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Damage evolution in neutron-irradiated Cu during neutron irradiation

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Abstract

We fabricate Cu of residual-gas-free by melting them in vacuum of 10^{-5} Pa. Both residual-gas-free specimen and as-received specimens which were estimated to contain 4 ppm hydrogen atoms were neutron-irradiated at 200°C and 300°C with temperature-controlled rig in Japan Material Testing Reactor (JMTR). Neutron fluence ranges from 5.3×10^{18} to 1.0×10^{20} n/cm^2. Irradiated specimens were observed by electron microscopy. In copper, both stacking fault tetrahedron (SFT) and voids were observed. The number density of voids decreased with increasing the fluence. The size of voids increased with the fluence. The voids formed uniformly in specimens at the low fluence, while some of voids were observed near dislocations at the high fluence. The number density of SFT increased with the fluence at 200°C. The number of vacancies which are accumulated in a void is 350 times larger than that in a SFT in a specimen irradiated to 5.3×10^{18} n/cm^2 at 200°C. At low fluence the number density of voids is same for as-received specimens and residual-gas-free specimens. The difference of the number density of voids between these two specimens was observed at high fluence in which the density is low in the residual-gas-free copper. Results are modeled as follows. Small vacancy clusters move during an irradiation. Voids nucleate when the coalescence of small vacancy clusters occurs. The mobility of voids with gas atoms is lower than that without gas-atom. This causes the number density of voids in as-received copper to be larger than that in residual-gas-free copper.

1. Introduction

Voids are representative vacancy clusters in neutron-irradiated metals at high temperature. Voids cause significant swelling and degrade the mechanical property. The preferential formation of voids was explained previously by the dislocation bias with which interstitial atoms are absorbed by dislocations due to their high mobility [1,2]. A considerable amount of experimental studies have been reported in low dose neutron irradiated fcc metals [3,4]. It pointed out these results cannnot be relationalized in terms of conventional mean-field approach and dislocation bias as the only driving force. At high temperature, small vacancy clusters break thermally into freely migrating vacancy. Some of voids grow to a large void by absorbing freely migrating vacancy. Voids are thought to nucleate in small vacancy clusters which trap gas atoms. Helium atoms are believed to be the most important gas atom [5]. The effects of gas atoms such as hydrogen and helium on the void formation was examined in ion- or electron-irradiated Cu and Ni by Lanore et al. they concluded that gas is necessary for void formation [6]. Zinkle et al. concluded the important role of oxygen and helium on the void formation in copper. Oxygen atoms are predicted to stabilize void formation and helium also tends to stabilize void formation [7]. In fission neutron irradiation experiments at the JMTR (Japan Material Testing Reactor) and FFTF reactors by the present authors [8,9], it was recognized that residual gaseous atoms (mainly hydrogen atoms) play an important role in the formation of voids. We reported that the number density of voids formed in neutron-irradiated copper decreased when residual gas atom were removed in pure Cu and Cu–Al alloy [10,11].

The present work is carried out to examine the evolution of point defect clusters in neutron-irradiated copper at elevated temperatures. To examine precisely,

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the irradiation was carried out at the temperature controlled irradiation facility in the JMTR reactor [12–15]. The temperature of specimens were controlled to the pre-set temperature during a neutron irradiation including the start-up and shut down period of the reactor power. The temperature was set to be 200°C and 300°C. We discuss on the relationship of damage structure and residual gas atoms in pure copper.

2. Experimental procedures

The copper of 99.9999% nominal purity supplied by Dowa Ministry Ltd. was used as as-received copper. To reduce gas atoms dissolved in specimens, copper of 10 g was melted in high vacuum of 10^{-5} Pa. Copper was melted on alumina Al_2O_3. The resistivity ratio $R_{300\,K}/R_{4.2\,K}$ of as-received copper and residual-gas-free copper were 300 and 100, respectively. Small amount of aluminum atom is picked up from alumina because aluminum peak was detected on the PIXE spectrum of remelted specimen. The concentration of aluminum atom in remelted copper was estimated to be below 10 ppm. Both kinds of specimens were cold-rolled to 0.1 mm and punched out to disks of 3mm in diameter, and annealed in vacuum at 700°C for 5 h. Specimens were sealed in aluminum capsule which was evacuated to 10^{-3} Pa. Neutron irradiation was carried out in the temperature-controlled capsule 94M-15u at JMTR reactor [14,15]. Temperature was controlled within ±10°C during a period that a reactor power is on. A capsule could be pulled out from the irradiation position at the intermediate time. Neutron irradiation was performed at 200°C and 300°C. The irradiation condition at JMTR 94M-15u were summarized in Table 1. Neutron flux (E > 1 MeV) was constant at each temperature. After a radiation cooling, specimens were thinned by electropolishing and observed by an electron-microscope JEM-2000EX operated at 200 kV. The specimen thickness was estimated by an equal-thickness contour line. Voids were observed by so-called void contrast and SFT were observed by weak beam images from [1 1 0] direction.

