar{1}0]}) \quad (6.1)$$

$$\rho_{100} = 2N_{[1\bar{1}0]} - N_{[002]} \quad (6.2)$$

$$\rho_{\text{both}} = \rho_{111} + \rho_{100} = 1/3 (4N_{[1\bar{1}0]} + N_{[002]}) \quad (6.3)$$

At the local damages of 50 dpa and 72 dpa, the total number densities of both $1/2\langle 111 \rangle$ and $\langle 100 \rangle$ loops were $(1.4 \pm 0.2) \times 10^{22} \text{ m}^{-3}$ and $(4.1 \pm 0.7) \times 10^{22} \text{ m}^{-3}$, respectively, with the corresponding $1/2\langle 111 \rangle$ loop fractions of 90% and 79%, as shown in Fig. 6.9(a). The size distribution of dislocation loops imaged by using $\mathbf{g} = [002]$ at 72 dpa is shown in Fig. 6.9(b) and the averaged size was 2.8 ± 0.7 nm.

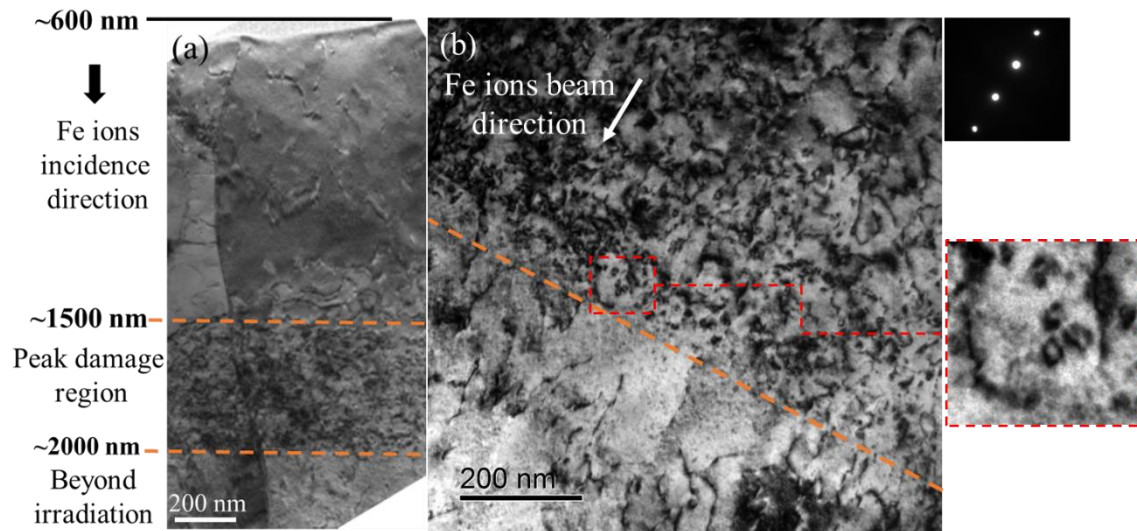


Fig. 6.7 (a) Microstructures of whole area including both the irradiated area and unirradiated area, and (b) a magnified microstructural morphology at the depth of ~2000 nm imaged by using $g = [110]$ close to zone [001] at a two-beam dynamical condition for Y-Ti-ODS irradiated at a nominal damage of 50 dpa.

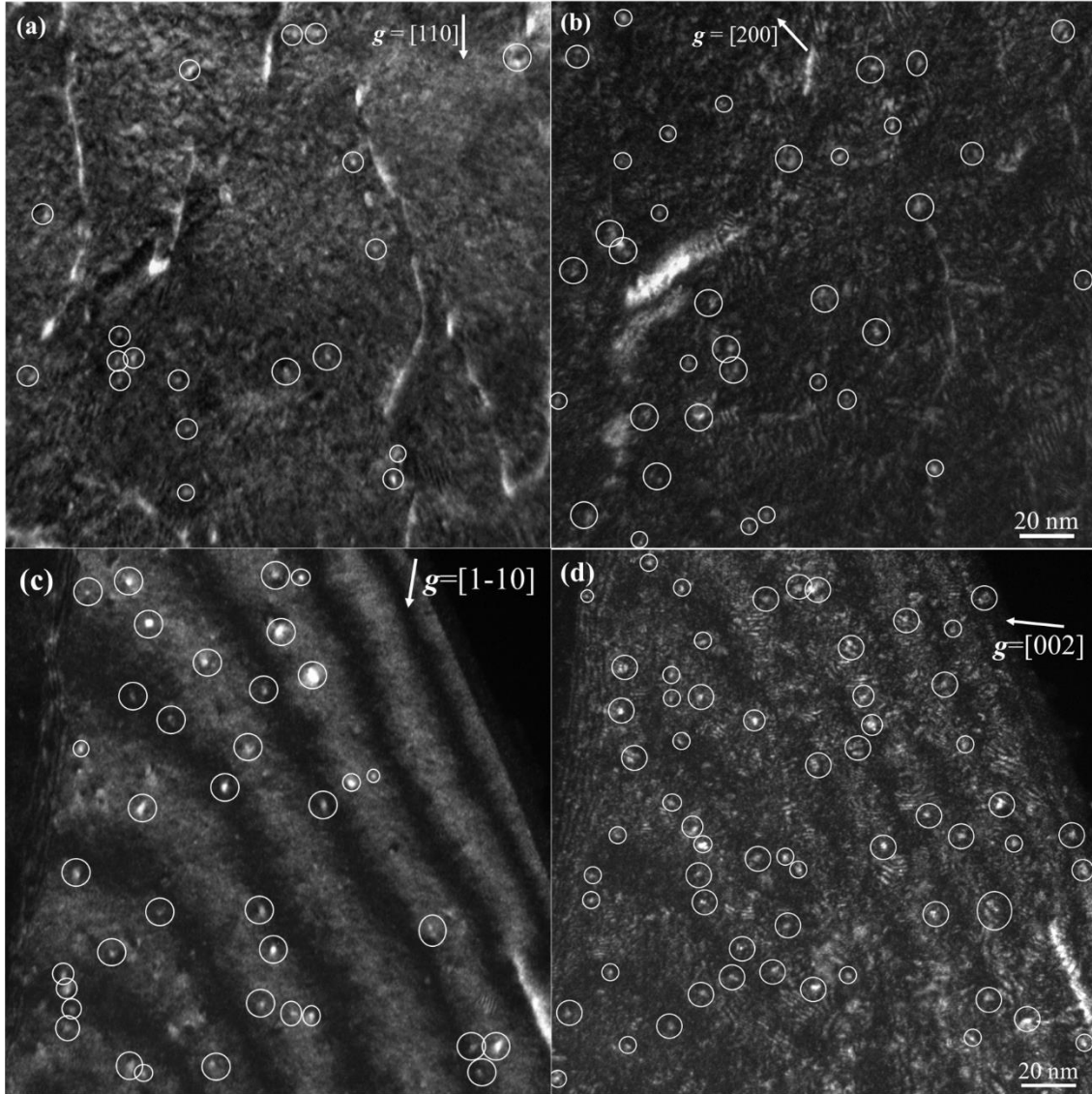


Fig. 6.8 (a) Weak beam dark field ($g, 3g$) image by using $g = [110]$ and (b) $g = [200]$ close to pole $[001]$ in an identical region at ~ 600 nm (~ 50 dpa); (c) WBDF ($g, 5g$) image by using $g = [1\bar{1}0]$ close to pole $[110]$ at ~ 900 nm (~ 72 dpa) and (d) WBDF image ($g, 4g$) by using $g = [002]$ in an identical region for Y-Ti-ODS irradiated at a nominal damage of 50 dpa; Dislocation loops circled were used for computing number density; The thickness of the investigated region of the top and the below were measured to be 49 ± 9 and 42 ± 8 nm, respectively.

The $1/2\langle 111 \rangle$ and $\langle 100 \rangle$ loops observed were probably interstitial-type rather than vacancy-type because of the low mobility of vacancies at RT and the preference for vacancies to congregate as voids [36]. Actually, $1/2\langle 111 \rangle$ loops could be directly produced by cascade collisions in pure Fe at a very low damage (0.5 dpa) with rare overlap of the individual cascades at RT [35] and the initial $\langle 100 \rangle$ loops should stem from the mutual interaction of the glissile $1/2\langle 111 \rangle$ loops, so

called “111 mechanism” [37]. As for the impacts of Cr on the behaviors of dislocation loops, the solute Cr could bind interstitial defects and slow down their diffusion significantly [38], resulting in a lower fraction of $\langle 100 \rangle$ loops in Fe-Cr alloys than in pure Fe above 0.5 dpa [35]. Despite its pinning effects, Cr possibly favored the formation of $\langle 100 \rangle$ loops, showing more $\langle 100 \rangle$ loops in Fe-Cr alloys than in pure Fe at 0.05 dpa [35]. Considering the complicated roles of solute Cr, it was reasonable to reckon the limited fractions of the $\langle 100 \rangle$ loops (less than 20%) in the present ODS steel after irradiation. No cavities were observed in all the irradiated specimens.

It is not disputed that O/M interfaces can provide the trapping sites for self-interstitials (SIA) and vacancies, and then promote their recombination. As a detrimental result of the dissolution of oxide particles, more displacement defects may survive after the particle irradiations caused by the loss of a substantial sink strength of oxide particles. Previous research reported that the number density of open volume defects was obviously increased in 14YWTi ODS after heavy ion irradiation up to ~15 dpa at $-80\text{ }^{\circ}\text{C}$ according to positron annihilation spectroscopy (PAS), while no voids were visible by TEM [25].

