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Journal of Nuclear Materials 329–333 (2004) 1558–1562

journal of nuclear materials

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# Microstructural evolution and hardness changes in the interface of Cu/316L joint materials under aging and ion irradiation

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**Abstract**

The effects of aging and ion irradiation on microstructure stability and hardness change in the joint materials of CuNiBe/316L and CuAl25/316L have been investigated in the present study. The aging at 673 K for 1000 h or Ni ion irradiation at 573 and 673 K to 10 dpa did not promote the interdiffusion and void swelling at the interface. The hardness in both Cu alloys and stainless steel was increased by irradiation, however, it was decreased by aging except for CuNiBe alloy. The hardness change in CuNiBe alloy was larger than that in CuAl25 alloy. The hardness changes would have a significant effect on the mechanical properties of joint materials.


## 1. Introduction

Precipitation and dispersion strengthened Cu alloys have good thermal conductivity and high strength. Cu alloys joined with 316L austenitic stainless steel are expected to be used as heat sink materials in the first wall and divertor of ITER [1,2]. Relative to 316L stainless steel, limited and scarce data are available for the microstructural evolution and mechanical properties of Cu alloys [3,4] and Cu/316L joints, respectively, under the operation condition of ITER. It is, therefore, important to investigate the effects of irradiation and heat treatment on microstructural change in the joint materials since poor properties at the interface can degrade the entire properties of the first wall.

In the previous study [5], annealing experiments showed that the microstructures in the interface of CuNiBe/316L and CuAl25/316L joints were thermally stable and did not cause interdiffusion during annealing at 573 and 673 K for 100 h. In the present study, the effects of aging at 673 K for 1000 h and irradiation with Ni ions on the microstructural and hardness changes in GlidCop CuAl25, CuNiBe alloys and their joint with 316L stainless steel materials were investigated.

## 2. Experimental procedure

GlidCop CuAl25/316L and CuNiBe/316L, which were made utilizing a hot isostatic pressing (HIP) technique to join the Cu alloy to the stainless steel of 316L, were examined in this study. The GlidCop CuAl25 alloy (0.25 wt% Al in the form of $Al_2O_3$) and CuNiBe (1.98 wt% Ni and 0.32 wt% Be) alloy were produced by SCM Metals Inc. and Brush Wellman Inc., respectively. The joint materials were fabricated at bonding temperature

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0022-3115/$ - see front matter 
doi:10.1016/j.jnucmat.2004.04.326

of 1255 K for CuAl25/316L, and at 1245 K for CuNiBe/316L. The pressure and the holding time for the HIP process were fixed at 101 MPa and 2 h [6].

The joint materials were thinned to 0.1 mm, and cut into 3 mm discs for transmission electron microscope (TEM) observation. The interface was at the center of discs. Aging experiment and ion irradiation were carried out to investigate the microstructural stability of the joint. The samples were aged at 673 K for 1000 h or irradiated by 4 MeV Ni ions perpendicular to surface of samples using a Tandem type accelerator in the University of Tokyo. The irradiation temperatures were 573 and 673 K, and irradiation rate at the damage peak region (about 550 nm in depth) was $1 \times 10^{-3}$ dpa/s. The irradiation dose was 10 dpa for Cu alloys. After aging or irradiation, the microstructural evolution and hardening change were examined. TEM specimens were prepared by ion milling. The interfaces were observed using TEM (JEOL 2010) and scanning electron microscopy (SEM, JEOL JSM-5800LV) to characterize the interfacial and the overall microstructure. TEM observation was performed at the maximal damaged area. Hardness measurement, which was carried out by an Elionix ENT-1100, was done from irradiated surface of samples without thinning. The diamond indenter was the Berkovich geometry, and the indenter load ($L$) and indenter displacement ($d$) were accurately monitored with a computer system. The relation between Vickers hardness and indenter load and indenter displacement is given by [7]

$$Hv = 3.484A(\mathrm{GPa}), \tag{1}$$

$$L/d = Ad + B, \tag{2}$$

where $A$ and $B$ are dependent on materials but independent of indenter load and indenter displacement.

