

Microstructure Development in Neutron Irradiated Tungsten Alloys

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The aim of this work is to investigate the influence of neutron irradiation condition, especially temperature, on irradiation hardening and microstructure development in irradiated tungsten-rhenium (W-Re) alloys. Neutron irradiations were carried out in JOYO at the range of 400 to 750°C, up to 1.54 dpa. Micro Vickers hardness tests and micro structural observations using a TEM were performed. Irradiation hardening of W-Re alloys irradiated at 538°C were clearly larger than those irradiated at other temperatures. Fine voids and fine needle- or plate-like precipitates were observed in pure W and W-Re alloys irradiated at 538°C, respectively, with high number density. The fine complex microstructure seems to be the cause of the characteristic irradiation hardening. [doi:10.2320/matertrans.MBW201025]

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1. Introduction

Tungsten (W) is one of the candidate materials for the plasma facing component of fusion reactors because of its high melting point, high sputtering resistivity, and high temperature strength. During fusion reactor operation, it is anticipated that not only displacement damage but also solid transmutation elements, such as rhenium (Re), and osmium (Os), will be induced in W by fusion neutron irradiation. Consequently, by increasing the neutron fluence, solid transmutation elements will accumulate and the original pure W will change to W-Re or W-Re-Os alloys. For example, calculations predicted that pure W changes to a W-18Re-3Os alloy after 50 dpa irradiation, corresponding to a neutron fluence of 10 MWy/m².¹⁾

It is well known that W shows brittle behavior at room temperature though it has excellent high temperature strength, and the low temperature embrittlement can be improved by thermo-mechanical treatment and Re addition.^{2,3)} It was reported that the creep strength of W irradiated with thermal neutrons is higher than that of unirradiated W. This indicates that the substantial solid solution Re, transmuted from W, can increase the creep strength of W.⁴⁾ Re and Os also change the physical properties of W. For example, W has a high thermal conductivity, however it decreases to half of pure W by the addition of 5 mass% Re.^{5,6)} Despite the solubility limit of Re in W is about 26 mass%, χ phase precipitates (Re₃W) were formed in the W-5Re and W-10Re alloys after 0.5–0.7 dpa irradiation at 600–1500°C without void formation and affected the bulk properties.⁷⁾ Heavy neutron irradiation induced large irradiation hardening in the W-26Re alloy by irradiation induced precipitation.⁸⁾ Even though Re and Os are the main transmutation elements from W, the property change behaviors of W alloys containing these elements, and the effects of the elements themselves under irradiation, have not been adequately reported.

For materials used in fusion reactors, mechanical properties such as strength and ductility are important when the

large electromagnetic force and thermal stress are loaded in the components as a result of instability of plasma such as disruption. We reported the differences in the irradiation hardening of W-Re and W-Os alloys, due to irradiation induced precipitation.⁹⁾ In order to investigate the influence of the irradiation condition on irradiation hardening and microstructure development in pure W and W-xRe alloys, hardness and microstructures have been evaluated after the neutron irradiation. Especially, this work is focusing on irradiation temperature effects.

2. Experimental Procedure

In order to simulate composition changes due to nuclear transmutation by neutron irradiation, W-xRe ($x = 0, 5, 10, 26$) model alloys were fabricated. The model alloy fabrications were carried out using an argon arc furnace. The raw materials were pure W (99.96%) and W-26Re (W: 74.0 ± 0.2%, Re: 26.0 ± 0.2%) rods supplied by Plansee Ltd. Interstitial impurity levels of the fabricated alloys were in the range of 40–200 wppm for carbon (C), 20–40 wppm for oxygen (O), and <12 wppm for nitrogen (N). Disk-shaped specimens with a diameter of 3 mm and a thickness of 0.3 mm were cut from the ingots using an electro discharge machine. The disks were mechanically ground and polished to a thickness of 0.2 mm, and finally annealed at 1400°C for 1 h in a vacuum (<10⁻⁵ Pa) prior to the neutron irradiation.¹⁰⁾

Neutron irradiation was performed in a fast test reactor, JOYO, at the Japan Atomic Energy Agency (JAEA). The irradiation conditions are shown in Table 1. Displacement damage (dpa) was calculated using the NPRIM-1.3 code¹¹⁾ with a displacement threshold energy of 90 eV.¹²⁾ In this calculation, fluence of 8 × 10²⁵ n/m² ($E_n > 0.1$ MeV) corresponds to 1 dpa approximately. The nuclear transmutation by neutron capture reaction is mainly caused by a low energy neutron ($E_n < 1$ keV). Greenwood *et al.* calculated the composition change due to transmutation during irradiation in another fast reactor.¹³⁾ According to the results, the transmutation of W to Re is negligibly small, even after 1.54 dpa irradiation in JOYO, because after the irradiation,

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Table 1 The neutron irradiation conditions in JOYO.

