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Effects of hydrogen and helium produced by transmutation reactions on void formation in copper isotopic alloys irradiated with neutrons

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ABSTRACT

Three kinds of copper isotopic alloys ^{63}Cu, $^{63+65}$Cu (50 at.% ^{63}Cu + 50 at.% ^{65}Cu) and ^{65}Cu were used to investigate the intrinsic effects and the synergetic effects of transmutation productions, hydrogen and helium, on void swelling. Helium is produced from ^{63}Cu by (n,α) reaction and hydrogen by ^{63}Cu and ^{65}Cu by (n,p) reaction under the fission neutron irradiation. It was found that both hydrogen and helium enhanced the void swelling of copper. Although production of hydrogen was higher than that of helium in the present work, the effect of hydrogen was only prominent at 646 K but not at 683 K. The effect of helium on void swelling appeared at 683 K.

1. Introduction

In the future fusion reactor, the 14 MeV neutrons generate transmutation products as well as high energy collision cascades. Helium and hydrogen produced by nuclear reactions of (n,α) and (n,p) promote the swelling and degrade mechanical properties of structural materials. In most of candidate first wall and divertor materials for fusion system, such as austenitic steels, ferritic steels and copper alloys, helium and hydrogen are produced simultaneously by not only fission neutrons but also fusion neutrons. Consequently, it is impossible to know how helium or hydrogen influences nucleation and growth of voids, and whether there is an interaction between helium and hydrogen or not during void formation. To separate the intrinsic effects of helium or hydrogen and the synergetic effects of helium and hydrogen on nucleation and growth of voids, ion accelerator has been usually used so far for irradiation experiments [1–4]. The main advantage of ion accelerator is the easy control of experimental conditions and high damage rate. It is not easy, however, to evaluate the mechanical property changes of structural materials in reactors based on ion irradiation data because the microstructure changes cannot be the same at the same irradiation temperature and the same dpa. For example, compared with neutron irradiation, the void swelling peak temperature shifts to high temperature in the ion irradiation [5].

Boron addition and isotopic tailoring are other methods to investigate the helium effect on void swelling [6–10]. A large amount of helium is produced by reaction of ^{10}B (n,α) ^{7}Li only at the early stage of irradiation, since the cross section of (n,α) reaction is very larger in ^{10}B. The amount of helium produced from ^{10}B decreases with decreasing amount of ^{10}B in matrix during irradiation. In some isotopic tailoring experiments, a part of Ni in austenitic stainless steel is replaced by ^{59}Ni isotope to get high production of helium during irradiation. Although the production of helium in doped ^{59}Ni alloy is more than one order of magnitude higher than that in undoped alloy, hydrogen also affects the void swelling because hydrogen is produced in both alloys during irradiation.

In this work, we used a unique method, which was one of the isotopic tailoring method, to investigate the helium and hydrogen effects. Copper isotopes ^{63}Cu and ^{65}Cu were employed here. Helium is generated by the reaction of ^{63}Cu (n,α) ^{60}Co, and hydrogen by the reaction of ^{63}Cu (n,p) ^{63}Ni and ^{65}Cu (n,p) ^{65}Ni under fission neutron spectra. The cross sections of ^{65}Cu (n,α) are very small, and these nuclear reactions can be ignored.

2. Experimental procedure

Natural copper is composed of 69.1 at.% ^{63}Cu and 30.9 at.% ^{65}Cu. In the present study, pure ^{63}Cu and pure ^{65}Cu were made by reductive reaction described as follows:

$$^{63}\mathrm{CuO} + \mathrm{H} \rightarrow {}^{63}\mathrm{Cu} + \mathrm{H_2O}$$
$$^{65}\mathrm{CuO} + \mathrm{H} \rightarrow {}^{65}\mathrm{Cu} + \mathrm{H_2O}$$

Three kinds of copper isotopic alloys, ^{63}Cu, ^{65}Cu and 50 at.% ^{63}Cu and 50 at.% ^{65}Cu named $^{63+65}$Cu were used. The impurities were less than 0.02%. After rolled and punched into 3 mm discs with 0.1 mm thickness, the specimens were annealed at 1173 K for 1 h. The irradiation was conducted in Fast Flux Test Facility (FFTF) reactor using the Materials Open Test Assembly (MOTA) below core

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canister during its cycle 2B operation. The irradiation temperatures were 646 K and 683 K, and the doses were 15.4 dpa for the former temperature and 9.7 dpa and 14.9 dpa for the latter temperature using the threshold energy of 19 eV. The amount of helium and hydrogen produced in three isotopic alloys during irradiation are listed in Table 1 which were estimated based on neutron cross section library JENDL-3.3 [11]. The results show that the production of hydrogen in ^{63}Cu was about two orders of magnitude higher than that of helium in ^{63}Cu. After irradiation, the microstructures were analyzed through microscopic examination using a JEOL 2010.

