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Effect of Applied Stress on Nucleation and Growth of Precipitates in a Cu-Be-Co Alloy

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Abstract. The influence of an external stress on the nucleation and growth of disk-shaped G.P. zones has been investigated for a Cu-1.2wt%Be-0.1wt%Co alloy aged at 220 °C. A compressive stress applied in the [001] direction during aging preferentially accelerates the nucleation and growth of the G.P. zones perpendicular to the [001] axis, whereas a tensile stress does not significantly affect those of G.P. zones. The promotion of the nucleation and growth of the G.P. zones perpendicular to the compressive-stress axis can be well understood through the interaction energy between the applied stress and the misfit strains of G.P. zones. The critical diameter of the disk-shaped G.P. zone nucleus was estimated as about 1.3 nm from evaluation of the interaction energy.

Introduction

It is well known that application of an elastic stress during the aging process of many age-hardenable alloy systems significantly affects the resulting microstructures, particularly the distribution of strengthening precipitates [1-4].

Monzen *et al.* have found by transmission electron microscopy (TEM) that application of the external stress during aging at 200 °C induces the oriented precipitation of disk-shaped G.P. zones, monolayers of Be atoms, on $\{100\}_\alpha$ in single crystals of a Cu-0.9wt%Be alloy [4]. Compressive stress along the [001] direction induces preferential formation of the G.P. zones perpendicular to the stress axis and tensile stress induces the same parallel to the stress axis. It has been shown that the oriented-formation of G.P. zones under stress is owing to the stress-aided formation of particular nuclei. However, it was not studied whether external stress during aging affects the nucleation and growth of particular G.P. zones out of G.P. zones parallel to three $\{100\}_\alpha$.

In this work, the influence of an applied compressive or tensile stress on the nucleation and growth of G.P. zones is examined for a Cu-1.2wt%Be-0.1wt%Co alloy aged at 220 °C. In addition, the critical diameter of the disk-shaped G.P. zone nucleus is determined.

Experimental Details

Cu-1.2wt%Be-0.1wt%Co alloy ingots were prepared from 99.99wt%Cu and Cu-3.81wt%Be and Cu-10.45wt%Co master alloys by melting in a vacuum. The alloy ingots were homogenized at 900 °C for 48 h in a vacuum, cold-rolled to 50% reduction in thickness and then spark-cut into specimen strips. For compressive aging, the specimens had a cross-section of 3 mm × 6 mm and a length of 6 mm. For tensile aging, the specimens had the same cross-section but a gauge length of 20 mm. All the specimens were solution-treated at 820 °C for 2 h in a vacuum and quenched into water. The solution treatment also caused complete recrystallization of the specimens. The solution-treated specimens were then aged at 220 °C for various times either under an applied stress of 70 MPa (stress aging) or under no stress (free aging). The applied stress of 70 MPa is about half of the yield strength of the solution-treated specimen at 220 °C.

Thin foils for TEM observations were prepared by slicing the aged specimens with a spark cutter and

by electropolishing using a solution of 67vol% methanol and 33vol% nitric acid at -30°C and 6.5V in a twin-jet electropolisher. Microscopy was carried out using a HITACHI H-9000NAR at an operation voltage of 300 kV.

Results and Discussion

Nucleation and growth of G.P. zones. Figure 1 shows the number density of disk-shaped G.P. zones as a function of stress aging time t for the specimens, compressive-stress-aged and tensile-stress-aged at 220°C for various times t and then free-aged at 220°C for times t' , the sum of t and t' being 48 h. The number density of G.P. zones is defined as the volume fraction of G.P. zones divided by the average volume per one G.P. zone. The volume fraction was determined by applying the lattice constants of the stress-aged and free-aged specimens measured by an X-ray analysis to the experimental data on the dependence of the lattice constant on the Be concentration in the literature [5]. The disk-shaped G.P. zones are assumed to have a thickness of 0.226 nm, equal to the diameter of Be atoms [6]. It is seen in Figure 1 that the density of G.P. zones in the compressive-stress-aged specimen increases and then becomes constant after about 18h. This observation indicates that the formation of the G.P. zones favored by the compressive stress is completed after 18h. On the other hand, the tensile-stress-aged specimen reveals no significant change in the number density with t . No difference in the number density was found between the specimens aged at 24 and 48 h under tensile stress or under no stress, indicating that aging for 24 h under tensile stress or no stress is long enough to cause the nucleation of G.P. zones to be finished.

