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Voids in fast-neutron-irradiated Cu, Ni and Cu–Ni concentrated alloys studied by TEM and positron annihilation methods

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Abstract

The effect of concentrated Ni and Cu solute atoms in the Cu–Ni system on the formation of voids has been examined using Cu, Cu–8 at.% Ni, Ni–8 at.% Cu and Ni irradiated with fast-neutrons in the FFTF-MOTA. Both solute atoms introduced smaller voids in the grains of the concentrated alloys than voids in the normal grains of pure-Cu and pure-Ni. Slight increase of irradiation temperature and the higher dose of fast-neutrons induced coalescence of voids in the grains of Ni–8 at.% Cu, but it resulted in the abrupt decrease of the concentration of small voids in the grains and the formation of heterogeneously distributed larger voids near grain boundaries in Cu–8 at.% Ni. Heterogeneous distribution of larger voids was also observed in other materials. Annealing at higher temperatures induced segregation of impurity atoms at a void surface in Ni–8 at.% Cu.

1. Introduction

Recent results of transmutation calculation for Cu [1] showed that about 1 at.% Ni and about 0.5 at.% Zn would be produced in the first wall of a fusion reactor during one year operation. The results were experimentally supported [2], and the effect of Ni addition on the formation of voids in Cu alloys has been studied [3]. In the present study, we examined voids formed in Cu and Ni, and their concentrated alloys containing 8 at.% solute atoms. 8 at.% was chosen because one of the nearest neighbor atoms of a vacancy is statistically a solute atom ($1/12 = 0.083$) in the FCC lattice.

It is well known that a positron is very sensitive to the vacancy-type defects especially micro voids in metals [4,5]. Positron annihilation method cannot examine the local and heterogeneous distribution of voids which transmission electron microscope (TEM) can observe, but it can give us information of smaller voids that TEM hardly observe.

2. Experimental procedure

Starting materials were 5N Cu and 4N Ni purchased from Johnson Matthey Chemicals Ltd. Cu–8 at.% Ni and Ni–8 at.% Cu alloys were made by melting and mixing these Cu and Ni using a boron-nitride crucible in a vacuum of the order of 10^{-4} Pa. The sheet specimens of 0.25 mm in thickness were made by cold-rolling, and the disk specimens of 3 mm in diameter were punched out from the sheet specimens. The disks were annealed at 1125 K for Cu and Cu–8 at.% Ni, and at 1375 K for Ni and Ni–8 at.% Cu, for 6 h in a vacuum of the order of 10^{-4} Pa.

Specimens were irradiated with fast-neutrons at 683 K to 6 dpa in the FFTF-MOTA below-core and at 703 K to 26 dpa in the FFTF-MOTA level-4 during cycle-11. After irradiation and shipment to Japan, TEM observation was carried out. Positron annihilation Doppler-broadened line-shape measurements were made for Cu, Cu–8 at.% Ni and Ni–8 at.% Cu irradiated at 683 K to 6 dpa, using the same specimens observed by TEM. The isochronal annealing was performed in steps of 100 K and 1 h. The positron source was ^{65}Zn produced by the transmutation of Cu in the specimens during neutron-irradiation.

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3. Results

Fig. 1 shows the typical void structures observed by TEM in the normal grains of the specimens. These bright-field micrographs were imaged with $\boldsymbol{g} = 002$ and $(0, 6\boldsymbol{g})$ where $6\boldsymbol{g}$ satisfied Bragg condition. The size distribution of voids in Fig. 2 was measured using TEM images of voids in nearly the same area as shown in Fig. 1. In the specimens irradiated to 6 dpa, the average void diameter in the alloys was smaller than that in pure metals. Increase in neutron-dose and a slight increase of irradiation temperature resulted in the enlargement of void size in pure-Cu and Ni–8 at.% Cu. For Cu–8 at.% Ni, the size of voids was nearly the same in both irradiation conditions, but the concentration of voids became smaller in the specimen irradiated to higher dose and at slightly higher temperature.

