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Precipitation Process in a Cu-Ni-Be alloy

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Abstract. The precipitation process in an aged Cu-1.9wt%Ni-0.3wt%Be alloy has been examined by high-resolution transmission electron microscopy. The precipitation sequence found is: Gunier-Preston (G.P.) zones → γ'' → γ' → stable γ. The disk-shaped G.P. zones and the disk-shaped γ'', γ' and γ precipitated phases are composed of monolayers of Be atoms on $\{100\}_\alpha$ of the Cu matrix and alternative Be and Ni matrix layers parallel to $\{100\}_\alpha$. The γ'' phases consisting of two to eight Be-layers has a body-centered tetragonal (bct) lattice with a=b=0.24 nm and c=0.28 nm. The γ' or γ phase is bct with a=b=0.24 nm and c=0.26 nm or a=b=0.26 nm and c=0.27 nm. The γ'', γ' or γ phase aligns with the matrix according to the Bain orientation relationship. The growth kinetics of disk-shaped γ precipitates on aging at 500°C has been also investigated. The $\{001\}_\alpha$ habit planes of the γ precipitates migrate by a ledge mechanism. The average thickness of the γ disks increases with aging time t as $t^{1/2}$. An analysis of experimental data using a kinetic model yields the diffusivity of solute in the Cu matrix, which is in agreement with the reported diffusivity of Ni in Cu.

Introduction

The precipitation behavior in Cu-Be binary alloys have been extensively investigated [1-4]. It is recognized that, in this alloy system, the precipitation sequence from the supersaturated solid solution (α) includes four stages: Gunier-Preston (G.P.) zones → γ'' → γ' → γ. The G.P. zones are composed of disk-shaped monolayers of Be atoms parallel to $\{100\}_\alpha$ of the Cu-rich matrix. The metastable γ'' or γ' phase or the stable γ phase has a CuBe structure consisting of alternative Be and Cu matrix layers [4]. The G.P. zones and the γ'', γ' and γ phases have been characterized by X-ray diffraction [1], transmission electron microscopy (TEM) [2, 3] and high-resolution TEM (HRTEM) [4]. In the precipitation sequence in Cu-Ni-Be alloys also, it is accepted that the sequence may include the same four stages [5, 6]. Guha [6] has reported, by X-ray diffraction, that the stable γ phase is a NiBe intermetallic and has a body-centered tetragonal (bct) lattice with a=b=0.26 nm and c=0.27 nm. It is generally recognized that the G.P. zones are similar to those in the Cu-Be system, and the metastable γ'' or γ' phase is the nickel-beryllide, similar to the structure of γ'' or γ' in the Cu-Be system [6, 7]. However, the structure, morphology and crystallography of the metastable precipitated phases have not been clarified yet. The aim of this work is to investigate the precipitation behavior in an aged Cu-1.9wt%Ni-0.3wt%Be alloy in detail by HRTEM. In addition, the growth mechanism and kinetics of γ precipitates are examined.

Experimental Procedure

A Cu-1.9wt%Ni-0.3wt%Be alloy (Ni : Be = 1 : 1 in atomic ratio) was prepared by casting in an Argon atmosphere from Cu (purity, 99.99%), a Cu-30wt%Ni mother alloy and a Cu-3.81 mass% Be mother alloy. The alloy ingots were homogenized at 900 °C for 24 h in a vacuum and then cold-rolled to 50% reduction in thickness. The cold-rolled alloy sheets were solution-treated at 1000 °C for 8 h in the vacuum and quenched into cold water. The specimens were then aged at the temperatures ranged from 375 to 575 °C for various times in the Argon atmosphere. A part of specimens were directly quenched into a salt bath with 500°C from the solution-treating temperature, and then aged at 500°C.

Thin foils for TEM observations were prepared by slicing the aged specimens with a spark cutter and by electropolishing using a solution of 50% methanol and 50% nitric acid at -25^{o}C and 6.5 V in a twin-jet electropolisher. HRTEM and TEM observations were carried out in a JEOL 2010FEF microscope and a JEOL 2000EX microscope operated at 200 kV. HRTEM images were taken with the objective lens at or near to Scherzer defocus. Small variations in the defocus did not significantly affect the appearance of lattice fringes of precipitates.