Capsule	Irrad. Temp. [°C]	Fluence* [$\times 10^{25}$ n/m ²]	dpa**
JNC-60	400	1.3	0.17
JNC-50	500	2.9	0.37
JNC-61	740	3.1	0.40
JNC-63	538	7.8	0.96
JNC-54	750	12.0	1.54

* $E_n > 0.1$ MeV, **1 dpa = 8×10^{25} n/m² ($E_n > 0.1$ MeV, $E_d = 90$ eV)

micro Vickers hardness (H_v) tests were carried out 5 times for each specimen, using MM-2 micro hardness tester produced by Taiyo Tester Ltd., with a load of 1.98N. Irradiation hardening (ΔH_v) was defined as the difference between the H_v of both before and after the irradiation. Microstructural observations were carried out with JEM-2000FX and JEM-2010 transmission electron microscopes (TEM) operating at 200kV. Thin foil specimens for the observations were prepared by electro-polishing with a 2 mass% NaOH solution using a twin-jet polishing machine operating at room temperature and 25–30 V. The thickness of the observed foil specimens were estimated with the thickness fringe method at $g = 110$ diffraction conditions for measurements of the number density of irradiation damage clusters such as voids, loops, and precipitates.

3. Results and Discussion

3.1 Irradiation hardening

Figure 1 shows the irradiation hardening of the specimens irradiated at various temperature conditions as a function of dpa. Comparing the pure W and W-Re alloys, the irradiation hardening behaviors of W-Re alloys were more sensitive to irradiation temperature than those of pure W. The absolute irradiation hardening of pure W was small and did not increase drastically with dpa.

In the case of irradiation at around 750°C, the irradiation hardening of W-26Re was larger than those of other alloys over at 0.4 dpa. The irradiation hardening increment of W-10Re was larger than those of the others from 0.4 to 1.5 dpa. This means that the threshold displacement damage level of the irradiation hardening exists, and it depends on the Re concentration. This threshold may be connected with the microstructure developing behavior, that is, switching over from the nucleation state to the growing state in precipitation.

In the case of irradiation at around 500°C, the irradiation hardening of W and W-Re alloys were about H_v 200, and the difference among these alloys was not significant at 0.4 dpa. The irradiation hardening of these alloys increased from 0.4 to 1.0 dpa, and the increments were much larger than those in the cases of around 750°C. Especially, the increments of W-Re alloys were very large, and that of W-26Re was over H_v 800. This means that the threshold displacement damage level at around 500°C, must be between 0.4 and 1.0 dpa. The hardening ratio “ ΔH_v per dpa” was much larger than that in the case of irradiation at around 750°C. Furthermore, the hardening ratio depended on Re concentration.

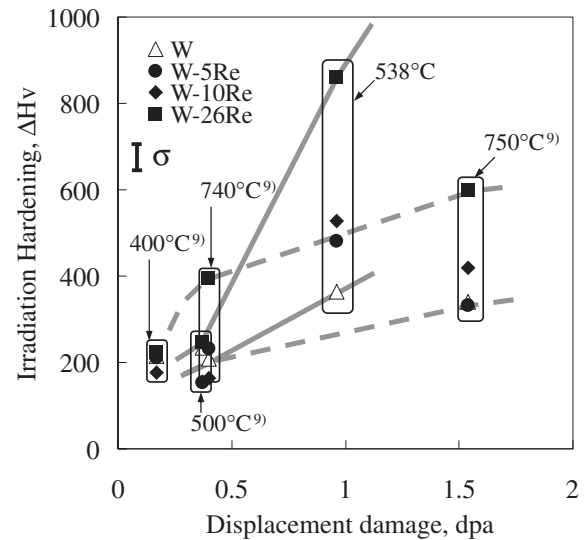


Fig. 1 Irradiation hardening of W-Re alloys irradiated in JOYO at several conditions. The solid lines indicate the trend of irradiation hardening at around 500°C. The dotted lines indicate the trend of irradiation hardening at around 750°C. The upper line is W-26Re, and the lower line is pure W, in both cases.