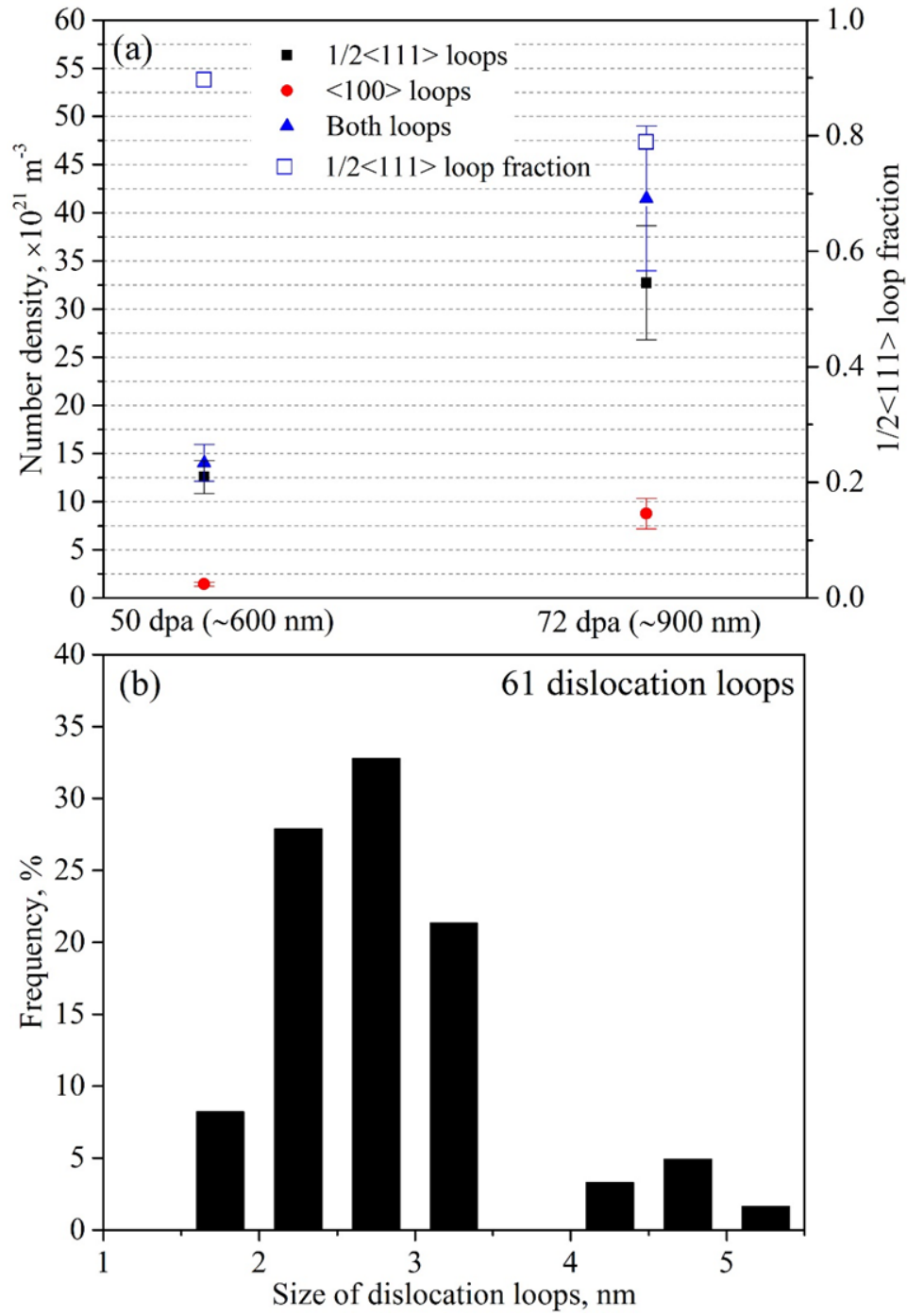
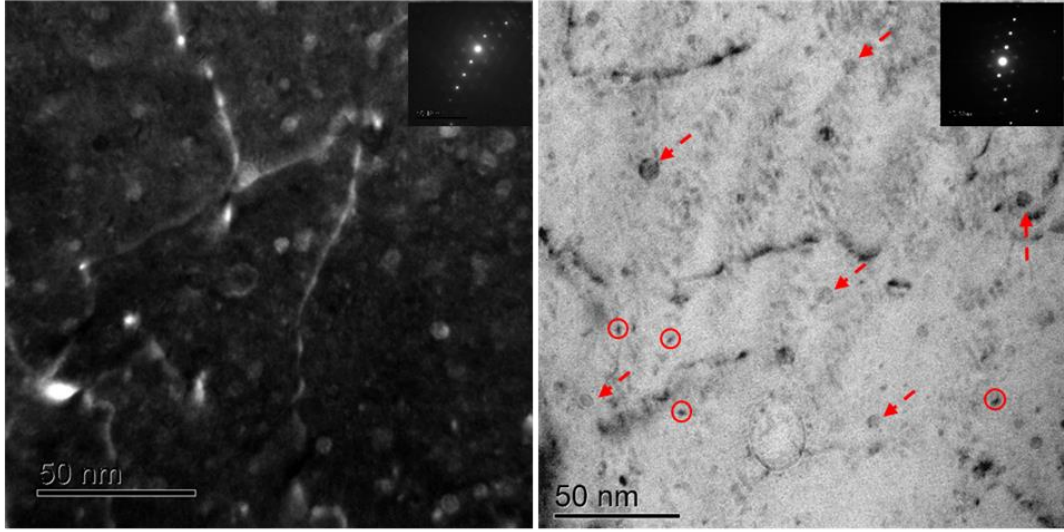


Fig. 6.9 (a) Number densities of the $1/2\langle 111 \rangle$ loops, the $\langle 100 \rangle$ loops and the both, as well as the $1/2\langle 111 \rangle$ loop fraction at ~50 dpa and ~72 dpa for Y-Ti-ODS; (b) Size distribution of dislocation loops imaged by using $\mathbf{g} = [002]$ at ~72 dpa shown in Fig. 6.8(d) and averaged size of dislocation loops is 2.8 ± 0.7 nm.

6.3.1.4 Comparison of ion-irradiation induced microstructural evolution in the three ODS steels

After ion irradiations up to the nominal damage levels of 2, 10 and 50 dpa, the microstructures including the dispersion morphology of oxide particles in Y-Al-ODS and Y-Al-Zr-ODS were characterized by using $g = \langle 110 \rangle$ under KBF imaging conditions, which were shown in Fig. 6.10 and Fig. 6.11, respectively. In Fig. 6.10(b) and Fig. 6.11(b), there are nano-features observed in two shapes: round plate (marked with arrows) and black dots (marked with circles). The round plate nano-features should be oxide particles, which became sparser with increasing the damage level in both of Y-Al-ODS and Y-Al-Zr-ODS. At high damage levels (~ 42 dpa/local for Y-Al-ODS in Fig. 6.10(d) and ~ 50 dpa/local for Y-Al-Zr-ODS in Fig. 6.11(d)), it was difficult to find the nano-features shaped by the round plate. The black dots, as discussed in the section of 6.3.1.2, can be considered to be tiny oxide particles or dislocation loops although it was hard to distinguish between them. The oxide particles, which were featured by round plate, were taken into account for investigating the changes of size and number density versus dpa for Y-Al-ODS and Y-Al-Zr-ODS. Fig. 6.12 shows that the size and number density of oxide particles in Y-Ti-ODS, Y-Al-ODS and Y-Al-Zr-ODS decreased gradually with dpa. Above about 20 dpa, the number density of oxide particles became similar in these three ODS steels, and much lower when compared to the corresponding number densities in the un-irradiated ODS steels.

(a) 4 dpa/local, 2 dpa/nominal (b) 11 dpa/local, 10 dpa/nominal



(c) 29 dpa/local, 10 dpa/nominal (d) 42 dpa/local, 50 dpa/nominal

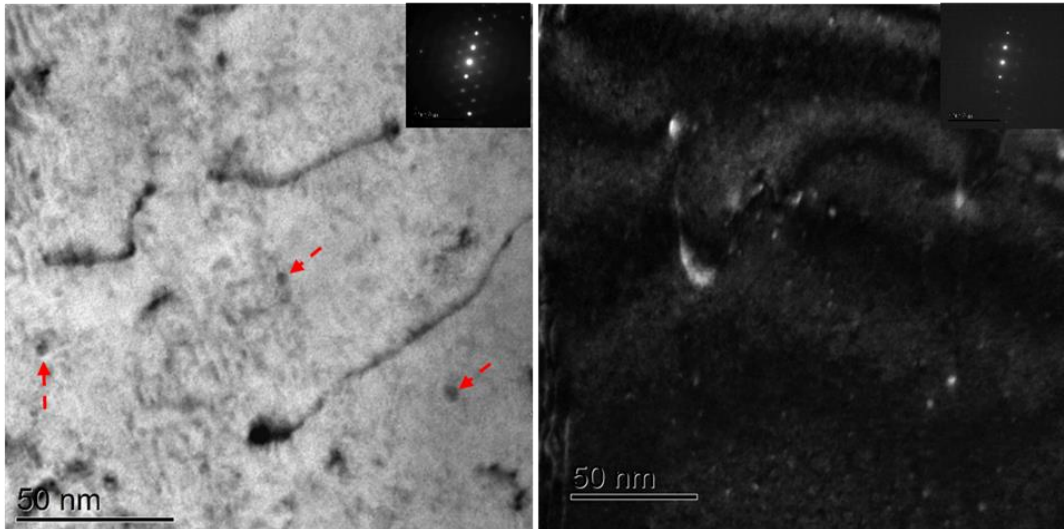
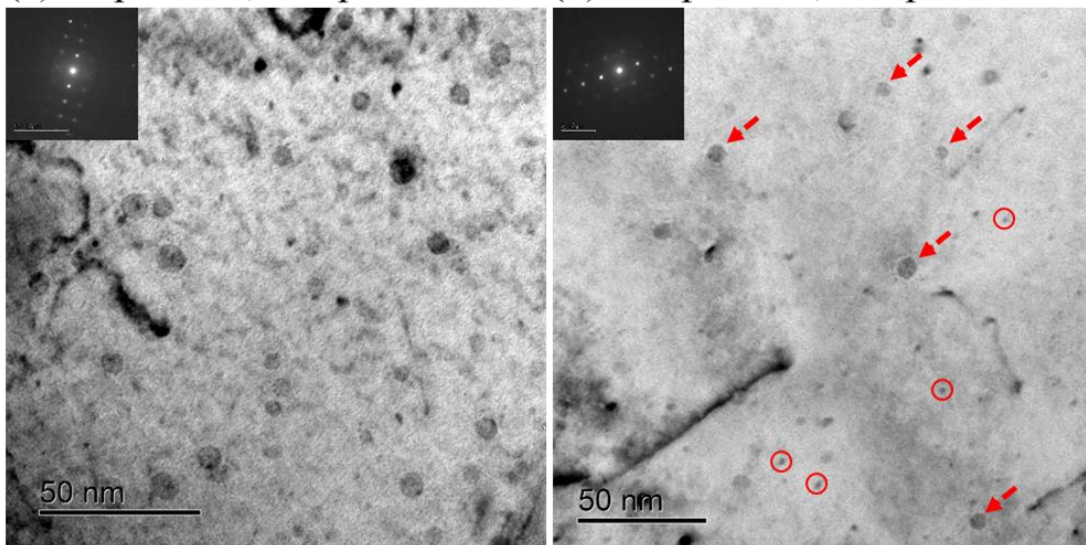