Results and Discussion

Structure and crystallography of precipitates. Aging of the Cu-Ni-Be alloy produced so-called G.P. zones first. As seen in Fig. 1, the G.P. zones are composed of disk-shaped monolayers of Be atoms on $\{100\}_\alpha$, similar to the G.P. [I] zones in the Al-Cu system [8] and the G.P. zones in the Cu-Be system [4]. The number of Be-atom layers increased as precipitates grew. Figure 2(a) shows a HRTEM image of a precipitate, taken along the zone axis parallel to $[110]_\alpha$. The precipitate has a two Be-layer structure separated by a Ni layer parallel to $(001)_\alpha$. Figure 2(b) is the selected area diffraction pattern (SADP) corresponding to (a). Intensity maxima in the streaks along the $[001]_\alpha$ 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 in Cu-Be alloys, according to Rioja and Laughlin [3]. In the two Be-layer precipitate of Fig. 2(a), lattice fringes parallel to the $(1\bar{1}0)_\alpha$ plane is faintly visible. The average spacings between the lattice fringes parallel to $(1\bar{1}0)_\alpha$ and $(001)_\alpha$, corresponding to $(010)_p$ and $(001)_p$ of the precipitated phase, were measured as b=0.244±0.08≈0.24 nm and c=0.282±0.12≈0.28 nm, respectively. Measurements of the precipitates reflections near the $1/2\{202\}_\alpha$ reciprocal-lattice positions in the Fig. 2(b) yielded almost the same value of 0.24 nm. A similar analysis of HRTEM images taken along the $[1\bar{1}0]_\alpha$ zone axis yielded the spacings of $(100)_\alpha$ ($//(110)_\alpha$) and $(001)_p$ ($//(001)_\alpha$), namely, a≈0.24 nm and c≈0.28 nm. About fifty precipitates viewed along the $[110]_\alpha$ or $[1\bar{1}0]_\alpha$ zone axis were examined. The angle α or β between the $(010)_p$ and $(001)_p$ or the $(100)_p$ and $(001)_p$ planes was nearly 90^{o} on average. The above measured values are similar to the lattice parameters of a=b=0.253 nm and c=0.29 nm for a bct lattice, having a Be atom at the body center, proposed as the crystal structure of γ" in a Cu-Be alloy by Shimizu *et al.* [2]. The multi-slice HRTEM image simulations of the G.P. zone and γ" phase were conducted. The structure of the γ" phase used for the simulation is based on this work. The parameters used were: high voltage HV=200 kV, spherical aberration C_s=1.0 mm, beam convergent semi-angle α=0.3 mrad and slice thickness=0.3 nm. The experimental and simulated images were in agreement with each other for the variation in the amount of defocusing. The simulated images of the G.P. zone and γ" phase obtained with specimen thickness t=20 nm and Scherzer defocus Δf=-60 nm are exemplified in the Fig. 1 and Fig. 2(a).

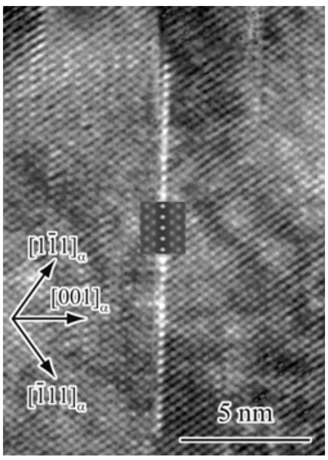

Fig. 1 HRTEM image of a G. P. zone in a Cu-Ni-Be alloy aged at 300^{o}C for 375 h. The

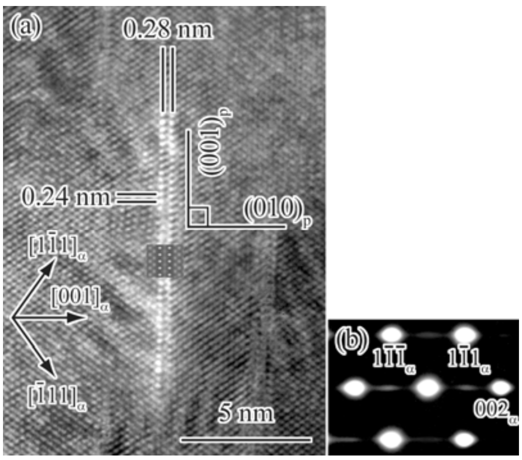

Fig. 2 (a) HRTEM image of a γ" precipitate in a Cu-Ni-Be alloy aged at 400^{o}C for 24 h. (b) $[110]_\alpha$

zone axis is along $[110]_\alpha$. SADP corresponding to (a).