The above results show a homogeneous distribution of voids, and the volume fractions of these regions are discussed in Section 4.1. There were, however, areas where heterogeneous distribution of voids was observed. Examples of these heterogeneous distributions are shown in Fig. 3. Fig. 3(a) shows the example observed in pure-Cu irradiated to 6 dpa at 683 K. The smaller voids of high density are the same kind of void discussed in the preceding paragraph. There is no void in the grain in the left part of the figure, and there are larger voids of about 500 nm in diameter in the right part of the figure. Fig. 3(b) shows larger voids along a grain boundary and smaller voids inside grains in pure-Cu irradiated to 26 dpa at 703 K. There was low concentration of very small voids in Cu–8 at.% Ni irradiated to 26 dpa at 703 K, but there were very large voids shown in Fig. 3(c) in the thicker part of the TEM specimen. These voids were arranged in chains as shown in Fig. 3(c), suggesting the formation of larger voids along grain boundaries. Fig. 3(d) shows a denuded zone of voids along a grain boundary in Ni–8 at.% Cu irradiated to 6 dpa at 683 K. The denuded zone was also observed in pure-Ni, and void-size was larger near the denuded zone than inside the grain.

Although the above results of a heterogeneous distribution of voids made it difficult to evaluate the swelling using TEM results, a rough estimation of the swelling was made and the results are shown in Table 1. For Cu–8 at.% Ni irradiated to 26 dpa at 703 K, the results include the swelling calculated from the values for heterogeneously distributed larger voids shown in Fig. 3(c). Dislocations were not distributed uniformly even in the same grain in pure-Cu irradiated to 6 dpa and Cu–8 at.% Ni irradiated to 6 and 24 dpa. Images of high density voids made it impossible to estimate dislocation density in Ni–8 at.% Cu irradiated to 26 dpa at 703 K. Because of these difficulties, dislocation densities

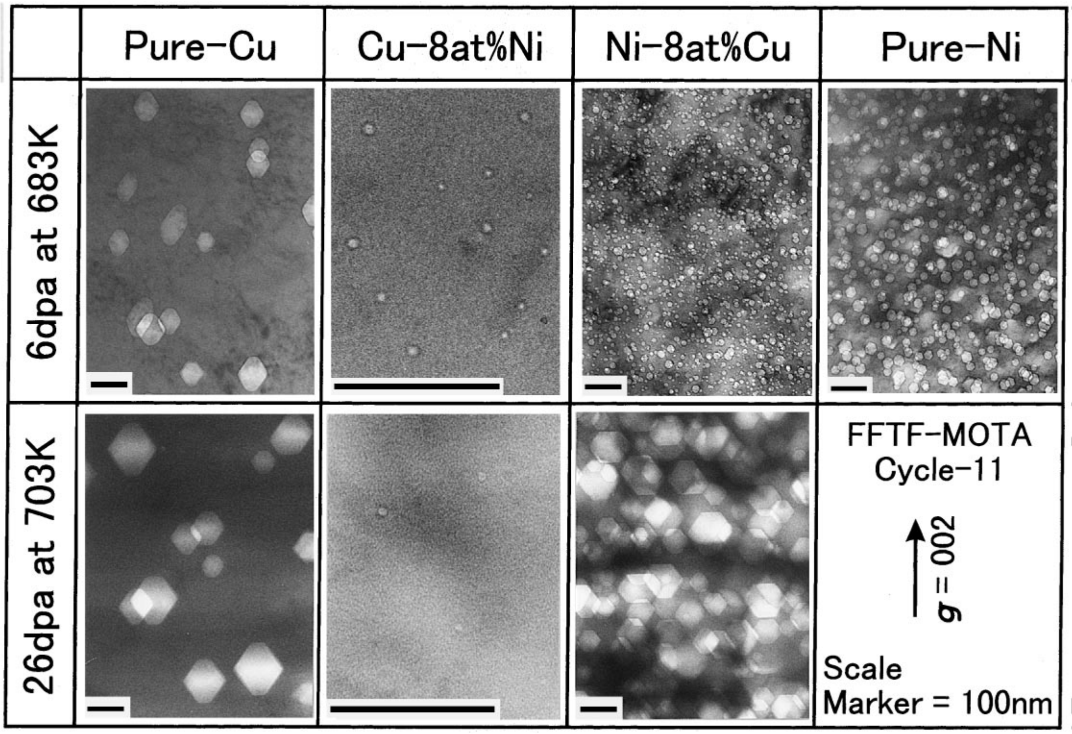

Fig. 1. Examples of TEM observed void images in the grain where voids were homogeneously distributed.