Fig. 6.10 Oxide particles and black dots in Y-Al-ODS imaged by using $g = [1\bar{1}0]$ under KBF ($s_g \neq 0$) for the irradiated grains at (a) 4 dpa/local: the dpa value is at the depth of 1150 nm in the specimen irradiated to 2 dpa/nominal, (b) 11 dpa/local: at 740 nm in 10 dpa/nominal, (c) 29 dpa/local: at 1600 nm in 10 dpa/nominal, (d) 42 dpa/local: at 450 nm in 50 dpa/nominal.

(a) 7 dpa/local, 10 dpa/nominal (b) 16 dpa/local, 10 dpa/nominal



(c) 29 dpa/local, 10 dpa/nominal (d) 50 dpa/local, 50 dpa/nominal

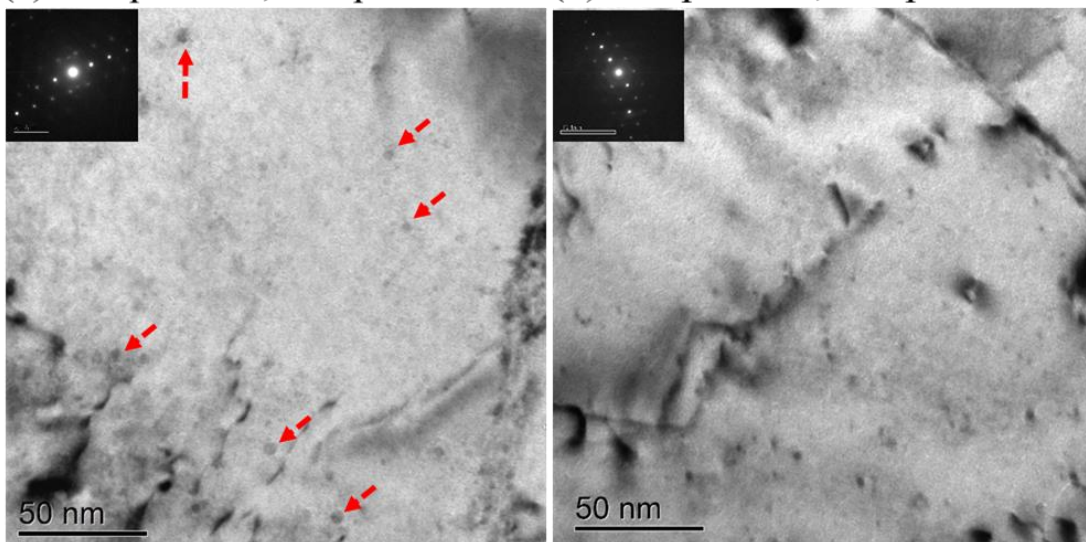


Fig. 6.11 Oxide particles and black dots in Y-Al-Zr-ODS imaged by using $g = [1\bar{1}0]$ under KBF ($s_g \neq 0$) for the irradiated grains at (a) 7 dpa/local: at 250 nm in the specimen irradiated to 10 dpa/nominal, (b) 16 dpa/local: at 1000 nm in 10 dpa/nominal, (c) 29 dpa/local: at 1500 nm in 10 dpa/nominal, (d) 50 dpa/local: at 600 nm in 50 dpa/nominal.

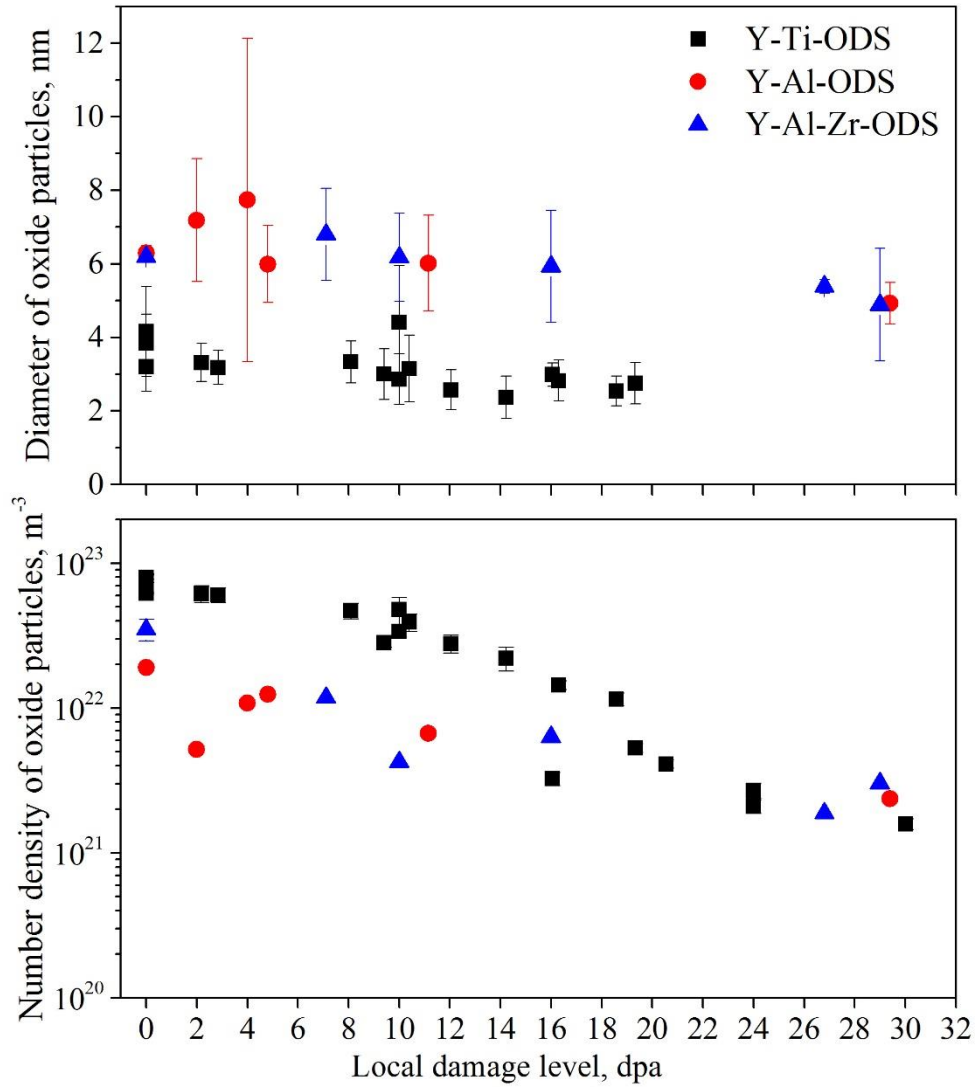


Fig. 6.12 (a) Averaged diameter and (b) number density of oxide particles as a function of dpa in Y-Ti-ODS (squares), Y-Al-ODS (circles) and Y-Al-Zr-ODS (triangles) irradiated to nominal displacement damages of 2 and 10 dpa.

6.3.1.5 Dissociation mechanism at RT

During cascade collisions, the ejected atoms out of precipitates or oxide particles may undergo three main processes: (i) dissolve into the matrix (ballistic dissolution); (ii) diffuse back into the parent particle or being absorbed by the other particles and (iii) re-nucleate to form a new particle with other solute atoms in the matrix. The last two processes depend much on the diffusion of solute atoms under irradiations, particularly the diffusion of Y in bcc Fe, which is slower than the other elements Ti and O. According to the vacancy mechanism, the radiation-enhanced diffusion coefficient of Y, D_Y^{irr} can be depicted by equation (6.4) [21]:

$$D_Y^{irr} = (C_v^{irr}/C_v^{eq})D_Y^h \quad (6.4)$$

where C_V^{irr} and C_V^{eq} are the vacancy concentration under irradiation and thermally equilibrium condition, respectively. D_Y^{th} is the thermal diffusion coefficient of Y, estimated to be $2.5 \times 10^{-42} \text{ nm}^2/\text{s}$ at RT [39]. On the basis of that the concentration of vacancies is equal to that of interstitials under irradiation [21], the C_V^{irr} is given by:

$$C_V^{irr} = (K_0/K_{IV})^{0.5} \quad (6.5)$$

where K_0 is the displacement rate, $1.3 \times 10^{-3} \text{ dpa/s}$ ($\sim 1200 \text{ nm}$ towards specimen surface) for this work and K_{IV} is the recombination rate of vacancies and interstitials. More details on related parameters are described in Ref. [21]. Consequently, the radiation enhanced diffusion coefficient of Y is estimated to be $5.3 \times 10^{-9} \text{ nm}^2/\text{s}$ and the diffusion distance during the irradiation period $\sim 5 \text{ h}$ is about 0.02 nm . Such a limited diffusion distance indicates that the ballistic dissolution should determine the microstructural evolution of oxide particles under irradiation. The rate of volume shrinkage for a spherical precipitate is described by Was [40] in the following equation:

$$dV/dt = -4\pi(r_p)^2\zeta K_0\Omega \quad (6.6)$$

where ζK_0 represents the outward flux atoms from the precipitate surface; r_p is the radius of a spherical precipitate; Ω is the atomic volume. This model does not account for the amorphization of oxide particles. The time dependent shrinkage in this model elucidates well the continuing reduction of the particle number density with increasing displacement damage in this study. Several large oxide particles still survived in the Y-Al-ODS and Y-Al-Zr-ODS specimens irradiated up to about 29 dpa/local, as shown in Fig. 6.10(c) and Fig.6.11(c). Since in this study it was rather difficult to conclude the difference in the phase stability among the three ODS steels, it can be said that the phase stability depends on the sort of oxide particles, chemical compositions and structures. More detailed investigations at higher temperatures than RT are necessary. Furthermore, in the previous studies, almost complete dissolution of nanoclusters without the formation of new clusters or precipitates was observed by APT after the heavy ion irradiations up to 150 dpa at RT [21] and lower temperatures [20, 24], whereas such a complete dissolution could not be found at irradiation temperatures above 100°C [17]. In contrast, an increase in number density of Y-Ti-O particles with $6 \pm 4 \text{ nm}$ in average size was observed by TEM in a 13.5Cr-0.3Ti ODS after heavy ion irradiation up to 0.8 dpa at RT [26], demonstrating a possible new nucleation of nanoclusters. Such discrepancy should be explained in association with the irradiation conditions like displacement damage and temperature, and the sort of oxide particles.

6.3.2 Irradiation hardening

6.3.2.1 Nanoindentation hardness measurement in Y-Ti-ODS

The depth profiles of the averaged nanoindentation hardness (H_{NI}) of as-received and irradiated specimens of Y-Ti-ODS are shown in Fig. 6.13(a), where the averaged H_{NI} continuously declined with increasing the indentation depth (h) to 2000 nm, which is known as the indentation size

effect (ISE) [41]. For a better understanding of depth dependence in radiation hardening, the ratios of the average hardness values of the irradiated specimens to the as-received were calculated and shown in Fig. 6.13(b). The measured nanoindentation hardness in the near surface region (shallower than around 150 nm), which is strongly affected by the specimen surface conditions such as oxidation, roughness [42], can be neglected. From approximately 150 to 330 nm, the hardness ratios increased quickly, and then decreased gradually from 330 to about 2000 nm, which explained that the measured H_{NI} at around 330 nm reflects the most obvious irradiation hardening. Beyond 330 nm, the hardness ratios decreased because the unirradiated region tended to occupy the major part of the deformation volume. Indeed, the depth of the plastic deformation region by the indentation is approximately 4–10 times of the indentation depth [43]. Therefore, we can select the hardness value at the indentation depth of 330 nm as a reference H_{NI} to estimate the radiation hardening. On the other hand, in order to avoid the ISE, Nix-Gao model was also adopted to assess the radiation hardening, which aims to evaluate a bulk equivalent macroscopic hardness for surface thin layer based on the concept of geometrically necessary dislocations (GNDs) [41], as given by:

$$H/H_0 = \sqrt{1 + (h^*/h)} \quad (6.7)$$

where H is the hardness at a certain indentation depth (h), and H_0 is the hardness that would only arise from the statistically stored dislocations (SSDs) in the absence of any GNDs. h^* represents for a characteristic length that depends on the indenter geometry, H_0 and the shear modulus of a given material. For the as-received ODS specimen, plotting the square of the measured hardness (H_{NI})² against the reciprocal of the indentation depth $1/h$ deserves a straight line with the slope being h^* , i.e. with a single value of h^* over the whole testing depth [41]. Fig. 6.13(c) shows each plot of (H_{NI})² versus $1/h$, where all the tangent lines in the indentation depth range of 150–330 nm were used to evaluate the bulk equivalent macroscopic hardness of the surface thin layers for the as-received and the as-irradiated specimen, and thus the averaged H_0 values were deduced.

All the measured hardness values (H) and hardenings (ΔH) obtained by the above two methods are shown in Fig. 6.14 and the numerical values are presented in Table 6.4. As shown in Fig. 6.14, the hardening was enhanced considerably with increasing the displacement damage irrespective of the analysis method used. At the nominal displacement damage of 50 dpa, the irradiation hardening was estimated to be 1.93 ± 0.20 GPa and 1.63 ± 0.39 GPa, which were measured at 330 nm and obtained by Nix-Gao model, respectively.

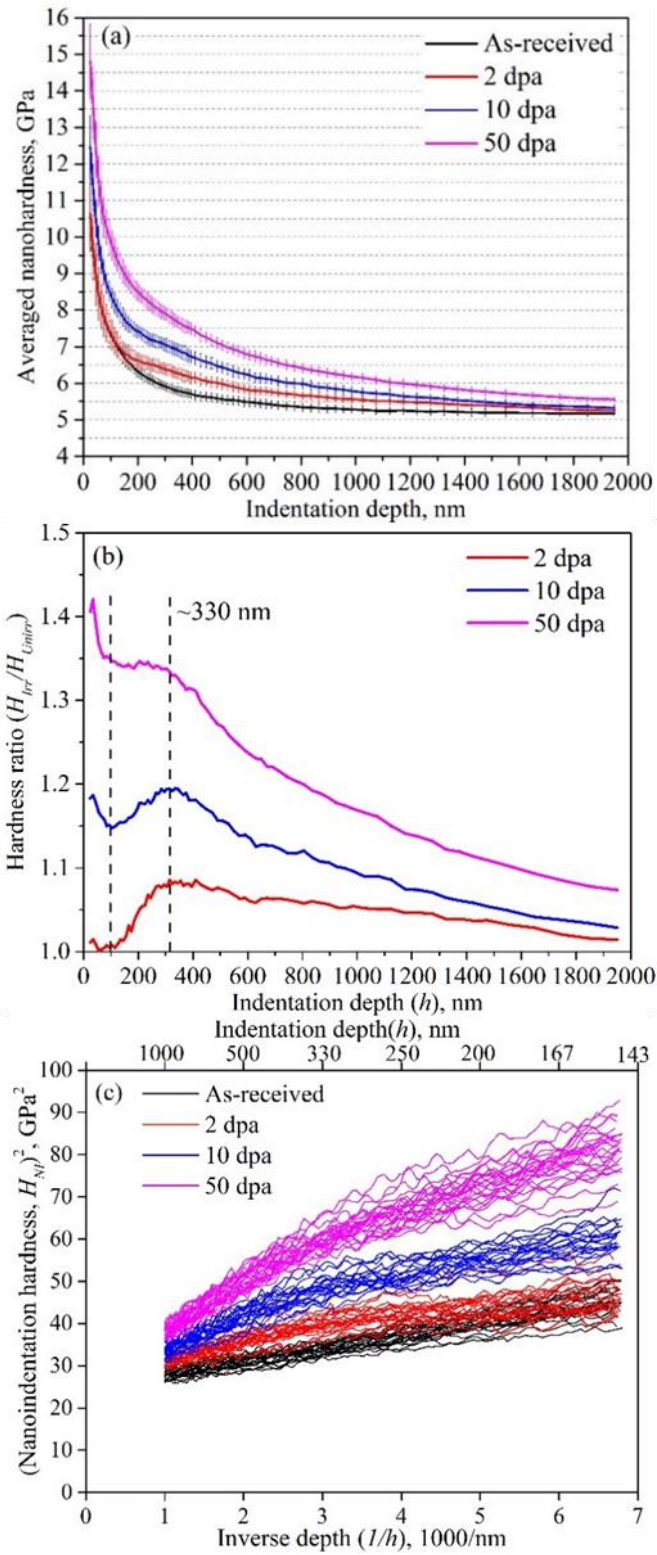


Fig. 6.13 (a) The average hardness profiles and (b) the ratio profiles of the averaged hardness of the irradiated to unirradiated versus indentation depth; (c) Each $(H_{NI})^2$ profile as a function of inverse depth $1/h$ in as-received and irradiated Y-Ti-ODS.

Table 6.4 Hardness values and hardenings of Y-Ti-ODS at roughly 330 nm and obtained by the Nix-Gao model

	Nanoindentation hardness (H_{NI}), GPa				Hardening (ΔH), GPa		
	As-received	2 dpa	10 dpa	50 dpa	2 dpa	10 dpa	50 dpa
At about	5.84 ± 0.11	$6.32 \pm$	$6.96 \pm$	$7.77 \pm$	$0.47 \pm$	$1.12 \pm$	$1.93 \pm$
330 nm		0.16	0.18	0.17	0.20	0.21	0.20
Nix-Gao	4.97 ± 0.18	$5.92 \pm$	$6.26 \pm$	$6.60 \pm$	$0.95 \pm$	$1.29 \pm$	$1.63 \pm$
model		0.37	0.31	0.34	0.42	0.36	0.39

