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Metastable Precipitates and Their Misfit Strains in a Cu-0.9wt%Be Single Crystal

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Abstract. The precipitation processes from G.P. zones to γ' in a Cu–0.9wt%Be alloy single crystal containing only the G.P. zones parallel to the matrix $(001)_\alpha$ plane are investigated by high-resolution electron microscopy. The precipitate phases follow a G.P. zone $\rightarrow$ γ" $\rightarrow \gamma_I +$ γ' sequence. The G.P. zone to γ_I phase transformation occurs successively via γ" during aging, while the γ' phase heterogeneously precipitates on the γ_I phase. From length-change measurements during aging, the misfit strains of γ' precipitates in directions perpendicular and parallel to $[001]_\alpha$ are estimated as $\varepsilon_{11} = \varepsilon_{22} = -0.03$ and $\varepsilon_{33} = -0.09$, respectively. The observation that the estimated absolute value of ε_{33} is much smaller than that of $\varepsilon_{33} = -0.25$ calculated using lattice parameters of the γ' phase and Cu matrix is understood in terms of the relaxation of ε_{33} by interfacial misfit dislocations.

Introduction

In a previous paper [1], we 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 on the Cu matrix $\{100\}_\alpha$ in single crystals of a Cu–0.9 wt% Be alloy. 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. We have also shown that the G.P. zones transform continuously to the following γ" phase during aging. It is generally accepted that the precipitation sequence during aging of Cu–Be alloys is G.P. zone $\rightarrow$ γ" $\rightarrow$ γ' $\rightarrow$ γ [2]. In addition, from an analysis of length-change measurement results, the misfit strains of the GP zone and γ" precipitate in directions parallel and perpendicular to the plate plane have been estimated.

In this work, the γ" to γ' transformation process is examined by high-resolution TEM (HRTEM) using a Cu–0.9 wt% Be single crystal containing only the G.P. zones perpendicular to the stress axis [001]. In addition, length-change measurements are undertaken to evaluate the misfit strains of γ' precipitates.

Experimental Details

Sheet-shaped single crystals, 2 mm thick, of a Cu–0.9wt%Be alloy were grown in a graphite crucible by the Bridgman method using a seed crystal. The surface of the single crystals was parallel to the (100) plane. Specimens with compressive axis along [001] were spark cut from the single crystals. The specimens had a cross-section of 2 mm $\times$ 4 mm and a length of 5 mm. All the specimens were solution treated at 820 °C for 2 h, quenched into water and subsequently aged at 200 °C for 120 h under a compressive stress of 50 MPa (stress aging). The stress aging produced the disk-shaped G.P. zones alone perpendicular to the [001] axis [1]. The stress-aged specimens were then aged at 275 °C for various times under no stress (free aging).

Length changes on aging were examined by measuring with a micrometer the distance between two scribed marks, about 4 mm apart. An X-ray analysis was performed to measure the lattice constants of the solution-treated and aged specimens. Thin foils for TEM observations were prepared by a standard electropolishing method. Microscopy was carried out using a HITACHI

H-9000NAR microscope operating at 300 kV.

Results and Discussion

γ" to γ' Phase Transformation. Figure 1(a) depicts a HRTEM image and a corresponding selected-area diffraction pattern (SADP) of the specimen, stress-aged at 200 °C for 120 h and then free-aged at 275 °C for 24 h. Fig. 1(b) is a magnified view of a precipitate with a five-layer structure of Be atoms separated by four matrix layers parallel to $(001)_\alpha$ in the same specimen. These HRTEM images were obtained with an incident beam parallel to the $[110]_\alpha$ direction. Intensity maxima in the streaks along the <002>$_\alpha$ direction in the SADP are seen near the 2/3{002}$_\alpha$ and 1/2{202}$_\alpha$ reciprocal- lattice positions. These are a feature of γ" precipitates [2]. In the five-layer precipitate of Fig. 1(b), lattice fringes parallel to the $(1\bar{1}0)_\alpha$ planes are visible. The average spacings between the lattice fringes parallel to $(1\bar{1}0)_\alpha$ and between the five layers of Be atoms were measured as 0.254 nm and 0.323 nm, respectively. The angle α between the five Be-layers and the lattice fringes was 86.8° on average. These measured values are in good agreement with the lattice parameters of a=b=0.253 nm and c=0.324 nm and α=85.4° for a body-centered tetragonal (bct) lattice, proposed as the crystal structure of γ" by Geisler *et al*. [3]. It is also apparent that the γ" phase does not independently nucleate but consecutively transform from the G.P. zones during aging, because all G.P. zones and γ" precipitates were perpendicular to the $[001]_\alpha$ axis.