Table 1
Amount of the transmutation products, helium and hydrogen, in copper isotopic alloys.

Isotopes	Irradiation Conditions	Amount of Helium	Amount of Hydrogen
^{63}Cu	646 K, 15.4 dpa	0.194 appm	12.0 appm
^{63}Cu	683 K, 14.9 dpa	0.189 appm	11.7 appm
$^{63+65}$Cu	646 K, 15.4 dpa	0.0975 appm	6.08 appm
$^{63+65}$Cu	683 K, 14.9 dpa	0.0950 appm	5.93 appm
^{65}Cu	646 K, 15.4 dpa	0.010 appm	0.161 appm
^{65}Cu	683 K, 14.9 dpa	0.010 appm	0.157 appm

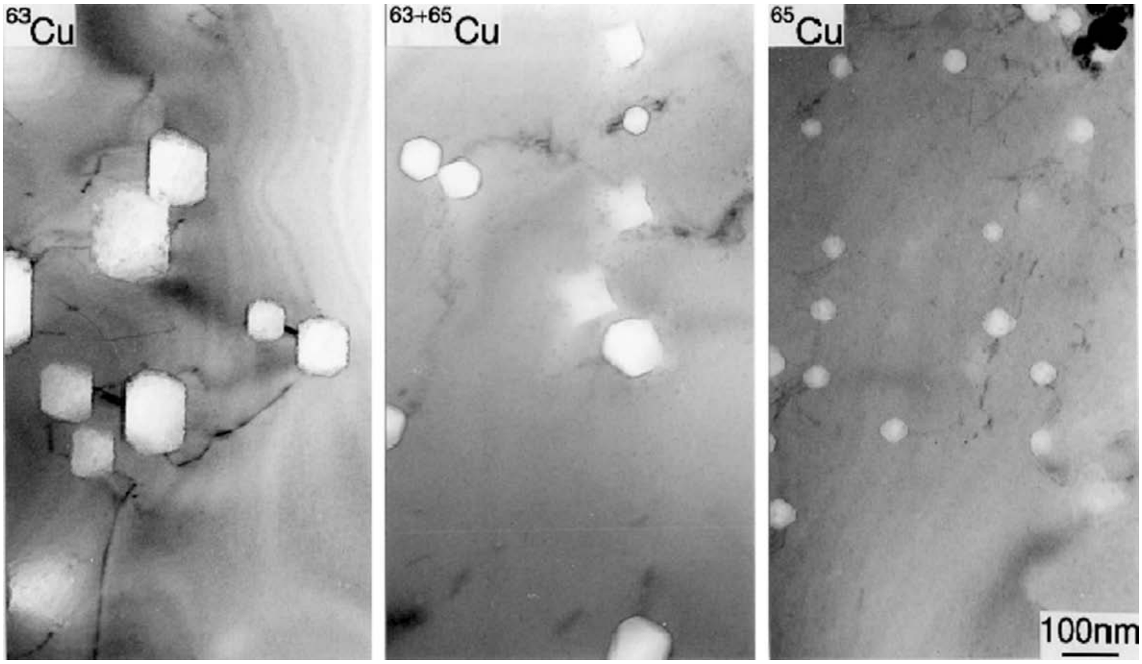

Fig. 1. Three kinds of neutron irradiated copper isotopic alloys. Void images at 646 K–15.4 dpa.