3. Experimental results

As reported previously by the present authors, interstitial clusters form their grouping which evolve to tangled dislocations. Interstitial clusters which form at displacement cascades are accumulated at dislocations by strain sensitive migration of interstitial clusters [16]. In copper interstitial clusters relax to a bundle of parallel ⟨1 1 0⟩ crowdions which moves with small migration energy of 0.001 eV. In area apart from tangled dislocation, vacancy clusters of SFT and voids uniformly form. Voids in pure Cu which were irradiated at 200°C and 300°C are shown in Fig. 1, where (a) and (c) show defects at low fluence and (b) and (d) show defects at high fluence at 200°C and 300°C, respectively. At both temperature irradiation, the number density of voids decreased with increasing the fluence, and the size of voids increased with the fluence. Voids were formed uniformly in the 200°C irradiation. On the other hands, some of voids were observed along dislocations in the 300°C irradiated copper. Fig. 3(a) and (b) shows the number density of voids and void swelling versus neutron fluence. The number density of voids is almost the same between the as-received specimen and the residual-gas-free specimen which were irradiated to the low fluence. The difference of the number density of voids between these two specimens increases with the fluence. The number density, the mean size and the swelling due to void formation are summarized in Table 2.

Weak beam images of SFT in as-received pure copper irradiated at 200°C and 300°C are shown in Fig. 2. At 300°C irradiation, the number density of SFT decreased with increasing of the fluence, while the number density of SFT increased with the fluence at the 200°C irradiation. At 200°C irradiation, size of SFT did not change with increasing of the fluence. Furthermore the number density of SFT were same for as-received and residual-gas-free copper as shown in Fig. 3(c). The number density and the mean size of SFT are summarized in Table 3.

In order to examine thermal stability of voids and SFT, annealing experiment of TEM thin foil was carried out. The specimen was pure copper irradiated to 5.3×10^{18} n/cm^2 at 200°C. Annealing temperature was 250°C, 300°C, 350°C, 400°C and 500°C. Fig. 4 shows defects which were observed by a weak beam image. In this area four voids were observed. During an annealing at 250°C for 70 min, SFT did not change their size and position as shown in Fig. 4(a) and (b). Voids moved slightly keeping their size as indicated with a black arrow in Fig. 4(b). After an annealing at 350°C for 30 min, all voids and smaller SFT disappeared. SFT did not shrink before disappearance.

Table 1
The irradiation condition of JMTR were summarized. Neutron flux was constant at each temperature (E > 1 MeV). Damage rate was 5.0×10^{-8} and 6.5×10^{-8} dpa/s of 200°C and 300°C irradiation, respectively

Irradiation time (h)	40.5	188.0	591.5
200°C fluence (n/cm^2) dose level (dpa)	5.3×10^{18}, 7.3×10^{-3}	2.5×10^{19}, 3.4×10^{-2}	7.7×10^{19}, 1.1×10^{-1}
300°C fluence (n/cm^2) dose level (dpa)	7.1×10^{18}, 9.8×10^{-3}	3.3×10^{19}, 4.6×10^{-2}	1.0×10^{20}, 1.4×10^{-1}