3.2 Microstructural observations

3.2.1 Pure W

Figure 2 shows the results of microstructural observations in W irradiated to 0.17–1.54 dpa at 400–750°C. In the specimen irradiated to 0.17 dpa at 400°C, fine and dense voids were observed. Dislocation loops were also observed and the geometric distribution was not uniform. In the specimen irradiated to 0.96 dpa at 538°C. Fine and relatively larger voids were observed. The minimum diameter of visible void was approximately 1 nm, and the observed maximum void diameter was about 6 nm. Dislocation loops were also observed. The mean diameter of loops was larger than that of those observed in the specimen irradiated to 0.17 dpa at 400°C. In the specimen irradiated to 0.40 dpa at 740°C, voids were observed. However, fine voids were barely observed and the minimum diameter of visible voids was about 2 nm. Dislocation loops were also observed, but the number density was much smaller than those irradiated at 400 and 538°C. In the specimen irradiated to 1.54 dpa at 750°C, large voids and a void lattice had been observed, and the diameters of the voids were in the range of 2–9 nm. The details were explained in a previous report.⁹⁾

Figure 3 shows the void size distribution of pure W observed in this work. The size distribution in the specimen irradiated to 0.17 dpa at 400°C was very narrow, and the average diameter and the number density were 1.8 nm and $1.9 \times 10^{23}/\text{m}^3$. The size distribution in the specimen irradiated to 0.40 dpa at 740°C was also narrow, and the average diameter and the number density were 2.9 nm and $1.3 \times 10^{23}/\text{m}^3$. The size distribution in the specimen irradiated to 1.54 dpa at 750°C was broad and in symmetry, and the average diameter and the number density were 4.7 nm and $1.2 \times 10^{23}/\text{m}^3$. These distributions suggest the behavior as follows. The void nucleation was dominant, and a number of fine voids were formed though the growth barely occurred at 400°C. Formed voids grew at 740°C above 0.40 dpa, and the

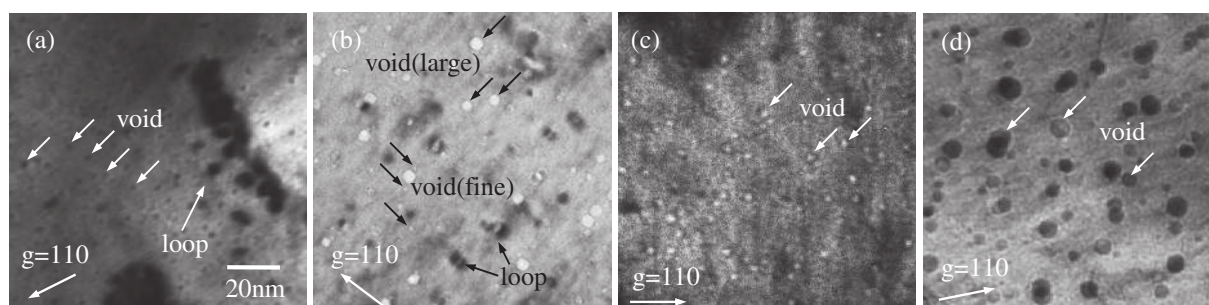


Fig. 2 Microstructural observations of pure W irradiated to (a) 0.17 dpa at 400°C, (b) 0.96 dpa at 538°C, (c) 0.40 dpa at 740°C and (d) 1.54 dpa at 750°C. The void images in (a) and (d) are black, because these were taken in an “over focused” condition.