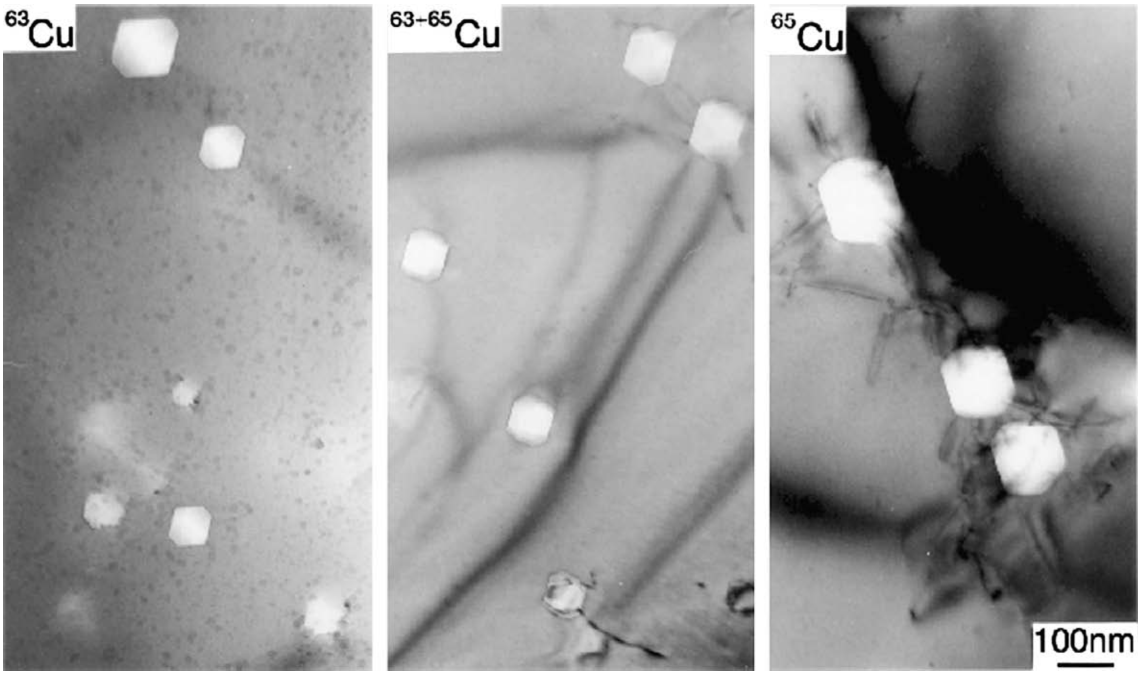

Fig. 2. Three kinds of neutron irradiated copper isotopic alloys. Void images at 683 K–14.9 dpa.

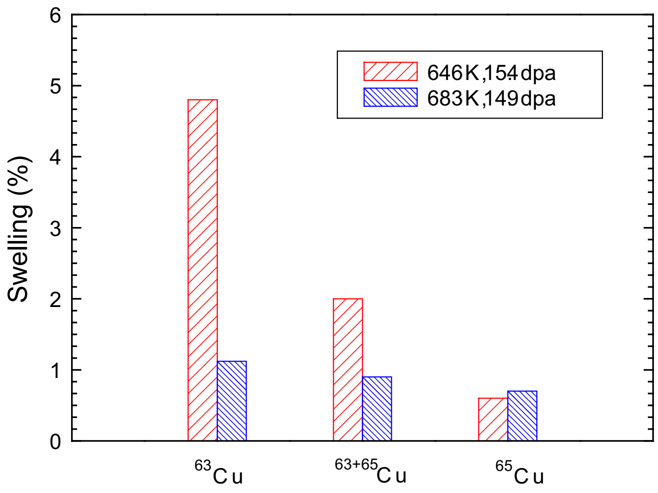

Fig. 3. Temperature dependence of void swelling in three copper isotopic alloys.

Table 2
Microstructures obtained in the present study.

	Void density (m^{-3})	Void size (nm)	Swelling (%)	Dislocation density (m^{-2})
646 K, 15.4 dpa				
^{63}Cu	4.3×10^{19}	130	4.8	5.2×10^{13}
$^{63+65}$Cu	8.6×10^{19}	70	1.9	6.9×10^{13}
^{65}Cu	1.0×10^{20}	50	0.6	6.2×10^{13}
683 K, 9.7 dpa				
^{63}Cu	2.1×10^{19}	70	0.4	2.6×10^{13}
$^{63+65}$Cu	1.4×10^{19}	80	0.3	2.0×10^{13}
^{65}Cu	3.5×10^{18}	100	0.2	3.3×10^{13}
683 K, 14.9 dpa				
^{63}Cu	3.9×10^{19}	80	1.1	2.0×10^{13}
$^{63+65}$Cu	2.8×10^{19}	85	0.9	2.2×10^{13}
^{65}Cu	1.0×10^{19}	110	0.7	4.1×10^{13}