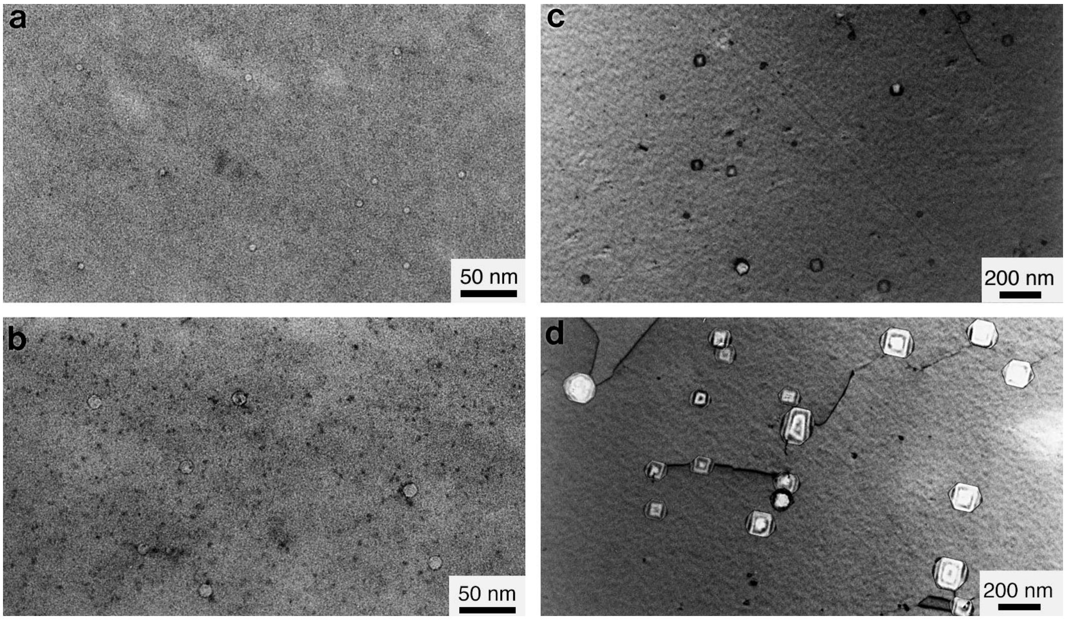

Fig. 1. Evolution of void structure with increasing the fluence at 200°C and 300°C for as-received pure copper. The number density of voids decreased with increasing of the fluence at both temperature. Void contrast images are shown irradiated at 200°C (a) 7.3×10^{-3} and (b) 1.1×10^{-1} dpa, irradiated at 300°C (c) 9.8×10^{-3} and (d) 1.4×10^{-1} dpa, respectively.

4. Discussion

There are many aspects to be discussed more closely based on the present experimental results. The first one is why the number of vacancy to be accumulated in a void is large comparing to that of SFT. The ratio of vacancy number which composes a void and an SFT is 350 for the irradiation of 5.3×10^{18} n/cm^2 at 200°C and 1300 for the irradiation of 1×10^{20} n/cm^2 at 200°C. The number density of SFT increases with the fluence and

Table 2
The number density (Nv), mean size (dv) and swelling of voids

Temperature dose (dpa) specimen	Nv (cm^{-3})	dv (nm)	Swelling (%)
200°C 0.0073			
Cu	4.0×10^{14}	7.2	7.8×10^{-3}
Cu(RGF)	2.6×10^{14}	7.1	4.9×10^{-3}
200°C 0.034			
Cu	3.1×10^{14}	10.1	1.7×10^{-2}
Cu(RGF)	2.3×10^{14}	11.4	1.8×10^{-2}
200°C 0.110			
Cu	2.2×10^{14}	11.7	1.9×10^{-2}
Cu(RGF)	9.7×10^{13}	11.5	7.7×10^{-3}
300°C 0.0098			
Cu	6.8×10^{12}	47.5	3.8×10^{-2}
Cu(RGF)	6.0×10^{12}	33.4	1.2×10^{-2}
300°C 0.046			
Cu	3.4×10^{12}	78.4	8.6×10^{-2}
Cu(RGF)	2.3×10^{12}	72.2	4.6×10^{-2}
300°C 0.140			
Cu	1.4×10^{12}	155	2.8×10^{-1}
Cu(RGF)	0.9×10^{12}	155	1.7×10^{-1}

RGF means residual-gas-free specimen.