## 3. Results

### 3.1. SEM micrograph and EDX line analyses of the joint interfaces

As reported in a previous paper [5], Fe–Cr precipitates formed in the Cu alloy side of the CuAl25/316L near the interface in a region 30 μm wide. In contrast, large Be particles were observed through the Cu alloy in the CuNiBe/316L except for the region near the interface, where a 30 μm region contained no beryllium. In addition, voids with average diameter of 2 μm were observed in Cu alloy side near the interface of CuAl25/316L, whereas voids with average diameter of 5 and 1 μm were observed at the interface and in 316L side near the interface of CuNiBe/316L, respectively. Fig. 1 shows the SEM micrographs and results of EDX line analysis near the interface of CuAl25/316L and CuNiBe/316L, which includes materials as-received, annealed at 673 K for 1000 h and irradiated at 673 K with Ni ions to 10 dpa. Other than the change in distribution of larger Fe–Cr precipitates and large Be particles, no significant microstructural or compositional changes were observed in the as-received, annealed and irradiated materials in either joint.

### 3.2. Effects of aging and irradiation on microstructural evolution in Cu alloys and joint interfaces

In the CuAl25 alloy, aging removed the small precipitates of average size of 4 nm while leaving behind larger precipitates, presumably oxide particles with average size of 15 nm. Stacking fault tetrahedra (SFT) with high density were formed during irradiation at 573 K to 10 dpa, with the density of SFT decreasing when irradiated at 673 K. Fig. 2 shows the microstructural evolution in CuNiBe substrate either aged at 673 K for 1000 h or irradiated at either 573 or 673 K to 10 dpa. SFT were also observed after irradiation, and the changes of size and density of SFT with temperature were similar to those in CuAl25 alloy. Besides large Be particles observed by SEM, as shown in Fig. 2, the precipitates $\gamma''$ were observed, and their size and density were not influenced significantly by the irradiation. However, aging led to a coarsening of the $\gamma''$ precipitates, and in fact the change in electron diffraction patterns taken from [0 1 1] zone axis along [2 0 0] direction showed that the $\gamma''$ precipitates changed to $\gamma'$ during aging at 673 K for 1000 h. This is evident from the diffraction patterns because the streaks produced by the $\gamma''$ precipitates in as-received sample have coalesced into discrete diffraction spots in the diffraction pattern after aging.

The interfaces of joints were also observed by TEM. Though the voids with average diameter of micrometer order were observed near the interface by SEM, no voids and precipitates were identified at the interfaces of annealed or irradiated CuAl25/316L and CuNiBe/316L by TEM. Dislocation loops and SFT were observed near the interfaces of irradiated samples.

### 3.3. Hardness changes induced by aging and irradiation in joints

Fig. 3 summarizes the results of hardness experiment in CuAl25/316L and CuNiBe/316L. On Cu side of CuAl25/316L, the hardness decreased slightly after aging for 1000 h at 673 K and increased after irradiation. The hardness of CuAl25 alloy irradiated at 573 K was 20 Hv higher than that at 673 K. The hardness changes in 316L stainless steel were similar to those in CuAl25 alloy. In contract to the hardness changes in CuAl25 alloy, the hardness of CuNiBe alloy increased