In the alloy aged at 400°C for 24 h and then aged at 550°C for 50 h, nearly disk-shaped precipitates, consisting of about ten to sixteen Be-layers, parallel to $\{100\}_\alpha$ were observed. Figures 3(a) and (b) depict a HRTEM image of a twelve Be-layer precipitate parallel to $(001)_\alpha$ and a $[110]_\alpha$ SADP of the region containing the precipitate. Analyses of the HRTEM image and the $[110]_\alpha$ SADP gave a=0.242±0.03≈0.24 nm, c=0.263±0.04≈0.26 nm and $\alpha=\beta=90^\circ$. When the disk-shaped precipitates parallel to $(001)_\alpha$ were viewed along the $[001]_\alpha$ zone axis, they were too thin to be detected. However, their extra reflections were observable, as depicted in the $[001]_\alpha$ SADP of Fig. 3(c). The precipitate reflections yield $a=b$≈0.24 nm and γ=90°. Here γ is the angle between the a and b axes. Geisler *et al.* [1] reported the γ' phase with a bct lattice with a=0.254 nm and $b=c$=0.279 nm in a Cu-Be alloy.

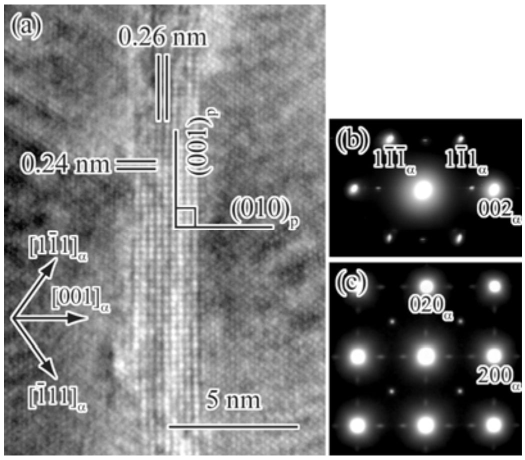

Fig. 3 (a) HRTEM image of a γ' precipitate in a Cu-Ni-Be alloy aged at 400°C for 24 h and then 550°C for 50 h. (b) $[110]_\alpha$ SADP corresponding to (a). (c) SADP taken from $[100]_\alpha$.

In the specimen, aged at 400°C for 24 h, 550°C for 50 h and then 575°C for 90 h, disk-shaped precipitates being composed of twenty four layers of Be atoms and more were observed. The precipitates consists of alternative Be and Ni matrix layers parallel to $\{100\}_\alpha$. Analyses of HRTEM images and $[110]_\alpha$ and $[001]_\alpha$ SADPs in the specimen revealed that the precipitates had a bct lattice with $a=b$=0.264±0.04≈0.26 nm and c=0.271±0.05≈0.27 nm. This structure is in agreement with the structure of the stable γ phase (NiBe intermetallic) in Cu-Ni-Be alloys, reported by Guha [6].

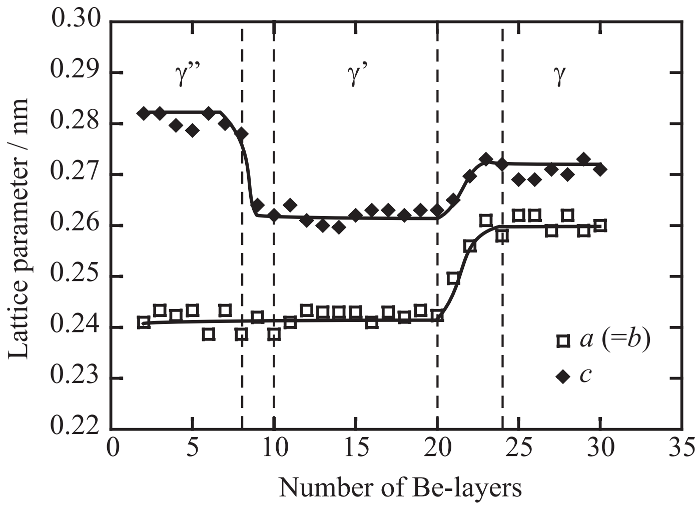

Fig. 4 Change in the lattice parameters of precipitated phases, a (= b) and c, with the number of Be atom layers.