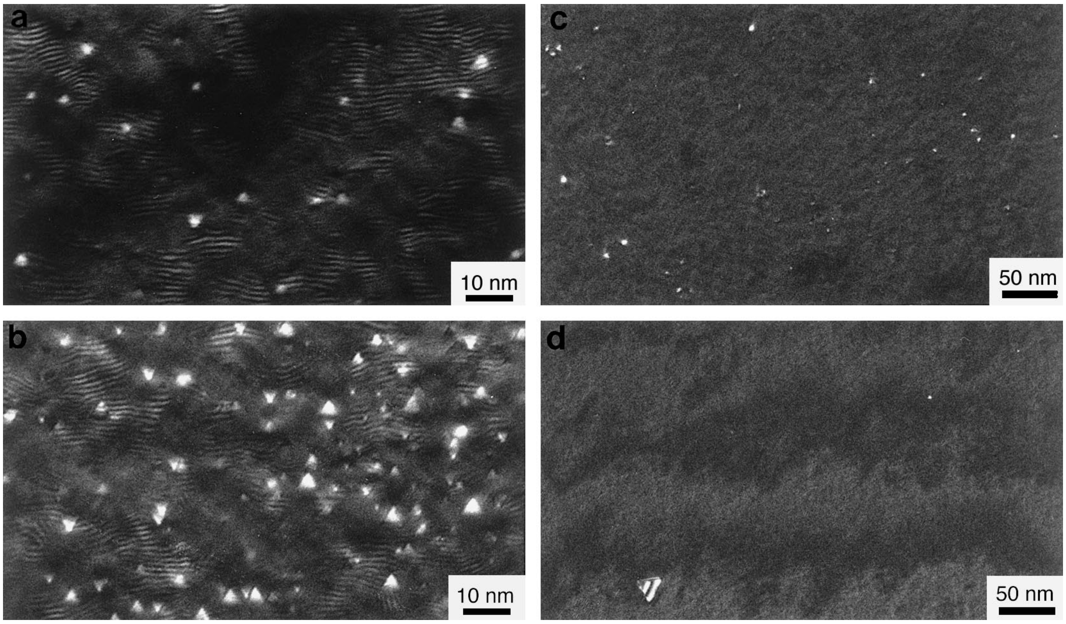

Fig. 2. Evolution of SFT structure with increasing of the fluence at 200°C and 300°C for pure copper. The number density of SFT increased with increasing of the fluence irradiated at 200°C (a) 7.3×10^{-3} and (b) 1.1×10^{-1} dpa. The mean size of SFT was about 3 nm, it did not depend on the fluence. However the number density of SFT decreased with increasing of the fluence irradiated at 300°C (c) 9.8×10^{-3} and (d) 1.4×10^{-1} dpa, respectively.

the size of SFT did not change much for the both irradiation at 200°C. This suggests that the growth of void occurs by the coalescence of vacancy clusters. If vacancy clusters grow by absorbing freely migrating single vacancy which were generated at cascade damage, voids and SFT grew with almost the same number of vacancies. The second result to be discussed is why the number density of voids decrease with the fluence in irradiated copper at 200°C. It is generally assumed that voids nucleate at vacancy clusters which are formed at the cascade core. In this case the number of voids should increase slowly with the fluence. And finally the number density of voids reach a constant due to a balance of generation and disappearance of voids. The present results show that the number density of voids in irradiated copper to 5.3×10^{18} n/cm^2 is larger than that in that to 1.0×10^{20}n/cm^2 at 200°C. We take a standpoint in which a formation of void nucleus was easy in copper which are irradiated to 5.3×10^{18} n/cm^2 and a formation rate of void nucleus become small in irradiated copper to 1.0×10^{20} n/cm^2. At present we can not propose the atomistic process of void nucleation. The present experiment suggests that voids are nucleated with no relation of gas atoms which are trapped in vacancy clusters. One possibility of void nucleation is that at the coalescence of several vacancy cluster in copper at 200°C vacancy clusters relax to a void rather than form a SFT. It is shown by the computer calculation that the formation energy of a SFT is small than that of a void. This suggests that voids can nucleate as a metastable vacancy cluster only at high temperature. Voids move as shown in thin foil annealing experiment. The movement is not due to Brownian motion as discussed frequently but strain field sensitive motion. The thin foil annealing experiment show that a SFT disappear thermally at 300°C. It is noted that a SFT break and disappear without showing the shrinking of the size. In copper irradiated at 300°C, SFT is nucleated by accumulating vacancies at the core of cascade damage in low fluence regime. The nucleation of SFT is not so significant at high fluence regime. This is due to the increase of dislocation density.

5. Conclusion

1. In pure copper, the number density of voids decreased with increasing the fluence, and the size of voids increased with the fluence at 200°C and 300°C irradiation. SFT could grow and the number density was decreased with increasing the fluence during 300°C.
2. The number of vacancies which aggregate to a void is much larger than that to a SFT. The difference increases with the neutron fluence and the irradiation temperature.
3. An annealing experiment of TEM thin foil suggests that thermal stability of SFT is larger than that of