3. Results

3.1. Temperature dependence of swelling

The dislocation density decreased with increasing irradiation temperature in three isotopic alloys. Figs. 1 and 2 show void image micrographs in three isotopic alloys irradiated at 646 K–15.4 dpa and 683 K–14.9 dpa. The density of voids increased and the size of voids decreased with increasing amount of ^{65}Cu, i.e. decreasing production of hydrogen and helium, in the irradiation at 646 K. Whereas the changes of void density and void size were reversed in the irradiation at 683 K. Namely with increasing irradiation temperature, the void density decreased, especially in ^{65}Cu where the void density decreased by one order of magnitude. The void size increased with decreasing production of helium and hydrogen. The void swelling in ^{63}Cu and $^{63+65}$Cu decreased also, but it increased slightly in ^{65}Cu as shown in Fig. 3. The void swelling was high in ^{63}Cu and low in ^{65}Cu at both temperatures. The microstructural parameters obtained are summarized in Table 2.

3.2. Dose dependence of swelling

Fig. 4 shows voids observed in three kinds of copper isotopic alloys irradiated at 683 K–9.7 dpa. The dose dependence of swelling in three kinds of copper isotopic alloys is shown in Fig. 5. With increasing irradiation dose, the void swelling increased because the void density increased and the voids grew larger. The void swelling was high in ^{63}Cu and low in ^{65}Cu in both doses.

4. Discussions

The effect of gas atoms formed by transmutation was clearly detected in three copper isotopic alloys. The swelling was highest in ^{63}Cu. The growth behavior was, however, different between 646 K and 683 K. The void size was largest and the density was lowest at 646 K in ^{63}Cu. On the other hand, the void size was smallest and the density was highest at 683 K.

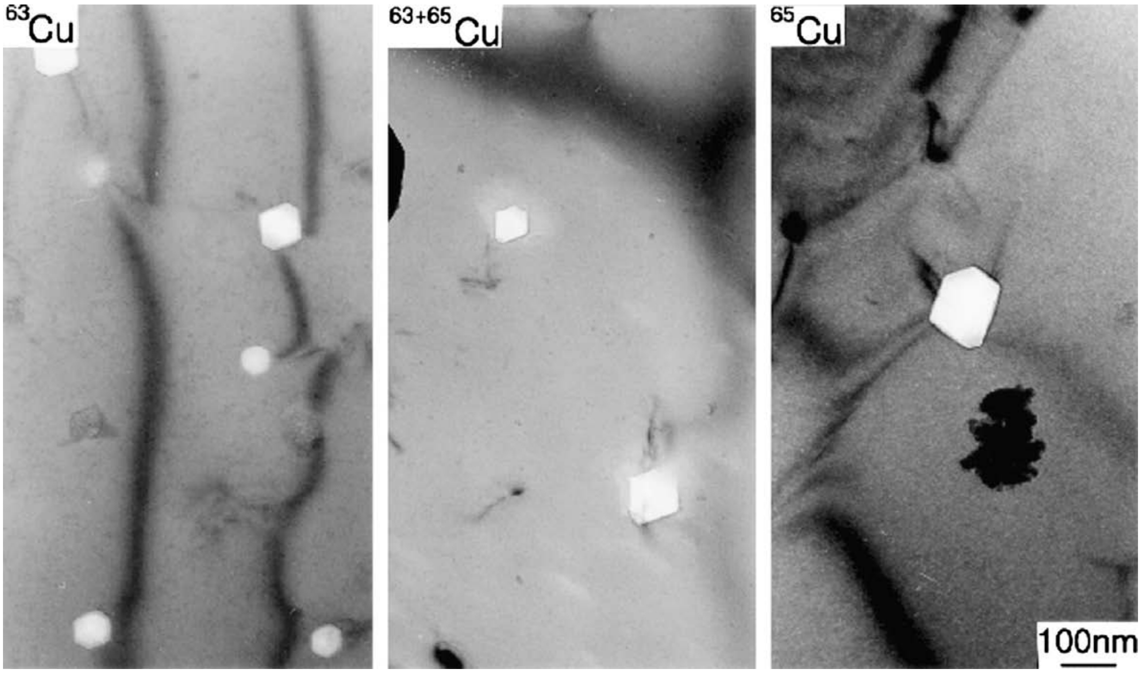

Fig. 4. Three kinds of neutron irradiated copper isotopic alloys. Void images at 683 K–9.7 dpa.