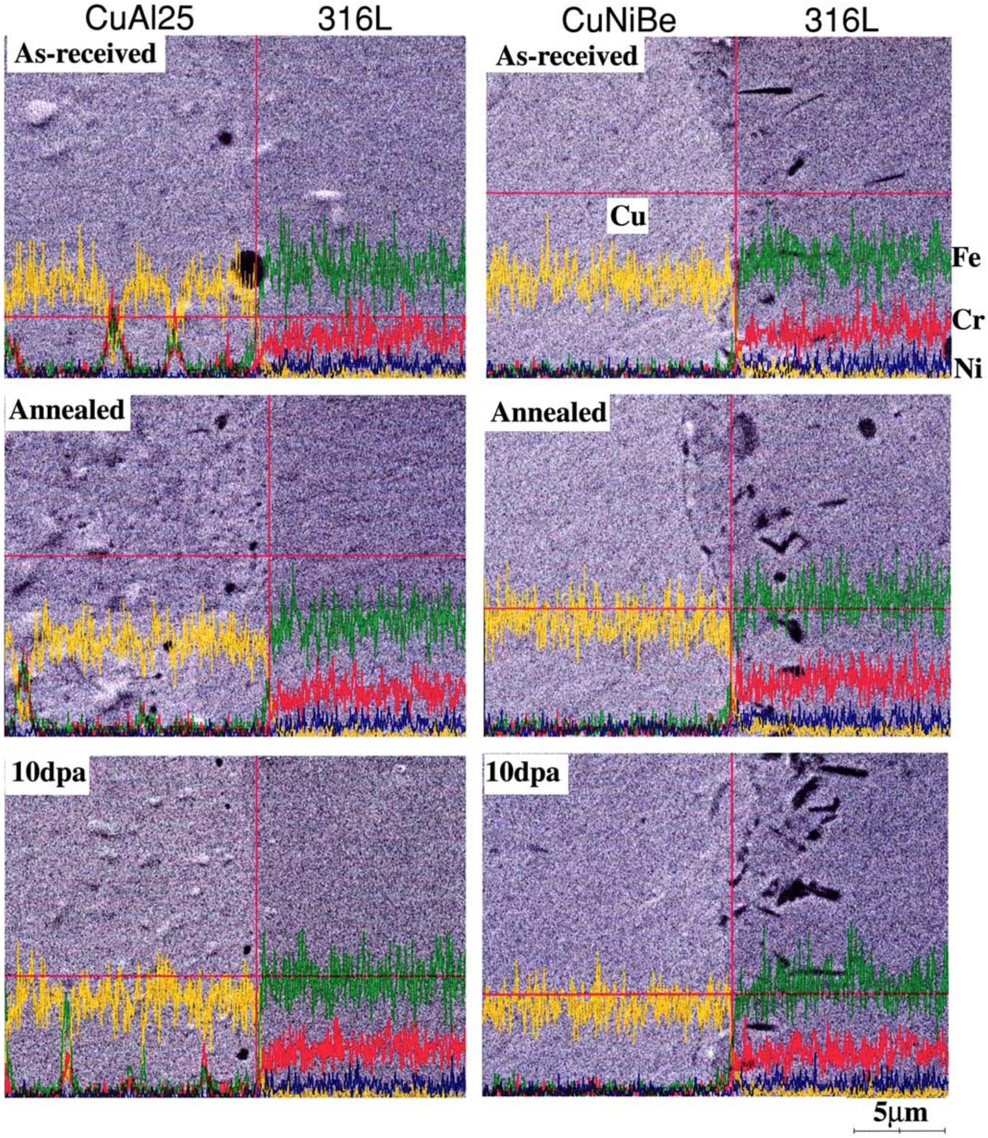


Fig. 1. SEM micrographs of as-received, annealed and irradiated joint materials of CuAl25/316L and CuNiBe/316L.

30 Hv during aging at 673 K. The trend of hardness changes induced by irradiation in CuNiBe alloy was the same as in CuAl25 alloy, but the hardness changes were larger in CuNiBe alloy than that in CuAl25 alloy.

## 4. Discussion

Bonded materials of Be (or W)/Cu alloys/316L stainless steel have been considered for use as the first wall and divertor in the ITER. Generally, the joint is the weak part of bonded material and often many of bonded materials fracture near the interface with and without neutron irradiation [6,8–11]. Therefore, it is necessary to study the microstructure changes near interface.