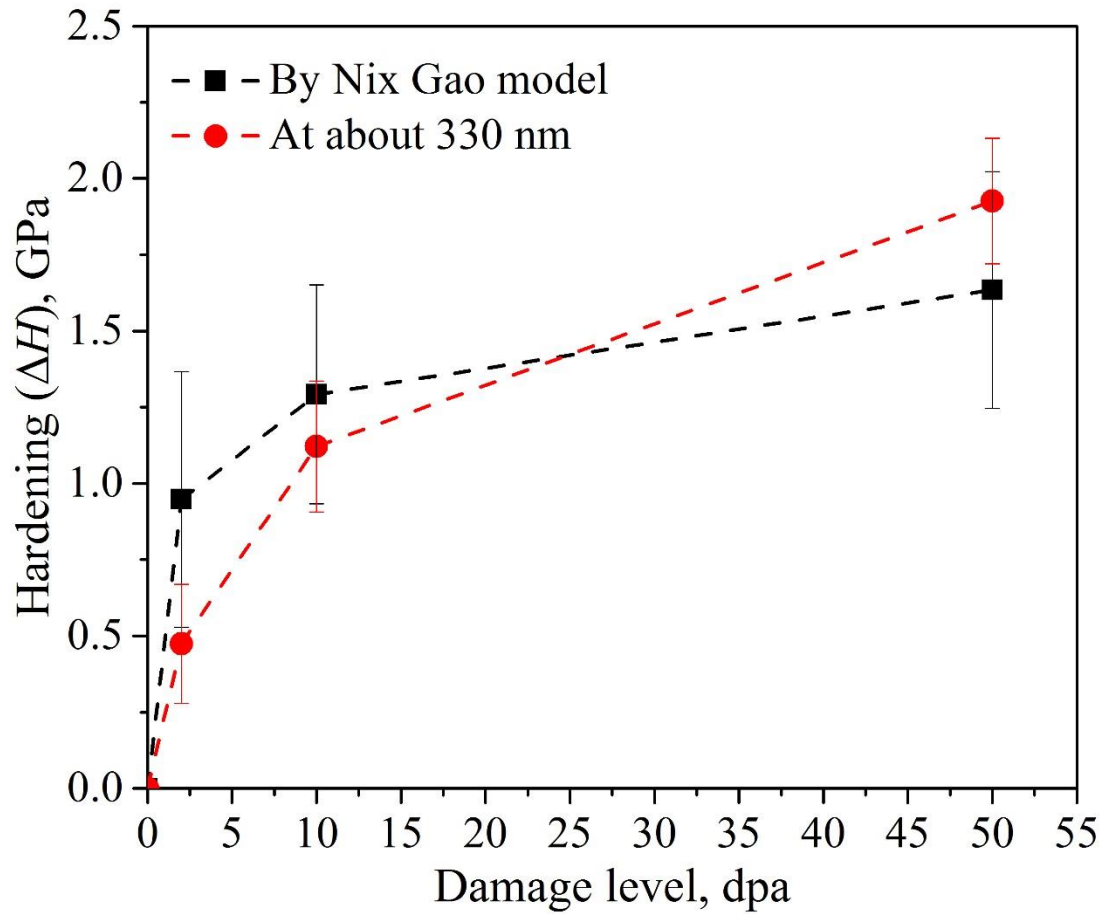


Fig. 6.14 Plots of hardening (ΔH) versus dpa of Y-Ti-ODS after ion irradiations.

6.3.2.2 Comparison of nanoindentation hardness changes among the ODS steels

Similar with Y-Ti-ODS, the depth profiles of the averaged nanoindentation hardness (H_{NI}) of as-received and irradiated specimens of Y-Al-ODS and Y-Al-Zr-ODS also revealed a gradual decreasing tendency, as shown in Fig. 6.15(a) and (c). Fig. 6.15(b) and (d) show each plot of $(H_{NI})^2$ versus $1/h$ for Y-Al-ODS and Y-Al-Zr-ODS, respectively. As discussed in the aforementioned section 6.3.2.1, the irradiation hardening values were obtained by two different methods based on the measured nanoindentation hardness at the indentation depth of 330 nm and by the Nix-Gao model. The hardness changes, namely irradiation hardening, versus the nominal dpa of these three ODS steels Y-Ti-ODS, Y-Al-ODS and Y-Al-Zr-ODS were displayed in Fig. 6.16. It revealed that the radiation hardenings in the three ODS steels elevated with increasing the nominal damage level irrespective of the method. Moreover, the irradiation hardenings deduced by the same method in Y-Ti-ODS and Y-Al-ODS were close to each other, which were slightly higher than the counterparts of Y-Al-Zr-ODS at the nominal damages of 2, 10 and 50 dpa.

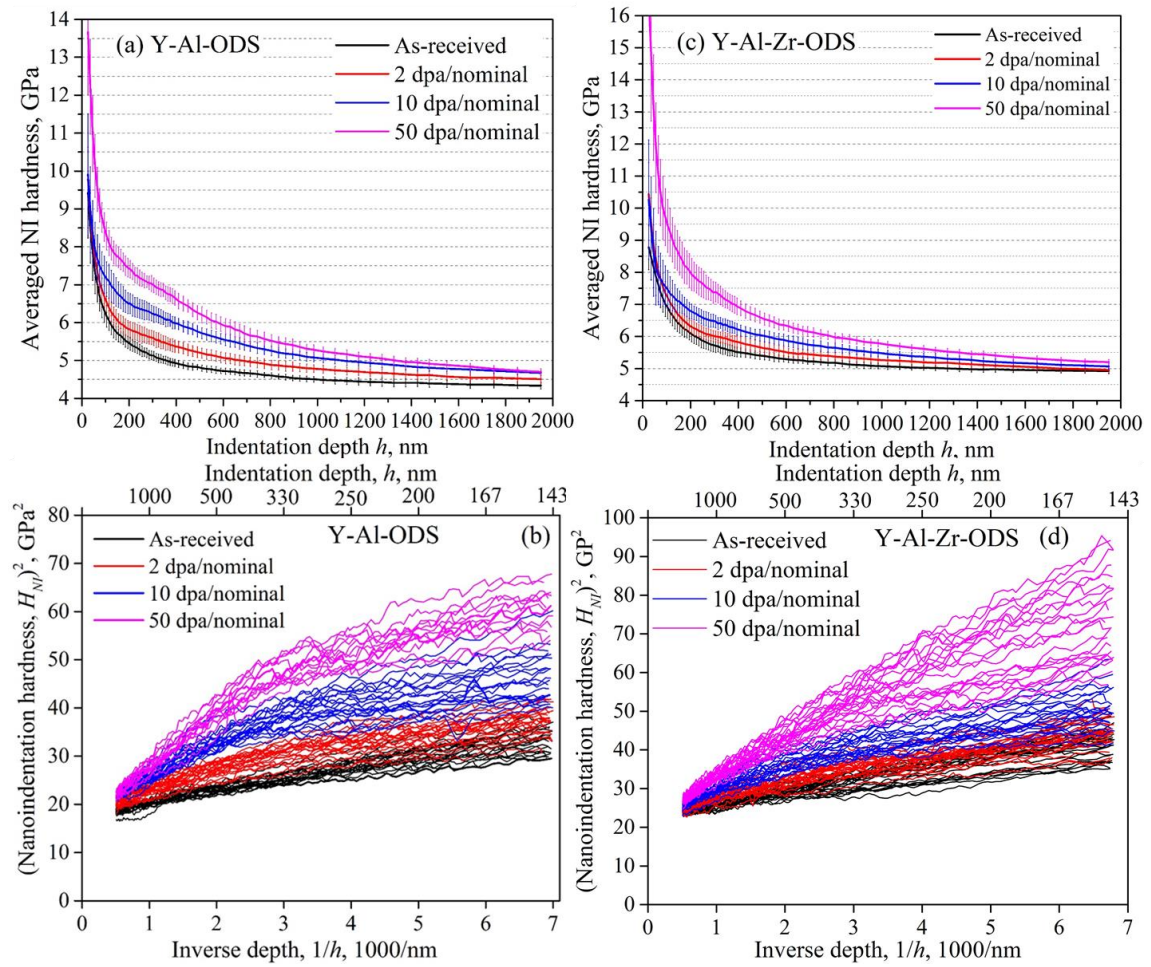


Fig. 6.15(a, c) The average hardness profiles and (b, d) Each $(H_{NI})^2$ profile as a function of inverse depth $1/h$ in as-received and irradiated Y-Al-ODS and Y-Al-Zr-ODS.

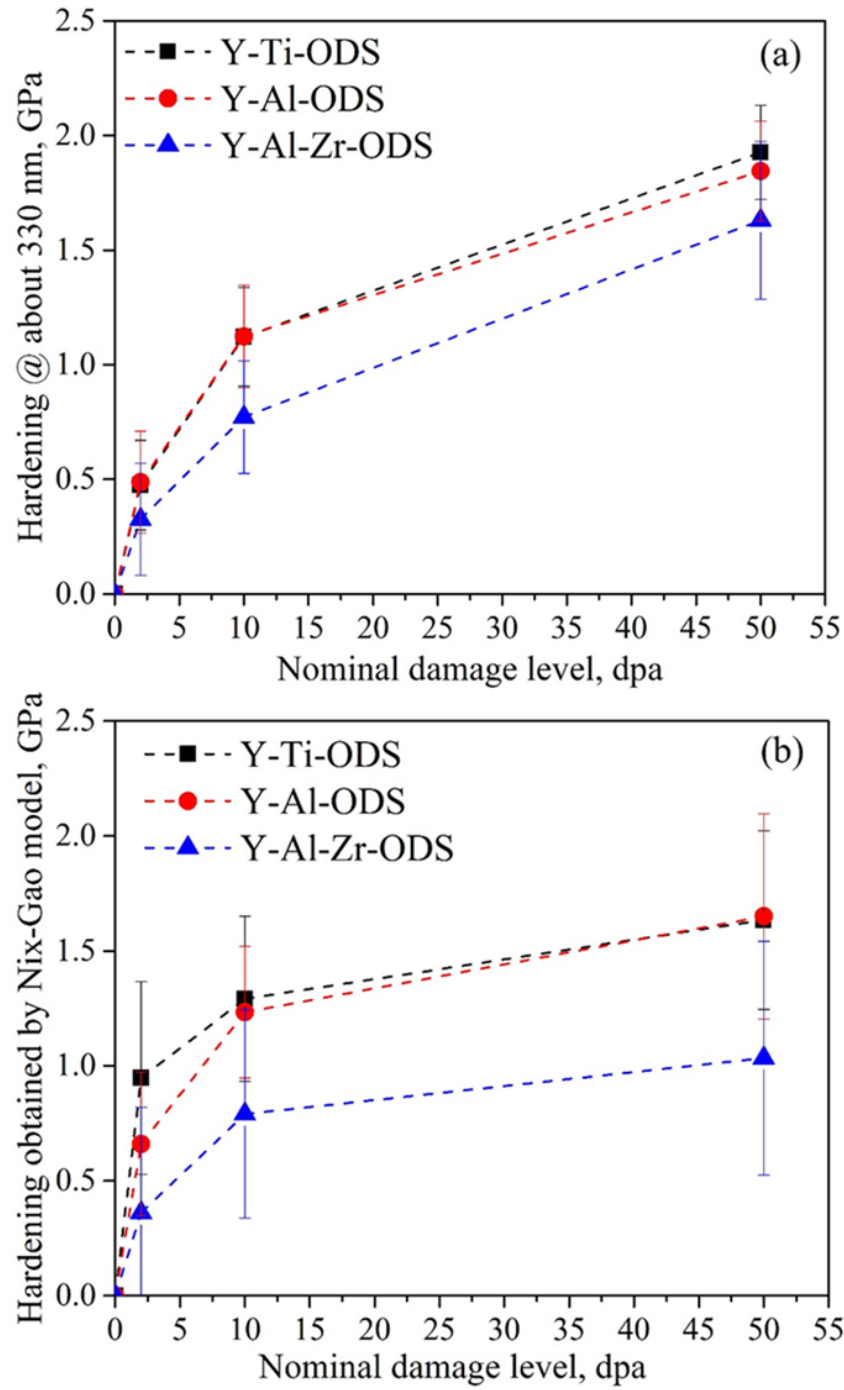


Fig. 6.16 Hardening (ΔH) versus dpa of Y-Ti-ODS, Y-Al-ODS and Y-Al-Zr-ODS after ion irradiations, obtained based on the measured nanoidentation hardness at the indentation depth of about 330 nm (a) and by the Nix-Gao model.