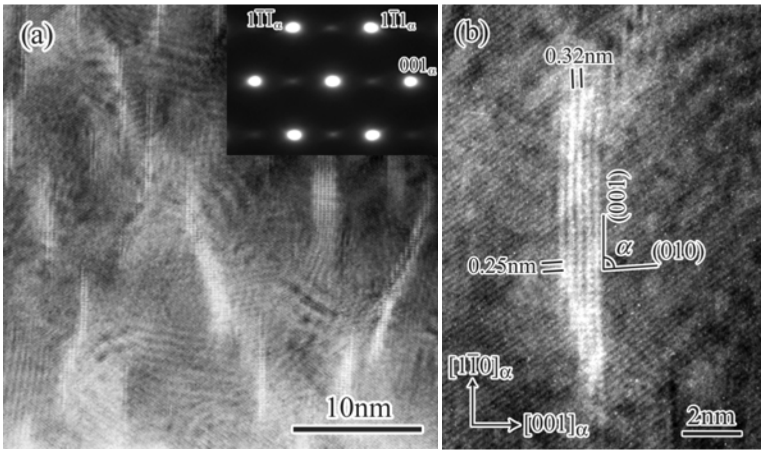

Fig. 1 (a) HRTEM image and corresponding $[110]_\alpha$ SADP of the specimen, compressive-stress-aged at 200°C for 120 h and then free-aged at 275°C for 24h. (b) Magnified image of a five-layer γ" precipitate in the same specimen.

Figure 2 shows a HRTEM image of a precipitate and a corresponding $[110]_\alpha$ SADP in the specimen, stress-aged and free-aged at 275 °C for 144 h. The precipitates were composed of about one hundred layers of Be atoms and were divided into two portions, upper major and lower minor portions, as shown in Fig. 2. Measurements on the spacings and angle of the precipitate {100} lattice fringes in the major portion of the precipitates yield b=c=0.269 nm and α=90° on average. Geisler *et al*. [3] reported the γ' phase of a bct lattice with a=0.254 nm and b=c=0.268 nm. Also, the {113}$_\alpha$ habit plane was observed, as shown in Fig. 2. On the other hand, analyses of the lattice fringes in the minor portion, consisting of about ten Be-layers reveal that the minor portion has b=0.251 nm, c=0.353 nm and α=90°. Gruhl and Wassermann [4] reported a bct phase which they called γ', with a=b=0.250 nm and c=0.354 nm. This phase is termed γ_I in the present study. The γ_I phase is not stable and no longer observed after aging at 275°C for 800 h. As shown in Fig. 1(b) or 2, the Bain orientation relationship is satisfied between the γ" or γ_I phase and the Cu matrix: $(001)_\alpha$ // $(001)_{\gamma" \text{ or } \gamma_I}$; $[110]_\alpha$ // $[100]_{\gamma" \text{ or } \gamma_I}$.

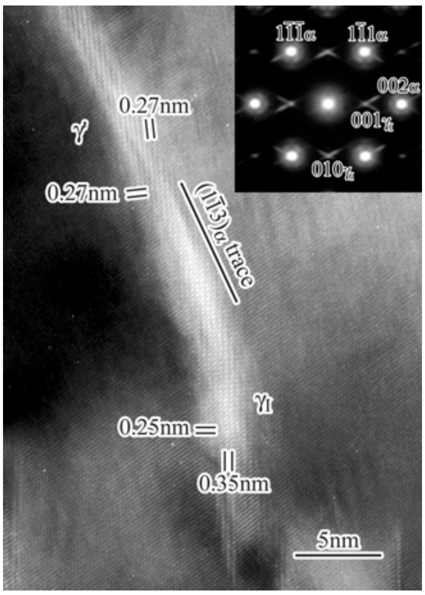

Fig. 2 HRTEM image of a precipitate in the specimen, stress-aged and then free-aged at 275°C for 144 h.

All plate-shaped γ" and γ_I precipitates were perpendicular to the $[001]_\alpha$ stress axis. Therefore, the structure of the γ" phase continuously changes into that of the γ_I. The γ" to γ_I transformation was complete prior to the appearance of γ’. It is thus apparent from Fig. 2 that the γ’ phase does not independently nucleate but heterogeneously precipitates on the γ_I phase.

Analyses of the dark-field micrographs taken with some reflections of the γ’ phase in the $[110]_\alpha$ and $[1\bar{1}0]_\alpha$ SADPs revealed that the γ’ precipitates exhibited the orientation relationship, $(1\bar{1}3)_\alpha // (0\bar{1}3)_{\gamma'}$; $[110]_\alpha // [100]_{\gamma'}$, $(1\bar{1}\bar{3})_\alpha // (0\bar{1}\bar{3})_{\gamma'}$; $[110]_\alpha // [100]_{\gamma'}$, $(113)_\alpha // (103)_{\gamma'}$; $[1\bar{1}0]_\alpha // [0\bar{1}0]_{\gamma'}$ or $(11\bar{3})_\alpha // (10\bar{3})_{\gamma'}$; $[1\bar{1}0]_\alpha // [0\bar{1}0]_{\gamma'}$, to the matrix [2]. There existed four variants in the present work. In the relationship, one directional parallelism has four planar parallelisms as represented. Since there are three independent directional parallelisms, the orientation relationship has twelve variants in total. Therefore, the orientations of the γ’ phase originate from that of the γ_I phase.