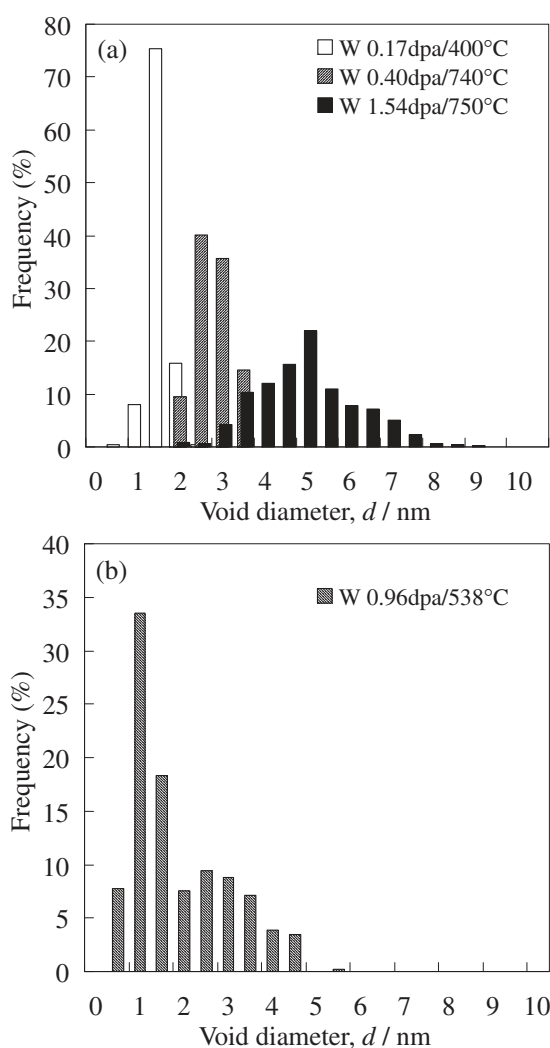


Fig. 3 The size distributions of voids in W after irradiation at (a) 400°C, 740°C, 750°C, and (b) 538°C. The distribution after irradiation at 538°C had a shape between those at 400°C and 740°C.

damaged structure tended to be stable at 1.54 dpa or higher because a void lattice was observed.

In the case of specimen irradiated to 0.96 dpa at 538°C, the distribution had a shape between those seen at 400°C and 740°C, and the average diameter and the number density were 2.1 nm and $4.9 \times 10^{23}/\text{m}^3$. More than half of the voids were smaller than 2 nm. Thus, most of the voids remained at the nucleation state. However, the largest diameter void at

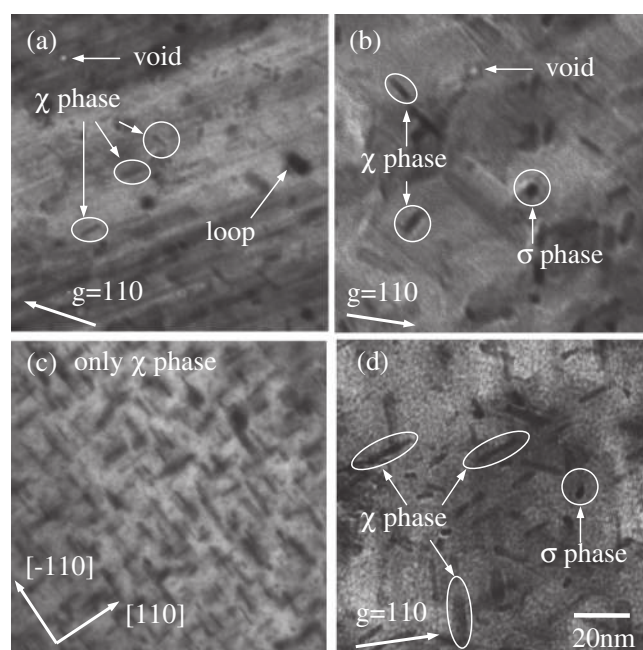


Fig. 4 Microstructural observations of (a) (b) W-5Re and (c) (d) W-10Re, irradiated to (a) (c) 0.96 dpa at 538°C and (b) (d) 1.54 dpa at 750°C. Plate-like precipitates were along {110} planes.

this irradiation condition was larger than that observed in the specimen irradiated to 0.40 dpa at 740°C. Consequently, it is considered that void nucleation is dominant, and that some voids can grow under irradiation at 538°C. Moteff *et al.* reported that di-vacancy recovered at 532°C, and tri-vacancy recovered at 715°C in annealing of pure W irradiated at 70°C.¹⁴⁾ Thus, vacancy mobility is considered to start to increase at temperatures over 530°C. In around this temperature, void nucleation frequently occurred, and most of the voids maintained as formed, and some of them grow due to the mobile vacancy. This seemed to be the cause of large irradiation hardening of pure W at 538°C.