Figure 4 presents the lattice parameter values of $a=b$ and c as a function of the number of Be-atom layers. In this study, the precipitated phase which has two to eight Be-layer, ten to twenty Be-layers or twenty four Be-layers and more is termed γ'', γ' or γ. As shown in Figs. 2 and 3, the γ'', γ' and γ phases exhibited the Bain orientation relationship to the Cu matrix: $(001)_\alpha$ // $(001)_p$; $[110]_\alpha$ // $[100]_p$.

Growth of disk-shaped γ precipitates. The specimens, solution-treated at 1000°C for 8h, were directly quenched into a salt bath heated to 500°C and then aged at the temperature. In this case, the stable γ phase directly nucleated from the solid-solution without precipitation of the metastable G.P.

zones and γ'' and γ' phases. A HRTEM observation of the broad faces of γ disks revealed the presence of small coherent ledges [9]. Figures 5 (a) and (b) show the coherent ledges observed on the face of a γ precipitate and its schematic illustration. The coherent ledges had a height of 0.27 nm, which matches the spacing of $(001)_p$ of the γ phase, d_p=0.27 nm. When the lattice parameter of 0.3615 nm for pure Cu is taken as the $(001)_\alpha$ spacing d_α, each coherent ledge produces a negative misfit of $(d_p - d_\alpha) / [(d_p + d_\alpha) / 2] \approx -0.29$. According to Fonda *et al.* [9], to reduce the overall misfit strain produced by the coherent ledges, the coalescence of coherent ledges takes place, resulting in a taller ledge containing misfit dislocations, which is called the misfit-compensating ledge. As γ precipitates grow, such misfit compensating-ledges were observed on the γ precipitates, as exemplified in Fig. 6. At the ledge in Fig. 6(a), six $(001)_p$ spacings on the γ phase side of the interface are matched with five $(001)_\alpha$ spacings on the Cu side of the interface. The average misfit strain associated with the ledge is given by $(6d_p - 5d_\alpha) / [(6d_p + 5d_\alpha) / 2] \approx -0.11$. This value is much smaller than the misfit strain of -0.29 produced by the coherent ledges.

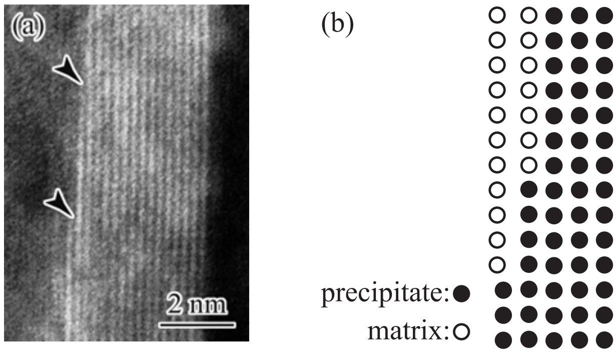

Fig. 5 (a) HRTEM image showing ledges on the side face of a γ precipitate in a Cu-Ni-Be alloy aged at 500°C for 1h. The height of the ledge corresponds to the $(001)_p$ spacing. (b) Enlarged schematic illustration of (a).

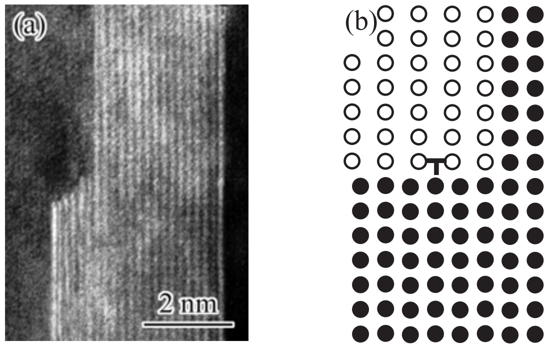

Fig. 6 (a) HRTEM image showing a ledge on the side face of a γ precipitate in a Cu-Ni-Be alloy aged at 500°C for 50h. The height of the ledge corresponds to the six $(001)_p$ spacings. (b) Enlarged schematic illustration of (a).