6.3.2.2 Hardening mechanism

Considering the similar radiation hardenings in Y-Ti-ODS, Y-Al-ODS and Y-Al-Zr-ODS, here, the hardening mechanisms were only discussed by correlating between the microstructural evolution and radiation hardening of Y-Ti-ODS after ion irradiation. The nanoindentation hardness can be converted to Vickers hardness by using the measured values of the Y-Ti-ODS. The Vickers hardness of as-received Y-Ti-ODS was measured to be $367.8 \pm 4.4 \text{ kgf/mm}^2$ [4] and the corresponding nanoindentation hardness was $4.97 \pm 0.18 \text{ MPa}$ in this work. The yield stress was calculated to be 1125 MPa on the basis of the correlation between yield stress, σ_y , and Vickers hardness, HV, where $\sigma_y (\text{MPa}) = 3.06\text{HV} (\text{kg/mm}^2)$ [44]. Similarly, for the 50 dpa (nominal displacement damage) irradiation, the stress increment $\Delta\sigma$ of Y-Ti-ODS can be estimated to be 369 MPa with the nanoindentation hardening value obtained by Nix-Gao evaluation method, as shown in Table 6.5. Furthermore, we adopted the equation (6.8) for combining the hardening contributors such as oxide particles, dislocation loops and solute atoms because they are short-range obstacles for dislocation motion [40]. Thus, the stress increment $\Delta\sigma$ in this study can be written as:

$$\Delta\sigma = \sqrt{(\Delta\sigma_l)^2 + (\Delta\sigma_{so})^2 - (\Delta\sigma_o)^2} \quad (6.8)$$

where $\Delta\sigma_l$, $\Delta\sigma_{so}$ and $\Delta\sigma_o$ represent the strengthening contributors by dislocation loops, solid atoms (Y, Ti, O) and oxide particles, respectively. Here, vacancy-type clusters were not taken into account because in our previous study [4] the formation of tiny cavities of $\sim 10^{23} \text{ m}^{-3}$ caused a softening instead of hardening in the Y-Ti-ODS. It is noted that the ion-irradiation results in a hardening accompanied by the dissolution of oxide particles which is well known as a contributor to the strengthening of ODS steels.

In the previous analytical study on solid solution hardening [45], the solid solution strengthening could be formulated linearly on the concentration of solute atom C_i in bcc alloys regardless of substitutional strengthening and interstitial strengthening, and shown as follows:

$$\Delta\sigma_{so} = k_i C_i \quad (6.9)$$

where k_i is the strengthening coefficient for alloying elements. At RT, k of carbon (C) and nitrogen (N) as interstitial atoms is $1103 \text{ MPa per at. \%}$, which is much greater than $18 \text{ MPa per at. \%}$ for Ti as a substitutional atom [46]. Considering the similar size misfit of oxygen (O) in the ferrite matrix with C and N, k of O is possibly set to be $1103 \text{ MPa per at. \%}$. According to the resultant chemical compositions of Y-Ti-ODS (see Table 6.1), the atomic percentages of Y, Ti and O in the ferritic matrix were roughly estimated to be $0.16 \text{ at. \%}$, $0.18 \text{ at. \%}$ and $0.38 \text{ at. \%}$, respectively. So the potential solid solution strengthening component was evaluated as 420 MPa for O, and 3 MPa for Ti, respectively. Meanwhile, Sun et al. [46] actually measured the strengthening by solid solution oxygen in pure titanium and reported the strengthening coefficient to be $262 \text{ MPa/at.\%O}$, smaller than the analytical value in bcc alloys obtained by Lu et al. [45].

Additionally, $\Delta\sigma_l$ and $\Delta\sigma_o$ can be expressed by the following equation based on Orowan type bypassing mechanism [40]:

$$\Delta\sigma = M\alpha\mu b(Nd)^{0.5} \quad (6.10)$$

where M is the Taylor factor (3.06); α is the barrier strength factor of the contributor, being 0–1; μ is the shear modulus (80 GPa for alpha iron); b is the Burgers vector (0.248 nm for $1/2\langle 111 \rangle$ dislocations in bcc iron); N and d are the number density and mean diameter of the contributor, respectively. Oxide particles of 5–10 nm in diameter possess the obstacle strength factors α_o of ~0.4–0.8 (0.63 on average), which was measured by Ijiri et al. [47] by means of in-situ TEM observation on the oxide particle-dislocation interaction. The strength factors of loops α_l were estimated to be about 0.3–0.4 for two neutron-irradiated Fe-9Cr alloys [48]. In this study, the irradiation hardening ($\Delta\sigma$) values were estimated by different combinations of barrier strength factors of oxide particles and dislocation loops, which are shown in Table 6.5. It turns out that for the case of $\alpha_o = 0.4$ and $\alpha_l = 0.5$, the stress increments measured by nanoindentation method and estimated from the TEM observation became close. The higher α_l value possibly arises from the decoration effect of solute atoms (O) on dislocation loops. For $\alpha_o \geq \alpha_l$, additional strengthening components are required.

Finally, in this study, we attempted to correlate the irradiation hardening with the microstructure change, which was mainly the dissolution of oxide particles, but the results of the present analysis indicated a significant solid solution hardening by oxygen (and possibly yttrium and titanium). It is considered that along with the ion-irradiation induced dissolution of Y-Ti-O particles, the constitution atoms may form locally condensed high entropy alloyed (HEA) regions where those atoms are distributed rather homogeneously. It is also expected that such HEA regions could not be detected by APT nor by TEM method nowadays, which makes the analysis difficult in this study. More detailed study is necessary.

Table 6.5 Comparison between the yield stress increment σ_y obtained from nanoindentation hardness and the stress increment $\Delta\sigma$ estimated from the microstructural observation by TEM.

	H_{NI} , GPa	H_V , kgf/mm ²	σ_y , MPa Estimated from H_V	Oxide particles		Dislocation loops		O solute atom, at. %	$\Delta\sigma$, MPa Estimated from TEM
				Diameter, nm	Number density, $\times 10^{22} \text{ m}^{-3}$	Diameter, nm	Number density, $\times 10^{22} \text{ m}^{-3}$		
As-received	4.97 ± 0.18	367.8 ± 4.4	1125	3.8 ± 1.0	7.4 ± 0.8	n.o.	n.o.	≈ 0	–
50 dpa (Nominal)	6.60 ± 0.34	488 ¹⁾	1494 ²⁾	n.o.	n.o.	2.8 ± 0.7	4.1 ± 0.7	0.38	–
Irradiation effects	$\Delta H_{NI} = 1.63 \pm 0.39$	$\Delta H_V = 120$	$\Delta\sigma_y = 369$	$\alpha_o = 0.4, \Delta\sigma_o = -407 \text{ MPa}$		$\alpha_l = 0.3, \Delta\sigma_l = 195 \text{ MPa}$		$\Delta\sigma_{so} = 420 \text{ MPa}^{3)}$	220
				$\alpha_o = 0.4, \Delta\sigma_o = -407 \text{ MPa}$		$\alpha_l = 0.5, \Delta\sigma_l = 325 \text{ MPa}$			341
				$\alpha_o = 0.5, \Delta\sigma_o = -509 \text{ MPa}$		$\alpha_l = 0.5, \Delta\sigma_l = 325 \text{ MPa}$			152

Note: Values with error bars were experimentally obtained. n.o.: not observed. 1) NI-HV conversion 2) HV-tensile stress conversion 3) reference [45]

6.3.3 Other issues

In addition, Lescoat et al. [49] investigated the amorphization of oxides in a DY (Y, Ti, O) ODS steel by using electron diffraction pattern, showing that large particles ($d \approx 50$ nm) underwent amorphization under irradiations with 92 MeV Xe ions to 0.1 dpa at 20 °C and 700 keV Kr ions to 47 dpa at 300 °C, which mainly brought about electronic excitations and ballistic damages, respectively. Skuratov et al. [50] also reported that to form the amorphous ion tracks inside the $\text{Y}_2\text{Ti}_2\text{O}_7$ pyrochlore nanoparticles, the threshold value of electronic stopping powers was estimated to be between 7.4 keV/nm and 9.7 keV/nm. Meanwhile, pyrochlore $\text{Y}_2\text{Ti}_2\text{O}_7$ was prone to be amorphous by displacement damages because of its high antisite formation energy [51], and was verified on bulk pyrochlore $\text{A}_2\text{Ti}_2\text{O}_7$ (A=Y, Lu, Sm, Gd) after 0.6 MeV Bi ion irradiations at ~ 0.18 dpa at RT [52]. In this study, it was challenging to characterize the amorphization of small dispersoids (~ 3 nm) in Y-Ti-ODS. Nevertheless, in Recry. Y-Ti-ODS, the oxide particles after the irradiation at nominal damage 2 dpa were characterized by using HRTEM and EFTEM, as shown in Fig. 6.17. Ti-, Y-jump ratio images demonstrated that the oxide particle contains both Y and Ti. The amorphous ring shown in Fig. 6.12(e) indicated a possible amorphization after irradiation, which might be produced by the atomic displacement rather than the electronic excitations (the maximum value ~ 6 keV/nm for this work shown in Fig. 6.1(b)). A simulation study on FFT information is required to confirm the amorphization. However, defect fluorite $\text{Y}_2\text{Zr}_2\text{O}_7$ was reported to be more resistant to amorphization by ion irradiation than pyrochlore $\text{Y}_2\text{Ti}_2\text{O}_7$ because the cation antisite defect energy of the former was calculated to be about half of the latter [53]. Such discrepancy in the structural stability of oxide particles did not produce a significant influence on the ion-irradiation induced particle dissolution at room temperature (RT). Therefore, more works at higher irradiation temperatures are necessary to uncover this issue.