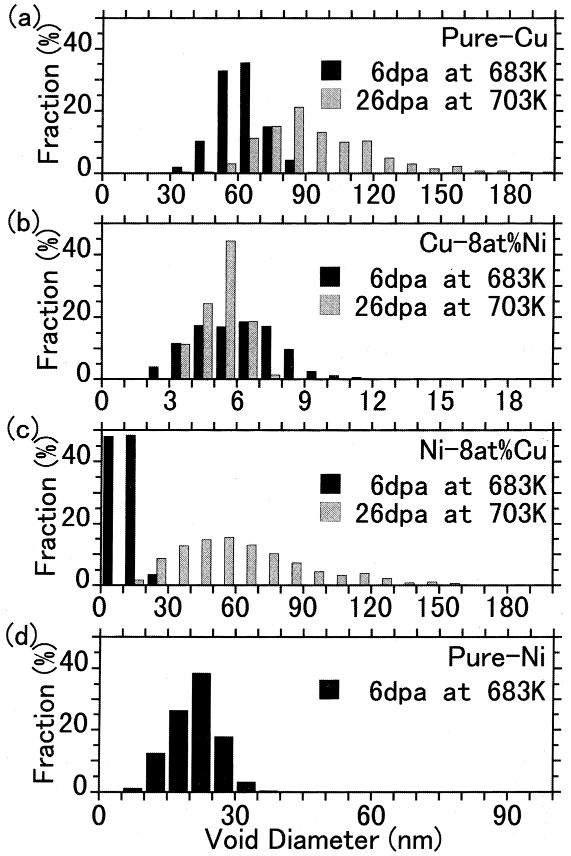

Fig. 2. Size distribution of voids in nearly the same areas as shown in Fig. 1.

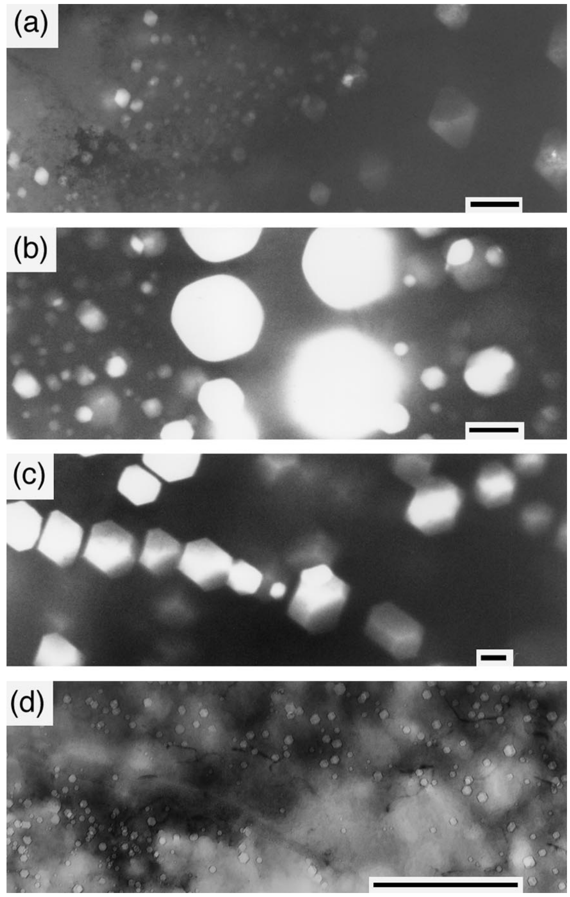

Fig. 3. Examples of the heterogeneously distributed voids in pure-Cu irradiated to (a) 6 dpa at 683 K and (b) 26 dpa at 703 K, (c) in Cu–8 at.% Ni irradiated to 26 dpa at 703 K, and (d) in Ni–8 at.% Cu irradiated to 6 dpa at 683 K. Scale-marker 500 nm.

in Table 1 have an experimental error of at least $\pm 2 \times 10^{13}$ m^{-2}. There was no strong evidence of an effect of alloying on dislocation density in the materials irradiated to 6 dpa at 683 K.