Fig. 1 Effect of free, compressive-stress and tensile-stress aging at 220°C on the number density of disk-shaped G.P. zones.

Table 1 Number density of G.P. zones on each $\{001\}_{\alpha}$ in the Cu-Be-Co specimens, free-aged (FA), compressive-stress-aged (CSA) and tensile-stress-aged (TSA) at 220°C for 48 h.

G.P. zone	Density [10^{23}m^{-3}]		
	FA	CSA	TSA
$(001)_{\alpha}$		4.0 ± 0.3	2.6 ± 0.2
$(010)_{\alpha}$	3.1 ± 0.2		
$(100)_{\alpha}$		3.0 ± 0.1	3.0 ± 0.3

We selected the grains in which the stress axis was nearly perpendicular or parallel to $(001)_{\alpha}$ or $(100)_{\alpha}$ and $(010)_{\alpha}$ of the Cu matrix, and determined the number density of G.P. zones on $\{001\}_{\alpha}$ from TEM observations using the electron beam parallel to $[110]_{\alpha}$ or $[101]_{\alpha}$ and $[011]_{\alpha}$ of the grains. In this case, the thickness of TEM foils was measured by utilizing the $\{111\}_{\alpha}$ coherent twin boundary, nearly parallel to the electron beam. Table 1 summarizes the number density of G.P. zones on each $\{001\}_{\alpha}$ in the specimens, free-aged (FA), compressive-stress-aged (CSA) and tensile-stress-aged (TSA) for 48 h. The density of the disk-shaped G.P. zones on $(001)_{\alpha}$ perpendicular to the stress axis in the CSA specimen is higher than those of the G.P. zones on $(100)_{\alpha}$ or $(010)_{\alpha}$ parallel to the stress axis in the CSA specimen and the G.P. zones on $\{100\}_{\alpha}$ in the FA and TSA specimens. The latter densities are nearly identical, except for that of the G.P. zones on $(001)_{\alpha}$ in the TSA specimen, which is lower.

Figure 2 depicts a TEM image of the specimen, free-aged at 220°C for 24 h and then compressive-stress-aged at 220°C for 24h. The image was taken using the electron beam parallel to $[100]_{\alpha}$. The diameter of disk-shaped G.P. zones perpendicular to the $[001]_{\alpha}$ stress axis is larger than that of G.P. zones on $(010)_{\alpha}$. Table 2 lists the diameter of G.P. zones on $\{001\}_{\alpha}$ in the specimens, free-aged 220°C for 24h and then free-aged (FA), compressive-stress-aged (CSA) or tensile-stress-

aged (TSA) at 220 °C for 24 h. The stress axis is parallel to $[001]_\alpha$. The diameter of the G.P. zones on $(001)_\alpha$ in the CSA specimen is larger than those of the G.P. zones on $(100)_\alpha$ or $(010)_\alpha$ parallel to the stress axis in the CSA specimen and the G.P. zones on $\{100\}_\alpha$ in the FA and TSA specimens. The latter diameters are almost the same.

Fig. 2 TEM image of the specimen, free-aged at 220 °C for 24 h and then compressive-stress aged at 220 °C for 24h. The arrow indicates the applied stress axis. The zone axis is parallel to $[100]_\alpha$.

Table 2 Diameter of disk-shaped G.P. zones on $\{110\}_\alpha$ in the Cu-Be-Co specimens, free-aged 220 °C for 24 h and then free-aged (FA), compressive-stress-aged (CSA) or tensile-stress-aged (TSA) at 220 °C for 24 h.