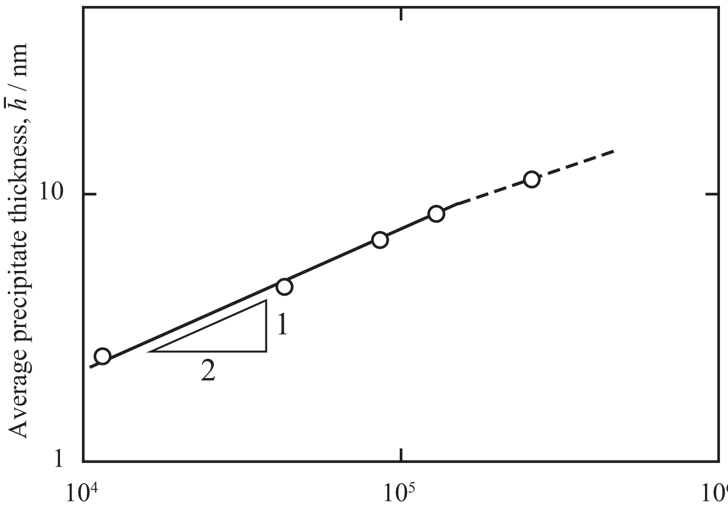

Fig. 7 Change in the average precipitate thickness $\bar{h}$ with aging time t for a Cu-Ni-Be alloy aged at 500°C. A solid line with slope 1/2 is superimposed.

The thickness h of γ disks was measured as a function of aging time t from TEM images of the plates in the edge-on orientation. Figure 8 displays the variation in average thickness $\bar{h}$ with t on logarithmic scales. In the early stage of aging, a liner relationship exists between log $\bar{h}$ and log t. The slope of the straight line was obtained by the least-squares method. The result shows that the thickening kinetics of γ disks follows a diffusion-controlled parabolic growth law:

$$\bar{h} = Kt^{1/2}, \tag{1}$$

where K is the parabolic rate constant and expressed as [10]

$$\frac{K}{2\sqrt{D}} \exp\left(\frac{K^2}{4D}\right) \operatorname{erf}\left(\frac{K}{2\sqrt{D}}\right) = \frac{\Omega}{\sqrt{\pi}}, \tag{2}$$

where D is the diffusion coefficient of solute atoms and Ω is the supersaturation of solute atoms (0.04 at 500°C for the present alloy). Using the experimentally obtained value of K, solving equation (2) numerically yields the value of D = 2.3 x 10^{-20} m^2s^{-1}. This value is relatively close to the reported diffusivity of Ni in Cu at 500°C, 5.3 x 10^{-20} m^2s^{-1} [11] but much smaller than that of Be in Cu at 500°C, 3.4 x 10^{-18} m^2s^{-1} [11]. It is thus concluded that the diffusion of Ni in the Cu matrix is the rate-controlling step for growth of the γ precipitates.

Summary

(1) The precipitated phases in a Cu-1.9wt%Ni-0.3wt%Be alloy follow a G. P. zone → γ'' → γ' → γ sequence. The disk-shaped G.P. zones and the disk-shaped γ'', γ' and γ phases are composed of monolayers of Be atoms and alternative Be and Ni matrix layers, parallel to $\{100\}_\alpha$ of the Cu matrix, respectively. The γ'' phases consisting of two to eight Be-layers has a body-centered tetragonal (bct) lattice with *a*=*b*=0.24 nm and *c*=0.28 nm. The γ' or γ phase is bct with *a*=*b*=0.24 nm and *c*=0.26 nm or *a*=*b*=0.26 nm and *c*=0.27 nm. The γ'', γ' or γ phase exhibits the Bain orientation relationship to the Cu matrix: $(001)_\alpha$ // $(001)_p$; $[110]_\alpha$ // $[100]_p$.
(2) Small coherent ledges were observed at the face of γ disks. The height of the coherent ledges is about 0.27 nm, which is in agreement with the $(001)_p$ spacing of the γ phase. The coherent ledges tend to coalesce to form a taller ledge containing a misfit dislocation.
(3) The thickening of γ disks occurs with parabolic growth kinetics. A kinetic analysis of experimental data using the growth model by Chen *et al.* [10] shows that the thickening of γ disks is controlled by the Ni diffusion in the Cu matrix.

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