The results of the isochronal annealing investigated by positron annihilation method are shown in Fig. 4. The H-parameter is the ratio of the total counts of 8 channels around the peak to the total counts of 44 channels of the Doppler-broadened 511 keV photo-peak after subtraction of the background. The decrease of the H-parameter after annealing mainly corresponds to a decrease in the concentration of voids that are deep traps for positrons. After annealing at 750 K, 48% and 43% of the effect of trapped positrons were recovered in Cu–8 at.% Ni and Ni–8 at.% Cu irradiated at 683 K, respectively. This stage may correspond to the annihilation of smaller voids observed by TEM and growth of larger voids. These larger voids were annihilated after annealing between 1150 and 1250 K in Cu–8 at.% Ni and Ni–8 at.% Cu. The main annealing stage of voids in pure-Cu was seen between 950 and 1150 K. The anomalous increase of H-parameter for Ni–8 at.% Cu between 850 and 1150 K indicates the formation of para-positronium at a void surface [6], which is introduced by the change of a void surface due to segregation of impurity atoms.

4. Discussion

4.1. Homogeneously distributed smaller voids

The volume fractions of regions where voids are homogeneously distributed were about 70% in pure-Cu irradiated to 6 dpa, about 95% in Cu–8 at.% Ni irradiated to 6 dpa, and about 85% in other materials. The results derived from voids in these regions are significant for the effects of neutron-dose and alloying elements. Very small voids of less than 10 nm in diameter were

Table 1
The evaluated data of void swelling and dislocation-density by TEM observation for the specimens examined in the present study

		Average void-diameter (nm)	Void-density ($\times 10^{19}$ m^{-3})	Swelling (%)	Dislocation-density ($\times 10^{13}$ m^{-2})
Pure-Cu	6 dpa at 683 K	62	9	1.1	6
	26 dpa at 703 K	97	8	3.8	8
Cu–8 at.% Ni	6 dpa at 683 K	6	200	0.02	5
	26 dpa at 703 K	5	8	0.0006	11
		[a]851	[a]0.04	[a]13	
Ni–8 at.% Cu	6 dpa at 683 K	11	1400	1.0	4
	26 dpa at 703 K	63	75	9.7	–
Pure-Ni	6 dpa at 683 K	21	130	0.64	4

[a] Estimated by heterogeneously distributed larger voids shown in Fig. 3(c).

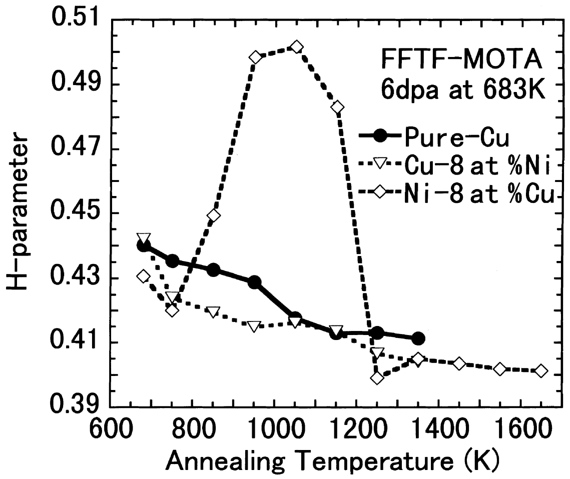

Fig. 4. The results of the isochronal annealing investigated by positron annihilation Doppler-broadened line-shape measurements.

formed in Cu–8 at.% Ni and Ni–8 at.% Cu irradiated to 6 dpa at 683 K. However, the concentration of these voids became very low in Cu–8 at.% Ni and these voids disappeared in Ni–8 at.% Cu irradiated to 26 dpa at 703 K. The results of positron annihilation also suggested the disappearance of these very small voids during the annealing at 750 K as discussed in the preceding section. Therefore, the stability of small voids of less than 10 nm in diameter is strongly dependent on the temperature in Cu–8 at.% Ni and Ni–8 at.% Cu between 683 and 703 K.