As reported in a previous paper [5], the main elements (Fe, Cr and Ni) of stainless steel diffused across the interface, reducing the concentrations of Fe, Cr and Ni near the interface in the stainless steel side and increased in the Cu alloy near the interface. Cu also diffused into the stainless steel side. Diffusion length was defined as $(D_0 \exp(-Q/RT)t)^{1/2}$, where $R$ is gas constant, $T$ absolute temperature, and $t$ the holding time at high temperature. Table 1 lists the estimation of diffusion length of Cr and Fe in Cu matrix and Cu in Ni matrix in place of stainless steel. It also lists the effects of heat

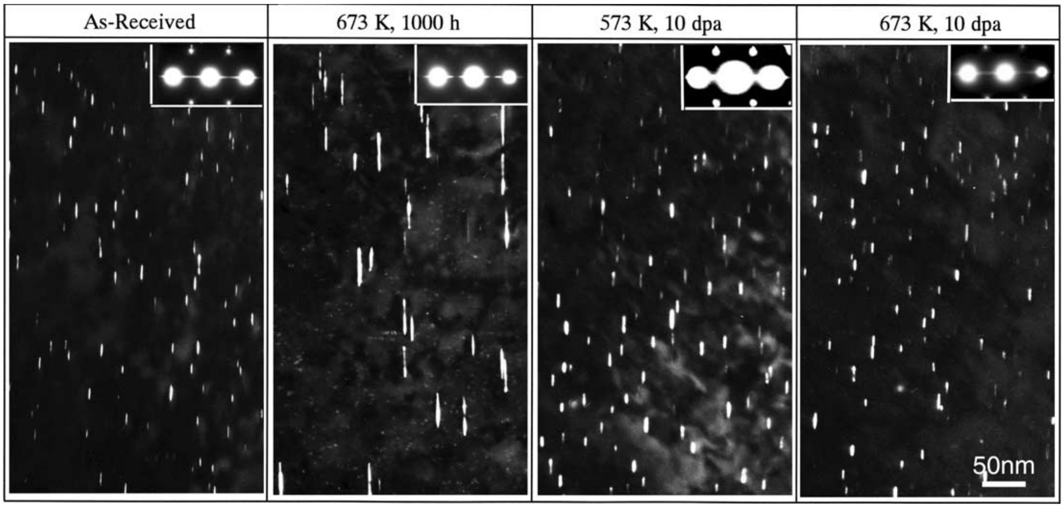


Fig. 2. Effects of aging and irradiation on precipitates in CuNiBe alloy, $\gamma''$ or $\gamma'$ precipitates were taken at a (g, 4g) weak beam condition using a $g = 2/3[200]_{Cu}$ reflection.

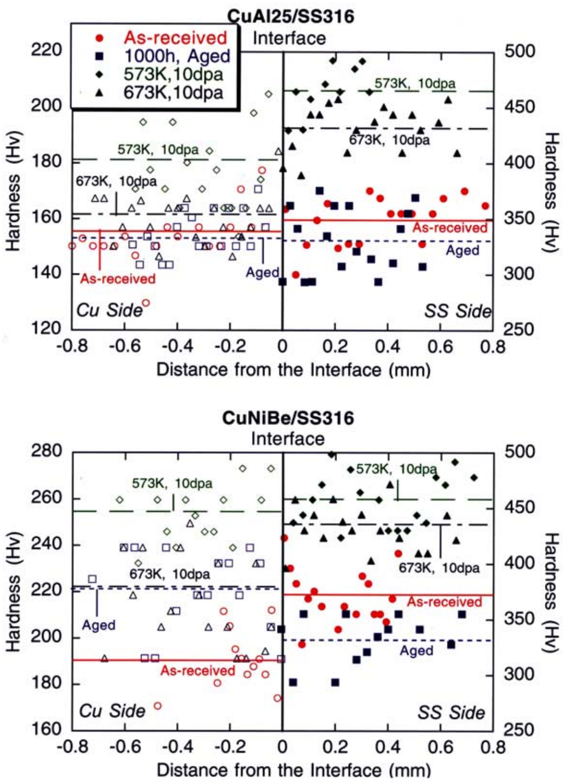


Fig. 3. Effects of aging and irradiation on hardness changes in CuAl25/316L and CuNiBe/316L joint materials.