3.2.2 W-xRe Alloys

Figure 4 shows the microstructures of W-5Re and W-10Re alloys irradiated to 0.96 dpa and 1.54 dpa, at 538°C and 750°C, respectively. Needle or plate-like irradiation induced precipitates (χ phase) were formed on {110} planes. The number densities of dislocation loops and voids were much lower than those in irradiated pure W. Especially, any void was not observed and very fine and dense precipitates were

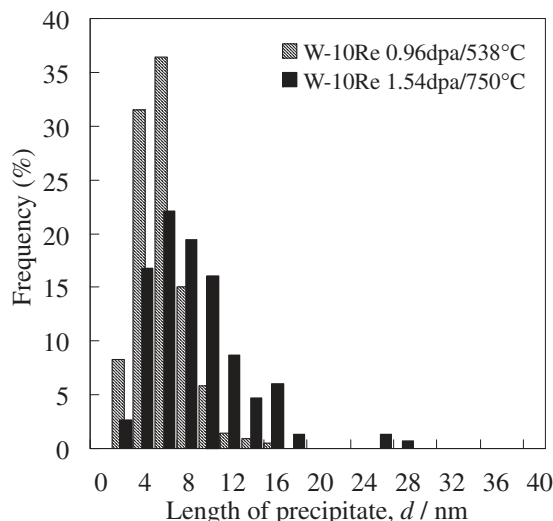


Fig. 5 The size distributions of precipitates in W-10Re after the irradiations at 538°C and 750°C. The distribution after irradiation at 538°C was relatively symmetrical, but that at 750°C was spread out longer.

observed in W-10Re irradiated to 0.96 dpa at 538°C. Small black spherical images were also observed in specimens irradiated to 1.54 dpa at 750°C. According to a previous report, the image seemed to be σ phase precipitates.⁸⁾

Figure 5 shows the length distribution of the χ phase precipitates observed in W-10Re irradiated to 0.96 dpa and 1.54 dpa at 538°C and 750°C. The length of the precipitates in the specimen irradiated at 538°C ranged from 2–18 nm, but most of the precipitates had a length less than 10 nm. On the other hand, the length distribution of precipitates irradiated at 750°C was broader than that irradiated at 538°C, and ranged 2–28 nm, and the size distribution. The number densities of precipitates were $8.4 \times 10^{23}/\text{m}^3$ and $4.2 \times 10^{23}/\text{m}^3$ in specimens irradiated at 538°C and 750°C, respectively. This means that precipitate nucleation was dominant at 538°C, though not only nucleation but growth also occurred at 750°C.

It was predicted that the χ phase precipitation is stable below 1500°C, in a phase diagram based on calculations with Gibbs energy and formation enthalpy.^{15,16)} However the χ phase precipitate was not observed in the unirradiated W-26Re alloy annealed at 650°C for 1000 h in this work. Furthermore, χ phase precipitation in the aged W-Re alloys containing up to 26% Re have not been reported. The χ phase precipitation has been observed in only the irradiated W-Re alloys. Thus, it is considered that Re cannot be segregated because of its slow diffusion rate, though the χ phase precipitation can occur in term of free energy. Irradiation should enhance the diffusion rate of Re and induce the χ phase precipitation.

The χ phase precipitates were observed in all of the W-xRe alloys irradiated at several conditions.^{9,17,18)} The precipitates in the specimens irradiated at 538°C were fine and dense, compared with other irradiation conditions. Williams *et al.* reported that interstitial-solute complexes (dumbbell) is very effective for solute enrichment at sinks. Especially for undersized solutes such as Re in W are bound strongly to self-interstitial atom (SIA). The Re-W dumbbell should

decrease the mobility of the SIA, and increase the probability of recombination of vacancy and interstitial. As a result, void formation will be suppressed in W-Re alloys.⁷⁾

Herchitz *et al.* observed Re depletion in the vicinity of precipitates in W-25Re irradiated in EBR-II at 575°C, 625°C, and 675°C, the maximum fluence was $4 \times 10^{26} \text{ n/m}^2$ ($E_n > 0.1 \text{ MeV}$).¹⁷⁾ When the irradiation temperature was high enough to move solute Re, Re could be supplied to the depletion region from the matrix, and precipitates could grow. In this case, the dragging field was considered to be broad, that is, large coarse precipitates formed and grew. On the other hand, when the irradiation temperature was not high enough to drag the solute Re to the depletion zone, precipitates could not grow. In this case, the dragging was considered to be local so that fine and dense precipitates could nucleate. It is considered that the irradiation at 750°C was the former case, and the irradiation at 538°C was the latter case.

The migration and recombination of the defects depend on the diffusion rate of SIA and vacancy. The results obtained in this work agree with the effect of the irradiation temperature. The cause of the fine and dense precipitates in the W-Re alloys irradiated at 538°C was proved to be the low diffusion rate of irradiation defects and solute Re. If the irradiation temperature is higher such as 750°C, the diffusion rate is high enough, and the coarse precipitates are formed because of the segregation of Re.