Increase in the neutron-dose resulted in the coalescence of voids and increased average void size and swelling for pure-Cu. The effect was more drastic in Ni–8 at.% Cu, since it contained high density of very small voids in the specimen irradiated to 6 dpa at 683 K and these voids were thermally not stable at 703 K as discussed above.

4.2. Heterogeneously distributed larger voids

Heterogeneous distribution of larger voids was mainly caused by the effect of grain boundaries that worked as efficient sinks of point defects. Therefore, we often found denuded zones of voids along grain boundaries like Fig. 3(d). In these regions, very large voids grew in the highly irradiated materials as shown in Fig. 3(b) and (c), which might suggest the biased sink efficiency of the grain boundary for interstitial atoms. These voids sometimes dominated the swelling and the properties of materials especially in Cu–8 at.% Ni irradiated to 26 dpa at 703 K. However, there were also grains that contained larger voids that were nearly 10 times as large as those in the normal grains in pure-Cu irradiated to 6 dpa at 683 K as shown in Fig. 3(a). There is no clear evidence of the effect of the morphology and density of dislocations on the difference in the evolution of these voids.

4.3. The effects of alloying

The addition of 8 at.% Ni in Cu stabilized very small voids. The results might suggest the strong binding between solute Ni atoms and vacancies and the increased number of nucleation sites of voids by solute Ni atoms. Vacancy-solute binding energies for Cu–Ni concentrated alloys were, however, estimated to be nearly zero according to the thermal equilibrium measurements of positron annihilation [7]. Nearly the same situation was found in Ni–8 at.% Cu. However, the slight increase of temperature and the higher dose of fast-neutrons drastically increased the average void diameters in the grain of Ni–8 at.% Cu, whereas the abrupt decrease in the density of small voids in the grain and the creation of larger voids near the grain boundaries were found in Cu–8 at.% Ni. Solute Cu atoms in Ni–8 at.% Cu stabilized the smaller voids, but the effect of solute Ni atoms in Cu–8 at.% Ni was different from the effects of solute Cu atoms.

4.4. Void surfaces

The result of the annealing experiments using positron annihilation showed the formation of positronium at voids in Ni–8 at.% Cu. Usually positronium is hardly formed at voids in metals, except in vanadium after annealing at high-temperatures where oxygen-impurity might segregate at a void surface [6]. In Ni annealed at 870 K, surface and grain boundary segregation of S was observed [8]. Segregation of other impurity atoms such as Sn and Sb were studied for Ni and Ni-based alloys [9]. Although the radiation induced segregation of Ni at voids in Cu–Ni alloys was reported [3], positron annihilation experiments did not show any effect of the radiation induced segregation. Equilibrium segregation of impurity atoms and co-segregation of impurity and gas atoms [10] at the surface might induce positronium state at a void surface in Ni–8 at.% Cu. Identification of the segregated impurity atoms was not possible in the present study.

5. Conclusions

1. Cu–Ni concentrated alloys containing 8 at.% solute atoms produced very small voids of less than 10 nm in diameter when they were irradiated with fast-neutrons to 6 dpa at 683 K. These voids were smaller than those in pure Cu and Ni, and thermally unstable at higher temperature. Slight increase of irradiation temperature and higher dose of fast-neutrons induced coalescence of voids in the grains of Ni–8 at.% Cu, but abrupt decrease of small voids in the grains and creation of heterogeneously distributed larger voids near grain boundaries in Cu–8 at.% Ni.
2. Heterogeneous distribution of voids was mainly related to the effect of grain boundaries. These voids dominated the swelling in Cu–8 at.% Ni irradiated to 26 dpa at 703 K.
3. Surface segregation of impurity atoms at voids in Ni–8 at.% Cu was introduced by the annealing at higher temperatures after fast-neutron-irradiation at 683 K. This resulted in the formation of positronium at a void surface.

Acknowledgements

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