G.P. zone	Size [nm]		
	FA	CSA	TSA
$(001)_\alpha$		9.0 ± 0.7	7.6 ± 0.6
$(010)_\alpha$	7.8 ± 0.6	7.8 ± 0.6	7.8 ± 0.5
$(100)_\alpha$			

The origin of the promotion of nucleation and growth of the G.P. zones only perpendicular to the stress axis under compression can be understood to arise from the interaction energy due to the presence of negative misfit strain ε_{ij} (stress-free transformation strain) between a G.P. zone and an external stress σ_{ij} . The interaction energy F_I is expressed as [1, 7]

$$F_I = -V\sigma_{ij}\varepsilon_{ij}, \quad (1)$$

where V is the volume of the G.P. zone. Since ε_{ij} of the G.P. zone, lying parallel to $(001)_\alpha$, has components of $\varepsilon_{33} = -0.10$ and $\varepsilon_{11} = \varepsilon_{22} = -0.01$ [8], equation (1) predicts that compressive stress along the $[001]$ direction during aging particularly accelerates nucleation and growth of the G.P. zones normal to the $[001]$ axis. This is in agreement with the results shown in Tables 1 and 2. In addition, the prediction of equation (1) that tensile stress along the $[001]$ direction particularly suppresses formation of the G.P. zones normal to the stress axis is coincident with the result of Table 1.

Critical size of G.P. zones. The number density of G.P. zones on $(001)_\alpha$ in the specimen, compressive-stress-aged for 48 h was determined from TEM observations using the electron beam normal to $(110)_\alpha$ on which the stress axis lies. The number density was plotted as a function of the angle θ between the stress axis and the plane normal of the G.P. zones. It decreased with increasing θ .

The energy change due to the nucleation of G.P. zones under a stress is given by equation (1). According to a classical nucleation theory [9], the interaction energy F_I affects the nucleation rate R as written by

$$R \propto \exp\left(-\frac{(G^* + F_I^*)}{kT}\right), \quad (2)$$

where G^* is the activation energy for nucleation in absence of a stress, F_I^* is the interaction energy associated with nucleation of the G.P. zone of a critical nucleus volume of V^* , k is Boltzmann's constant and T is the absolute temperature. When the nucleation rate at $\theta = 90^\circ$ and the applied stress are referred to as R_0 and σ_A , respectively, the nucleation rate normalized is written as

$$\ln\left(\frac{R}{R_0}\right) = -\frac{0.09\sigma_A V^*}{kT} \cos^2 \theta, \quad (3)$$

Fig. 3 Relative nucleation rate of G.P. zones plotted against $\cos^2\theta$.

This value is nearly identical to the nucleus diameter of about 1.0 nm estimated by Eto *et al.* [10] for the G.P. [1] zones in Al-Cu alloys.

Conclusions

- (1) Application of compressive stress in the [001] direction during aging a Cu-1.2wt%Be-0.1wt%Co alloy at 220°C promotes particularly the nucleation and growth of disk-shaped G.P. zones normal to the [001] axis, while tensile stress does not essentially affect those of G.P. zones.
- (2) The acceleration of the nucleation and growth of G.P. zones perpendicular to the compressive-stress axis can be well understood through the interaction energy between the stress acting on the G.P. zones and the misfit strains of G.P. zones.
- (3) By evaluation of the interaction energy, the critical size of the disk-shaped G.P. zone nucleus was estimated to be about 1.3 nm.

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using the misfit strains of the GP zone parallel to (001)_a, $\varepsilon_{33}=-0.10$ and $\varepsilon_{11}=\varepsilon_{22}=-0.01$ [8]. The logarithm of the number density of G.P. zones normalized by that at $\theta=90^\circ$, corresponding to the relative nucleation rate, is plotted against $\cos^2\theta$ in Figure 3. All the data points fall on a single straight line. The slope of the straight line gives $-0.09\sigma_{33}V^*/kT=0.27$, according to equation (3). Using $k=1.38 \times 10^{-23} \text{ JK}^{-1}$, $\sigma_A=-70 \text{ MPa}$ and $T=493 \text{ K}$, the activation volume for a critical nucleus is estimated to be $V^*=3.0 \times 10^{-28} \text{ m}^{-3}$. When the disk-shaped G.P. zones are assumed to have a thickness of 0.226 nm [6], equal to the diameter of Be atoms, the estimate of the nucleus diameter is about 1.3 nm.