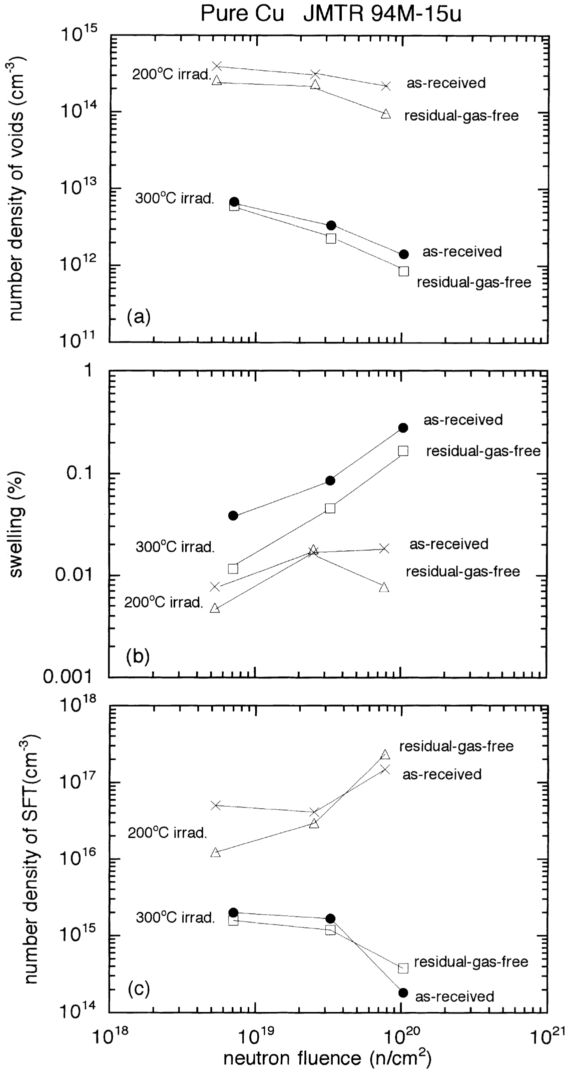

Fig. 3. The number density of void, the swelling and the number density of SFT versus neutron fluence was plotted for pure copper irradiated at 200°C and 300°C.

voids in copper. Void can move at above 250°C. SFT disappear at 300°C without showing decreasing their size.

4. The number density of voids is almost same in between as-received and residual-gas-free copper which were irradiated to the low fluence. The difference of the number density of voids between these two specimens increases with increasing of the fluence.

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Table 3
The number density (*Ns*) and mean size (*ds*) of SFT

Temperature dose (dpa) specimen	*Ns* (cm^{-3})	*ds* (nm)
200°C 0.0073		
Cu	5.1×10^{16}	2.7
Cu(RGF)	1.2×10^{16}	3.4
200°C 0.034		
Cu	4.2×10^{16}	3.1
Cu(RGF)	3.0×10^{16}	4.0
200°C 0.110		
Cu	1.5×10^{17}	2.7
Cu(RGF)	2.3×10^{17}	2.9
300°C 0.0098		
Cu	2.0×10^{15}	5.3
Cu(RGF)	1.6×10^{15}	4.8
300°C 0.046		
Cu	1.7×10^{15}	4.5
Cu(RGF)	1.2×10^{15}	5.5
300°C 0.140		
Cu	1.9×10^{14}	6.5
Cu(RGF)	3.8×10^{14}	6.0

RGF means residual-gas-free specimen.

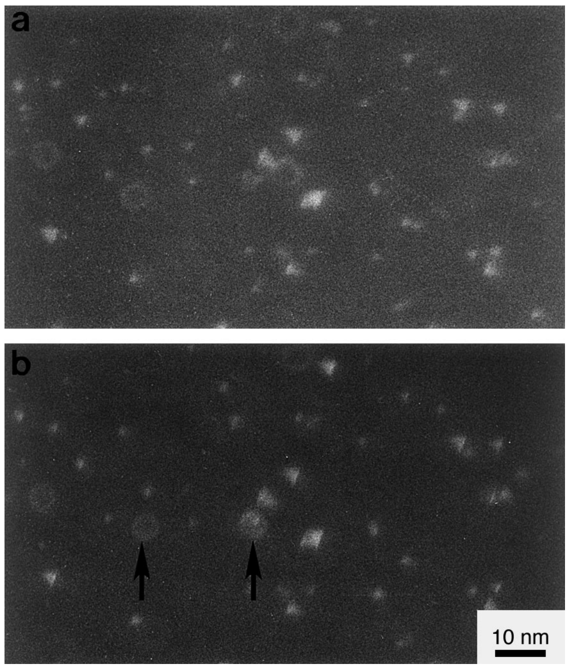

Fig. 4. The specimen was as-recieved pure copper irradiated to 5.3×10^{18} n/cm^2 at 200°C. Movement of void at 250°C for 70 min, clearly the void indicated black arrow moved, and it was kept conserving their size as shown in (a) and (b).

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