Misfit Strains of γ’ Phase. Figure 3 shows the elongations, plotted as a function of aging time, along the [001] stress axis for the specimen, free-aged at 200 °C up to 120 h and then free-aged at 275 °C, and along the [001] and [010] directions for the specimen, stress-aged at 200 °C up to 120 h and then free-aged at 275 °C. The elongation along [010] or [001] for the stress-aged specimen increases or decreases up to 120 h. The raising of the temperature from 200 to 275 °C causes initially a rapid increase or decrease in the elongation along [010] or [001] for the stress-aged specimen, and then the elongation along each direction remains almost constant. There existed the G.P. zones or γ” precipitates parallel to (001) in the specimens aged at 200 or 200 and 275°C up to 48 h, and primarily γ’ precipitates in the stage of constant elongation. On the other hand, the elongation of the specimen, free-aged at 200 and 275 °C slightly increases with time.

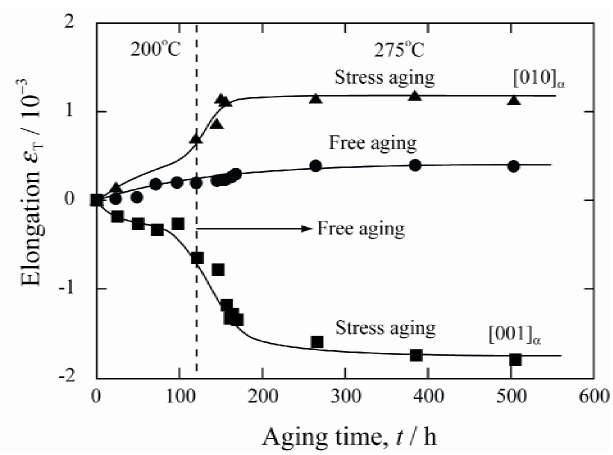

Fig. 3 Change in the specimen elongation during free aging and stress aging at 200°C up to 120h, and during subsequent free aging at 275°C.

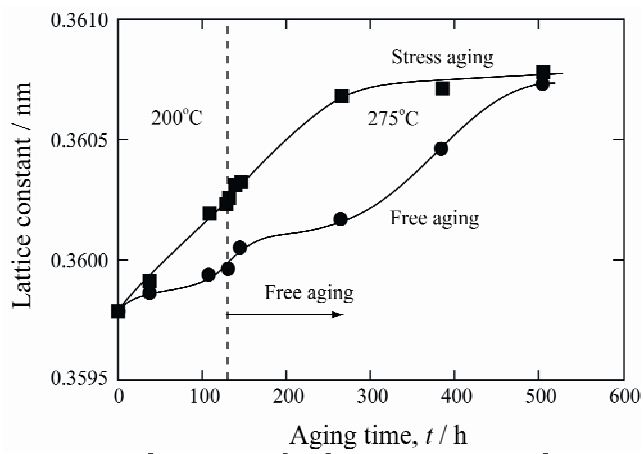

Fig. 4 Change in the lattice constant during free aging and stress aging at 200°C up to 120h, and during subsequent free aging at 275°C.

As in our previous study [1], the misfit strain ε_{ij} of the GP zone, lying parallel to $(001)_\alpha$, is assumed to have components of ε_{33} and $\varepsilon_{11}=\varepsilon_{22}$ from symmetry consideration. When the volume fraction of precipitates is f, the elongation ε_T of the stress-aged specimen along the [001] or [010] direction is written as [1]

$$\varepsilon_T = f\,\varepsilon_{33 \text{ or } 22} + (1-f)\,\varepsilon_a, \tag{1}$$

where ε_a is the dimensional change due to the loss of Be solute atoms from the solid solution. The elongation of the free-aged specimen is given as [1]

$$\varepsilon_T = f(\varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33})/3 + (1-f)\,\varepsilon_a. \tag{2}$$

This equation shows that there is no anisotropy in the elongation. The elongations along several directions on $(100)_\alpha$ of the free-aged specimen, containing the G.P. zones, γ” precipitates or γ’ precipitates, were measured. The measured values of ε_T for each specimen were identical within experimental error, indicating that if the shear components of ε_{ij} exist, they may be negligibly small.