According to the previous study that the particle coherency is size dependent [12, 15, 21], and most of fine nanoclusters are expected to be coherent with the matrix and of low O/M interfacial energy. Concerning the effect of coherency on the irradiation behavior of dispersoids, Chen et al. [54] explained it in a 12Cr ferritic-martensitic ODS alloy irradiated with 3.5 MeV Fe^{2+} at 325, 475, 625 °C up to 200 dpa, that fine and coherent dispersoids experienced modest size changes under ion irradiations, whereas semi-coherent and incoherent dispersoids shrank in size and were only observed to remain after the irradiation at 625 °C (elevated temperature). In situ TEM study also revealed that larger oxides seemed to be more affected by ion-irradiation at 45 dpa, 500 °C than Y-Ti-O nano-precipitates (5 nm in diameter) [55].

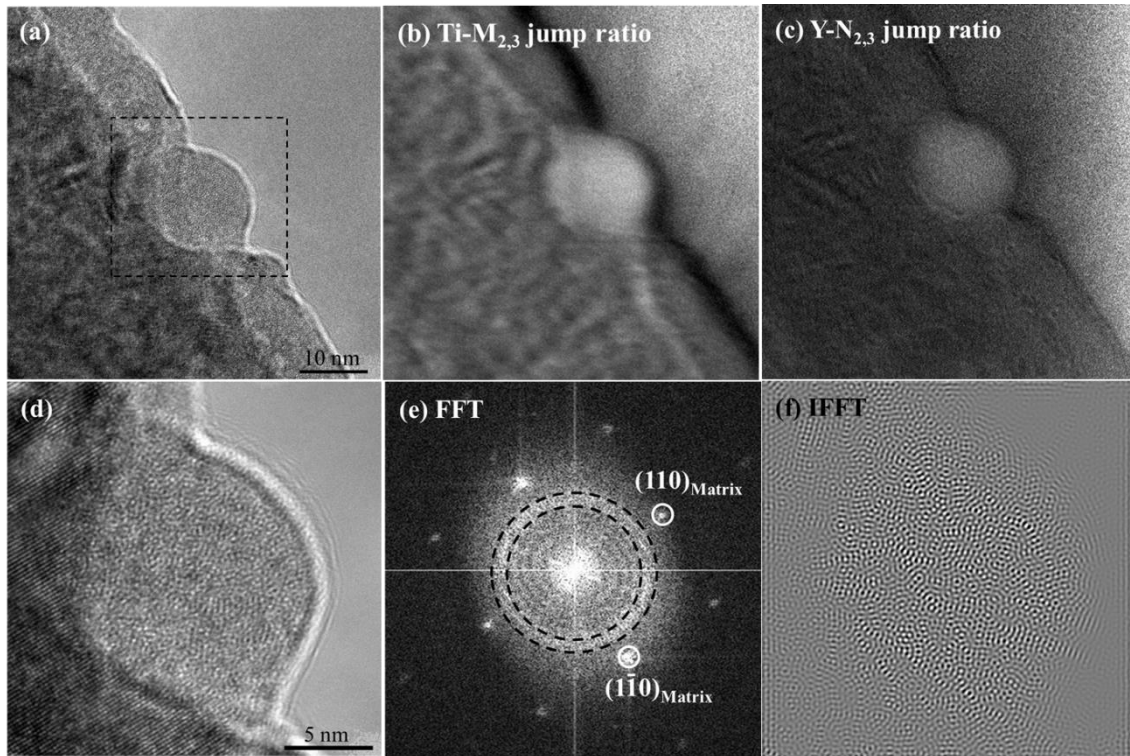


Fig. 6.17 (a) A zero-loss filtered image showing one nano-sized dispersoid (~ 10 nm diameter) in Recry. Y-Ti-ODS at the depth of ~ 720 nm (~ 2.3 dpa); (b)–(c) corresponding to jump ratio images of Ti-M_{2,3} and Y-N_{2,3}, respectively; (d) HRTEM lattice image of the dispersoid marked in 6.12(a); (e) FFT pattern of 6.12(d); (f) inverse FFT (IFFT) image reconstructed by the amorphous ring circled by two black dashes in 6.12(e).

6.4 Conclusions

FeCr-ODS steels strengthened by Y-Ti-O nano-particles (Y-Ti-ODS), Y-Al-O nano-particles (Y-Al-ODS), Y-Zr-O nano-particles (Y-Al-Zr-ODS) were irradiated with 6.4 MeV Fe ions up to nominal displacement damages of 2, 10 and 50 dpa at RT. Microstructure evolution and hardness changes after ion irradiations were investigated by TEM and nanoindentation hardness measurements. Coarsened oxide particles in the Y-Ti-ODS after recrystallization (named by Recry. Y-Ti-ODS) were also characterized by TEM techniques including HRTEM and EFTEM for understanding phase stability under the irradiation of a nominal 2 dpa at RT. The obtained main results are as followings:

- 1). Prior to the irradiation, the averaged diameter and number density of nano-sized oxide particles in Y-Ti-ODS were 3.8 ± 1.0 nm and $(7.4 \pm 0.8) \times 10^{22} \text{ m}^{-3}$, respectively. The majority of oxide particles were cubic pyrochlore $\text{Y}_2\text{Ti}_2\text{O}_7$.
- 2). In the Y-Ti-ODS, Y-Al-ODS, Y-Al-Zr-ODS steels irradiated to nominal displacement damages of 2 and 10 dpa, the averaged diameter of oxide particles slightly decreased with increasing dpa, while the corresponding number density was significantly decreased by almost two orders of

magnitude above ~20 dpa in the case of Y-Ti-ODS compared to that before irradiation, while the oxide particles in Y-Al-ODS and Y-Al-Zr-ODS steels, large oxides still remained even after irradiation to higher than 20 dpa. More investigations are necessary. Ballistic dissolution is considered to be responsible for this phenomenon.

- 3). Above ~2 dpa, most of coarsened (Y, Ti) oxide nanoparticles in Recry. Y-Ti-ODS might become amorphous, which is considered to be produced by displacement damages rather than electronic excitations.
- 4). In the case of 50 dpa, tiny dislocation loops of 2.8 ± 0.7 nm were formed in Y-Ti-ODS. More than 80% loops were $1/2\langle 111 \rangle$ type and the rest can be the $\langle 100 \rangle$ type. The total number density of these two types of loops was $(4.1 \pm 0.7) \times 10^{22} \text{ m}^{-3}$ at the local damage of ~72 dpa.
- 5). When the displacement damage is increased, the hardness values of Y-Ti-ODS, Y-Al-ODS and Y-Al-Zr-ODS continuously increased irrespective of the dissolution of oxide particles. At a nominal damage of 50 dpa, the radiation hardening of Y-Ti-ODS was 1.63 ± 0.39 GPa estimated by the Nix-Gao model, which was close to the counterpart of Y-Al-ODS 1.65 ± 0.44 GPa and slightly bigger than the counterpart of Y-Al-Zr-ODS 1.03 ± 0.51 GPa. The solid solution strengthening by oxygen and the dislocation loops could be responsible for the hardening accompanied by the dissolution of oxide particles.

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Chapter 7 Summary

Because of their superior tensile, creep and fatigue strength at elevated temperatures and excellent neutron radiation tolerance, ODS steels have been considered as a fusion blanket structural material and as a candidate fuel cladding for the next generation fission reactors and light water reactors with accident tolerant fuel. The Al-addition to FeCr-ODS steels altered the main particles from the ultrafine (Y, Ti) oxides to coarser (Y, Al) oxides, and a small addition of Zr to FeCrAl ODS steels altered the majority of oxide particles from Y-Al-O dispersoids to Y-Zr-O dispersoids. Considering the significance in the roles of oxide particles in radiation tolerance, in this research, the radiation effects such as He bubble formation behavior, swelling, hardening and phase stability were investigated for three different type of ODS steels (Y-Ti-ODS, Y-Al-ODS, Y-Al-Zr-ODS) with different sort of complex oxides.

Chapter 1: Chapter 1 introduces advanced nuclear energy systems, structural materials & fuel claddings in fission reactors, structural materials in fusion reactors together with the radiation effects on solids. Furthermore, current status of ODS steels which are the candidate structural material, is introduced and the objective of this study is described.

Chapter 2: Chapter 2 is experimental method, including the material information used in this study, such as the fabrication process, chemical compositions, grain morphology and so on. The experimental conditions such as ion irradiation, the annealing experiment, TEM observations and hardness measurements are described.