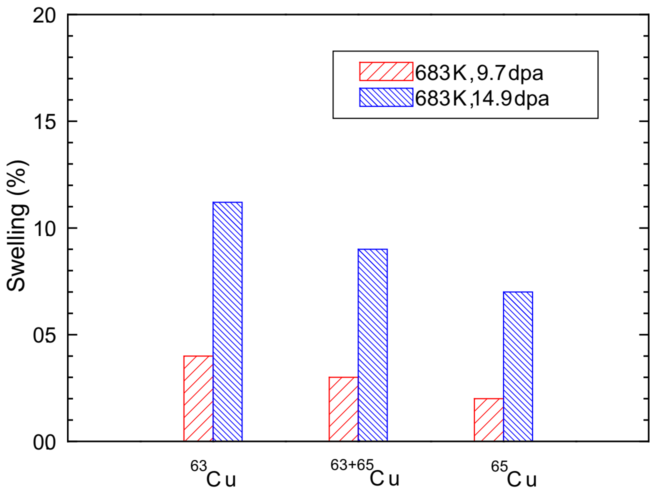

Fig. 5. Dose dependence of void swelling in three copper isotopic alloys.

Interactions of helium and hydrogen with radiation defects in metals and alloys have been reviewed by Mansur and Coghlan [12] and Condon and Schober [13], respectively. Many experiments and calculations show that helium enhances the void nucleation and growth [14]. The effect of helium on void formation and growth is greater than that of hydrogen [15].

Few data are available in literature for the interaction between gas atoms and vacancies in copper. Only the dissociation temperature of helium vacancy pairs was reported to be 785 K [16]. In general, the binding energy of hydrogen with vacancies is lower than 1 eV and helium has high binding energy higher than 2 eV in pure metals such as Ni and Fe [17–20]. Therefore it is concluded that the contribution of helium on the nucleation of voids dose not change in this temperature range.

The low density and large void size in ^{63}Cu at 646 K is explained by hydrogen effects. It is well know that voids with gas atoms (bubbles) in metals can move and make larger ones easily [21,22]. Bubble coalescence is expected by high production of hydrogen in ^{63}Cu at 646 K. At 683 K, hydrogen effects decreased remarkably by the escape of them from the matrix. The high concentration of small voids at 683 K must be mainly caused by helium. Helium trapped by vacancies and voids contributes to the stability of voids.

The available data of fission neutron irradiation show that the swelling peak of pure natural copper $^{63.55}$Cu is about 623 K [23]. As the swelling of ^{63}Cu is high at 646 K and decrease remarkably at 683 K, the swelling peak of natural copper may be dominated by hydrogen.

^{63}Cu and ^{65}Cu during neutron irradiation produce not only helium and hydrogen but also solid transmutants such as ^{64}Ni, ^{64}Zn, ^{68}Zn and ^{60}Co, with Ni and Zn reaching several tenths of percent in natural copper containing 69.1% and 30.9% of ^{63}Cu and ^{65}Cu, respectively [24]. Since ^{63}Cu produces ^{64}Ni and ^{64}Zn but ^{65}Cu produces only ^{66}Zn and ^{60}Co, there are differences in the solid transmutants produced in the three isotopic alloys. Although it can not be clearly concluded that these differences in solid transmutants contributed to the different swelling behavior, Satoh et al. have been showed that microstructural evolution in copper can not be influenced by alloying elements if the concentration of added element is less than 0.3 at.% [25]. Therefore, the swelling differences arose primarily from the differences in helium and hydrogen.

5. Conclusions

To investigate the intrinsic effects of hydrogen or helium and synergetic effects of hydrogen and helium on void swelling, copper isotopic alloys, ^{63}Cu, $^{63+65}$Cu and ^{65}Cu were irradiated by neutrons. The results can be summarized as follows:

1. Both helium and hydrogen enhanced the void swelling in copper.
2. The effect of hydrogen on void swelling was important at low temperature if the hydrogen production was much higher than helium production.
3. The swelling peak of natural copper ($^{63.55}$Cu) was related to hydrogen in the matrix.

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