The lattice constants of the solution-treated, free-aged and stress-aged specimens were determined from an X-ray analysis, as shown in Fig. 4. Using values of ε_a and f obtained from these values, the values of ε_{11}, ε_{22} and ε_{33} for the incoherent γ' precipitate are estimated as –0.03, –0.03 and –0.09 on average from Eqs. (1) and (2). These values are considerably identical to those of $\varepsilon_{11} = \varepsilon_{22} = -0.01$ and $\varepsilon_{33} = -0.11$ for the coherent γ" precipitate [1]. As mentioned above, the γ' precipitates exhibited the orientation relationship with the matrix: $(1\bar{1}3)_\alpha // (0\bar{1}3)_{\gamma'}$; $[110]_\alpha // [100]_{\gamma'}$. There were four variants of possible twelve ones. The elongation was measured along the $[001]_\alpha$ or $[010]_\alpha$ direction, which is parallel to four $<018>_{\gamma'}$ or four $<881>_{\gamma'}$ directions of the four variants. Usage of the lattice constants by Geisler *et al*. [3] gives $\varepsilon_{33} = -0.25$ and $\varepsilon_{11} = \varepsilon_{22} = -0.03$. The absolute value of ε_{33} is much larger than that of $\varepsilon_{33} = -0.09$ obtained from length-change measurements. Apparently, the misfit strain ε_{33} in $[001]_\alpha$ is released.

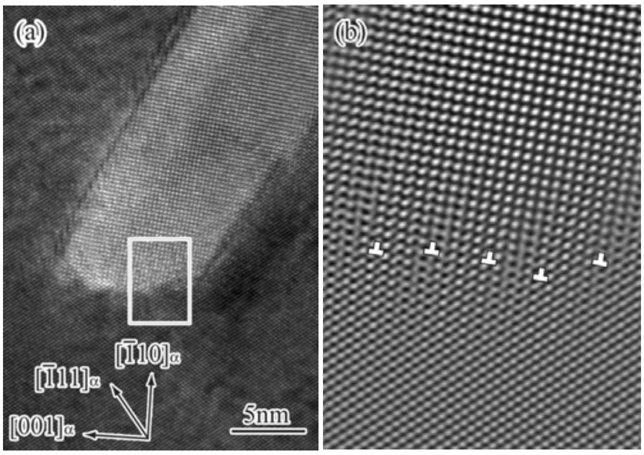

Fig. 5 (a) HRTEM image of a γ' precipitate in the specimen, free-aged at 275°C for 500 h after stress aging. (b) Enlarged HRTEM image of the outlined frame in (a) after noise filtering by means of fast Fourier transformation and inverse fast Fourier transformation.

Figure 5(a) presents a HRTEM image of the edge of a γ' precipitate in the specimen, free-aged at 275°C for 500h after stress aging. Fig. 5(b) is an enlarged image of the outlined frame in (a) after noise filtering by fast Fourier transformation and inverse fast Fourier transformation. The $[001]_{\gamma'}$ and $[001]_\alpha$ directions are nearly parallel. Misfit dislocations with a Burgers vector $\boldsymbol{b}=[001]_{\gamma'}$ observed at the interface between the γ' precipitate and the Cu matrix are spaced approximately five $(001)_{\gamma'}$ spacings of γ' apart, namely on average, five $(001)_{\gamma'}$ spacings on the γ' phase side of the interface are matched with four $(001)_\alpha$ spacings on the Cu side of the interface. The misfit strain in $[001]_\alpha$ should be relieved by the misfit dislocations. The averaged misfit strain ε_A in $[001]_\alpha$ after relaxation is given as $\varepsilon_A = (5d_{\gamma'} - 4d_\alpha) / [(5d_{\gamma'} + 4d_\alpha)/2] \approx -0.07$. Interestingly, this value is close to $\varepsilon_{33} = -0.09$ from length-change measurements. Here d_γ and d_α are the $(001)_{\gamma'}$ spacing (=0.268 nm) and $(001)_\alpha$ spacing (=0.361 nm), respectively.

Summary

The G.P. zone to γ' precipitation processes in a Cu–0.9wt%Be alloy single crystal containing only the G.P. zones parallel to the matrix $(001)_\alpha$ plane have been examined. The precipitation sequence found was: G.P. zone → γ" → γ_I + γ'. The γ_I phase continuously transformed from the G.P. zones via γ", whereas the heterogeneous formation of γ' occurred on the γ_I phase. An analysis of length-change measurement results revealed that the misfit strains of the γ' precipitate in $[100]_\alpha$, $[010]_\alpha$ and $[001]_\alpha$ are $\varepsilon_{11} = \varepsilon_{22} = -0.03$ and $\varepsilon_{33} = -0.09$. The absolute value of ε_{33} is much smaller than that of $\varepsilon_{33} = -0.25$ calculated from lattice parameters of the γ' phase and the Cu matrix. This result is understood through the relaxation by interfacial misfit dislocations.

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