3.3 Hardening mechanism

Irradiation hardening (ΔH_v) in Vickers hardness was calculated with the mean size (d) of defect cluster, and its number density (N). The estimations based on the follow equation summarized by Moteff *et al.*,¹⁹⁾ where α is a constant depending on the irradiated alloy and defect cluster type, μ is the shear modulus, and b is the Burgers vector.

$$\Delta H_v = 6\alpha\mu b(Nd)^{1/2} \quad (1)$$

The μ and b of W are 151 GPa and 0.2741 nm, respectively.¹⁹⁾ The $\alpha_1 = 0.02$ for the dislocation loop was referred to in a previous report.²⁰⁾ The $\alpha_v = 0.06$ and $\alpha_p = 0.027$ for the void and the precipitate were fixed by comparing the estimated values with measured irradiation hardening.

Table 2 shows the number density and the mean size of each induced defect cluster observed in some specimens. The irradiation hardening calculated by eq. (1) and the measured irradiation hardening in this work are also shown. In cases of the W-10Re irradiated to 1.54 dpa at 750°C, and pure W irradiated to 0.96 dpa at 538°C, the sums of the calculated irradiation hardenings were much larger than the measured ones. Moteff *et al.* applied the calculations to the void, which have a diameter in the range of 3–4 nm. Generally, a moving dislocation can be trapped at a trapping site that has a size of a few nanometers. If the trapping site was smaller than the necessary size (1–2 nm), the site could not contribute to the irradiation hardening effectively. In the two cases mentioned above, the mean sizes of the voids were 1.6 nm and 2.1 nm, so that most of the voids could not contribute to the irradiation hardening. On the other hand, the smallest void size in pure W irradiated to 1.54 dpa at 750°C was 2 nm, so that most of the voids could contribute to the irradiation hardening.

Table 2 The number density and size of irradiation induced defect clusters. ΔH_v (Calc.) and ΔH_v (Meas.) are the irradiation hardenings obtained by calculations based on microstructure and by measurement.

			N [10 ²² /m ³]	d [nm]	$(Nd)^{1/2}$ [10 ⁶ /m]	ΔH_v (Calc.)	ΔH_v (Meas.)
1.54 dpa	W	Void	12.0	4.7	23.8	355	341
750°C	W-10Re	Void	3.1	1.6	7.0	104	419
		Prec.	41.7	9.5	62.9	422	
0.96 dpa	W	Void	48.7	2.1	32.1	478	363
		Loop	4.7	4.7	14.9	74	
538°C	W-10Re	Loop	<0.2	~5	<2	<10	528
		Prec.	83.7	6.8	75.6	507	

Though shearing resistance due to the cutting of small voids might be a contribution, the influence was not confirmed in this work and did not seem to be major. Equation (1) can actually calculate the irradiation hardening due to precipitates with $\alpha_p = 0.027$. Consequently, the calculations were evidence that the large irradiation hardening of W-xRe alloys irradiated at 538°C was caused by fine and dense irradiation induced precipitates.

4. Summary

In order to investigate the influence of irradiation conditions on irradiation hardening and the microstructure development in pure W and W-xRe alloys, these alloys were irradiated in JOYO, and hardness tests and microstructural observations were carried out. Finally, it was concluded that irradiation temperatures could cause characteristic behaviors. The details of the results obtained in this work are as follows:

(1) Irradiation hardenings of W-xRe alloys show irradiation temperature dependence. The irradiation hardening increased slowly with dpa at 750°C. At around 500°C, the irradiation hardening increased rapidly from 0.4 dpa to 1.0 dpa, and the increment was strongly dependent upon the Re concentration.

(2) The number density of voids in pure W irradiated to 0.96 dpa at 538°C was the largest among all of the irradiation conditions in this study. A part of voids grew at this irradiation condition. The feature of void formation and growth correspond to the vacancy mobility that increased above approximately 530°C with the increasing temperature. Dislocation loops were not major defect clusters in this study.

(3) Fine and dense precipitates (χ phase) were observed in W-10Re irradiated to 0.96 dpa at 538°C. The same precipitates were also observed in W-10Re irradiated to 1.54 dpa at 750°C, though those were coarse and the number density was smaller. These behaviors seemed to correspond to the

mobility of vacancy and interstitial, depending on the irradiation temperature.

(4) Irradiation hardening calculations showed that small voids, such as those with a diameter less than 2 nm, did not practically contribute to the irradiation hardening. The calculations proved that the large irradiation hardening of W-Re alloys irradiated at 538°C was due to precipitation behavior.

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