treatments during HIP process and aging at 673 K for 1000 h on interdiffusion. In CuAl25/316L, the width of Fe–Cr precipitates in CuAl25 alloy is almost equal to the diffusion distance of Fe in Cu matrix at the temperature used during the HIP process. Therefore, the formation of Fe–Cr precipitates, which are insoluble in Cu, is a direct result of Fe and Cr diffusion into the copper alloy during the HIP process. Compared with diffusion length of Cr and Fe in Cu matrix, the diffusion length of Cu in stainless steel side was one order of magnitude lower. The nickel is thought to remain in solution in the copper matrix. In the case of the CuNiBe/316L, the large Be particles were not observed in the Cu matrix near the interface where Fe, Cr and Ni diffused from stainless steel side. It is thought that the Fe, Cr and Ni diffusing into the copper increased the solubility of Be, causing the Be particles disappear. Be and Cu also diffused from the Cu into the stainless steel, which may increase the changes for brittle behavior in the stainless steel due to the presence of Be [13].

The results of EDX showed that the aging at 673 K for 1000 h and irradiation at 573 and 673 K to a dose of 10 dpa did not influence the compositional change in the joint materials of CuAl25/316L and CuNiBe/316L. As shown in Table 1, the diffusion lengths of Cr and Fe in Cu matrix and Cu in stainless steel under the aging at 673 K are two and three orders of magnitude lower than that those during HIP process, respectively. Thus, the compositional change in joint by aging will be negligibly small. A model calculation showed that, in the ion irradiation, the vacancies cannot migrate to a long distance because of mutual annihilation of interstitials [14]. Since the diffusion of atoms is caused by vacancy migration, especially at high temperature, the compositional change is small in the case of ion irradiation. It is necessary, however, to consider the compositional change under neutron irradiation where the damage rate is low and the migration distance of vacancies is long.

Table 1
Estimation of diffusion length of elements in CuAl25/316L and CuNiBe/316L joints

| | HIP process (1250 K, 2 h) | Aging (673 K, 1000 h) |
|---|---|---|
| Cr in Cu matrix ($D_0$: $3.4\times10^{-5}$ m$^2$/s; $Q$: 195 kJ/mol) [12] | $4.17\times10^{-5}$ m | $3.00\times10^{-7}$ m |
| Fe in Cu matrix ($D_0$: $1.0\times10^{-4}$ m$^2$/s; $Q$: 231 kJ/mol) [12] | $3.02\times10^{-5}$ m | $1.03\times10^{-7}$ m |
| Cu in Ni matrix ($D_0$: $5.7\times10^{-5}$ m$^2$/s; $Q$: 258 kJ/mol) [12] | $2.61\times10^{-6}$ m | $1.39\times10^{-9}$ m |

The microstructural changes appear to correlate well with the changes in hardness. In the CuAl25/316L and the CuNiBe/316L, the hardness increased after irradiation due to the SFT defects produced during irradiation. The higher hardness after irradiation at 573 K correlates with the higher density of defects formed at 573 K compared to that at 673 K. The hardness change was greater in the case of the CuNiBe most likely as a result of additional changes in the precipitate composition or new invisible precipitates due to irradiation. The hardness of CuNiBe also increased after aging at 673 K for 1000 h, which is likely due to the $\gamma''$ change to $\gamma'$ precipitates and additional precipitation not easily measured from the micrographs. A similar increase in hardness induced by phase change has been reported in the reference [15].

In the present irradiation experiment, the irradiation time was less than 3 h to reach a dose of 10 dpa, so the effect of aging on precipitate stability could be ignored. In the operation condition of the ITER, however, the dose rate of irradiation is lower more than four orders of magnitude than that in the present ion irradiation [2], and it is thus expected that the microstructural evolution in CuAl25 and CuNiBe alloys will be affected by not only irradiation but also aging if the irradiation temperature is high enough.

## 5. Conclusion

Microstructural and compositional changes near the interface of CuAl25/316L and CuNiBe/316L were investigated by TEM and SEM. It was found that the voids were formed near the interface and compositions of Cu and stainless steel diffuse through interface to adjacent alloy during the HIP process. Also, it was found that the annealing at 673 K for 1000 h and irradiation at 573 and 673 K to 10 dpa did not cause the interdiffusion, but change the harness in CuAl25/316L and CuNiBe/316L. The hardness changes in CuAl25/316L were smaller than those in CuNiBe/316L.

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