Chapter 3: In this chapter, in order to investigate the effects of Al and Zr addition on He bubble formation behavior in ODS ferritic steel, two different type of ODS ferritic steels (Y-Al-Zr-ODS, Y-Ti-ODS) with/without Al and Zr co-addition were irradiated with He⁺ up to 0.2 dpa/3500 appm at 300 °C, 550 °C, 700 °C. The mean grain size of each ODS steel was about 370 nm. Al addition resulted in the formation of larger oxide particles with a lower number density in the ODS steel. After irradiation to 0.2 dpa/3500 appm He, dislocation densities in both ODS ferritic steels showed no change. However, the size and number density of He bubbles were increased and decreased, respectively, by the simultaneous addition of Al and Zr. Although both ODS steels showed good resistance to He-bubble induced swelling, the Y-Ti-ODS steel possessed a better swelling resistance than Y-Al-Zr-ODS steel. It was considered that the oxide particles were the main contributor for the swelling resistance of ODS steels by providing a number of defect sinks with a high sink strength. The swelling increased with increasing irradiation temperature in both ODS steels, indicating that the de-trapping He enhanced He-bubble swelling.

Chapter 4: In this chapter, He ion-irradiation hardening on an ODS steel was investigated. Y-Al-Zr-ODS ferritic steel was implanted with 3500 appm He (0.2 dpa) at 300, 550 and 700 °C. The post-implantation annealing (PIA) at 800 °C/100 h was conducted on the specimen implanted at 300

°C. Nanoindentation (NI) tests were carried out to investigate the temperature dependent hardening, and transmission electron microscopy (TEM) observation was performed to characterize the cavity evolution. A limited hardening was found in the as-implanted ODS specimens at all implantation temperatures, which tended to reduce with increasing the temperature. The PIA caused no further hardening, while TEM images revealed that there was an evident change in the cavity distribution morphology. The cavity diameter increased from 2.5 ± 0.4 nm to 5.0 ± 1.7 nm and the corresponding number density decreased from $(22.2 \pm 1.6) \times 10^{22} \text{ m}^{-3}$ to $(6.7 \pm 0.5) \times 10^{22} \text{ m}^{-3}$ before and after the PIA. The negligible hardness changes induced by the PIA were interpreted in terms of the Orowan-type dislocation barrier model with the corresponding barrier strength factor of cavities to be less than 0.1.

Chapter 5: In order to investigate the effects of oxide particles on radiation responses such as hardness change and microstructural evolution, three sorts of ODS ferritic steels, Y-Ti-ODS, Y-Al-ODS and Y-Al-Zr-ODS, mostly strengthened by (Y, Ti), (Y, Al) and (Y, Zr) oxide dispersoids, respectively, were simultaneously irradiated with iron and helium ions at 550 °C up to a damage of 30 dpa and a corresponding helium (He) concentration of ~3500 appm in the range of 1000 to 1300 nm. Single iron ion beam irradiation was also performed for reference. Transmission electron microscopy revealed that after the dual ion irradiation helium bubbles of 2.8, 6.6 and 4.5 nm in mean diameter with the corresponding number densities of 1.1×10^{23} , 2.7×10^{22} and $3.6 \times 10^{22} \text{ m}^{-3}$ were observed in Y-Ti-ODS, Y-Al-ODS and Y-Al-Zr-ODS, respectively, while no such bubbles were observed after single ion irradiation. About 80% of intragranular He bubbles were adjacent to oxide particles in the ODS ferritic steels. Although the high number density He bubbles were observed in the ODS steels, the void swelling in Y-Ti-ODS, Y-Al-ODS and Y-Al-Zr-ODS was still small and estimated to be 0.13%, 0.53% and 0.20%, respectively. The excellent swelling resistance is dominantly attributed to the high sink strength of oxide particles that depends on the dispersion morphology rather than the crystal structure of the particles. In contrast, no dislocation loops were produced in any of the irradiated steels. Nanoindentation measurements showed that no irradiation hardening but softening was found in the ODS ferritic steels, which was probably due to irradiation induced dislocation recovery. The helium bubbles in high number density never contributed to the irradiation hardening of the ODS steels at these irradiation conditions.

Chapter 6: Irradiation effects on hardness and phase stability were investigated for the Y-Ti-ODS ferritic steel strengthened by (Y, Ti) oxide nano-particles after irradiation with 6.4 MeV Fe^{3+} at room temperature (RT) up to nominal damages of 2, 10 and 50 dpa. With increasing displacement damage up to 18 dpa, nano-sized oxide particles slightly shrank, while the corresponding number density drastically reduced by almost two orders of magnitude compared to that of before irradiation. It is considered that ballistic dissolution should be responsible for such reductions in the particle size and number density. Dislocation loops consisting of $1/2\langle 111 \rangle$ type (> 80%) and $\langle 100 \rangle$ type were

observed under weak beam dark field (WBDF) condition in the specimen irradiated to a nominal damage of 50 dpa. The average size and number density of all the dislocation loops were 2.8 ± 0.7 nm and $(4.1 \pm 0.7) \times 10^{22} \text{ m}^{-3}$, respectively, at the local damage of ~ 72 dpa. Although the oxide particles were almost completely dissolved, nanoindentation hardness measurements revealed that the hardening went up continuously with increasing displacement damage and estimated to be 1.63 ± 0.39 GPa by the Nix-Gao model at a nominal damage of 50 dpa. The irradiation hardening accompanied by the dissolution of oxide particles was interpreted in terms of loss of oxide particles, solid solution hardening and formation of fine dislocation loops. The contribution of dislocation loops observed by TEM to the hardening was insufficient to overcome the loss of strengthening by dissolution, suggesting the importance of solid solution hardening and the possible existence of invisible additional hardening contributors.

Chapter 7: This chapter is the summary of the contents of this doctoral dissertation.

List of publications and presentations

1. Publications

- 1). **Peng Song**, Jin Gao, Kiyohiro Yabuuchi, Akihiko Kimura, “Ion-irradiation hardening accompanied by irradiation-induced dissolution of oxides in FeCr(Y, Ti)-ODS ferritic steel”, **Journal of Nuclear Materials** 511 (2018) 200–211.
- 2). **Peng Song**, Danniel Morrall, Zhexian Zhang, Kiyohiro Yabuuchi, Akihiko Kimura, “Radiation response of ODS ferritic steels with different oxide particles under ion-irradiation at 550 °C”, **Journal of Nuclear Materials** 502 (2018) 76–85.
- 3). **Peng Song**, Kiyohiro Yabuuchi, Akihiko Kimura, “Cavity evolution and hardness changes in a 15Cr-ODS ferritic steel by post He-implantation annealing”, **Nuclear Materials and Energy** 15 (2018) 115–121.
- 4). **Peng Song**, Zhexian Zhang, Kiyohiro Yabuuchi, Akihiko Kimura, “Helium bubble formation behavior in ODS ferritic steels with and without simultaneous addition of Al and Zr”, **Fusion Engineering and Design** 125 (2017) 396–401.
- 5). Eva Hasenhuettl, Zhexian Zhang, Kiyohiro Yabuuchi, **Peng Song**, Akihiko Kimura, “Crystal orientation dependence of ion-irradiation hardening in pure tungsten”, **Nuclear Instruments and Methods in Physics Research B** 397 (2017) 11–14.

2. Presentations at international and domestic conferences

- 1) **Peng Song**, Kiyohiro Yabuuchi, Akihiko Kimura, “Phase stability of a 14Cr-ODS ferritic steel strengthened by Y-Ti-O oxide particles under Fe ions irradiation at room temperature”, **Oral presentation**, The Nuclear Materials Conference (NuMat2018), 14–18 October, 2018, Seattle, WA, **USA**.
- 2) **Peng Song**, Kiyohiro Yabuuchi, Akihiko Kimura, “Cavity evolution and hardness change in a 15Cr-ODS ferritic steel under He-ion implantation & post-implantation annealing”, **Poster presentation**, The 14th Japan-China Symposium on Materials for Advanced Energy Systems and Fission & Fusion Engineering (JCS-14), 25–27 September, 2018, Sendai, **Japan**.
- 3) **Peng Song**, Kiyohiro Yabuuchi, Akihiko Kimura, “Cavity evolution and hardness change in a 15Cr-ODS ferritic steel under He-ion implantation & post-implantation annealing”, **Poster**

- presentation**, 12th Joint Conference on Fusion Energy, 28–29 June, 2018, Ohtsu, **Japan**.
- 4) **Peng Song**, Kiyohiro Yabuuchi, Akihiko Kimura, “Cavity evolution and hardness changes in a 15Cr-ODS ferritic steel with He implantation at 300–800 °C”, **Oral presentation**, 2018 JIM Spring Annual Meeting, 19–21 March, 2018, Chiba, **Japan**.
 - 5) **Peng Song**, Kiyohiro Yabuuchi, Akihiko Kimura, “Radiation responses of ODS ferritic steels with different oxide particles under single & dual beam irradiations”, **Poster presentation**, The 18th International Conference on Fusion Reactor Materials (ICFRM-18), 5–10 November, 2017, Aomori, **Japan**.
 - 6) **Peng Song**, Kiyohiro Yabuuchi, Akihiko Kimura, “Phase stability of oxide particles in ODS ferritic steels under ion-irradiation”, **Oral presentation**, 2017 JIM Autumn Meeting, 6–8 September, 2017, Sapporo, **Japan**.
 - 7) **Peng Song**, Kiyohiro Yabuuchi, Akihiko Kimura, “Swelling and hardening of ODS ferritic steels with different sorts of oxide particles”, **Oral presentation**, 2017 JIM Spring Annual Meeting, 15–17 March, 2017, Tokyo, **Japan**.
 - 8) **Peng Song**, Kiyohiro Yabuuchi, Akihiko Kimura, “Swelling and hardening of ODS ferritic steels with/without Al (Zr) addition under He⁺ irradiation”, **Poster presentation**, The 4th Nuclear Materials Conference, 7–10 November, 2016, Montpellier, **France**.
 - 9) **Peng Song**, Kiyohiro Yabuuchi, Akihiko Kimura, “Microstructure and swelling behavior of two oxide dispersion strengthened ferritic (ODS) steels with or without Al and Zr addition”, **Oral presentation**, The 13th China-Japan Symposium on Materials for Advanced Energy Systems and Fission & Fusion Engineering (CJS-13), 26–29 September, 2016, Hefei, **China**.

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