CHARACTERIZATION OF AGING BEHAVIOR OF PRECIPITATES AND DISLOCATIONS IN COPPER-BASED ALLOYS

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ABSTRACT

The growth of precipitates in a deformed Cu–Ni–Si alloy with an aging treatment and the rearrangement of dislocations were investigated using X-ray scattering methods. A small angle X-ray scattering (SAXS) method was used for characterizing the growth behavior of the precipitates with aging. The results showed that the precipitates grew gradually to a few nanometers in radius in the alloy aged under the condition that the alloy exhibited a maximum of the hardness due to precipitation hardening. The growth rate was prompted by the onset of the over aging, where the hardness starts to decrease. The line profile analysis of copper diffractions using modified Williamson-Hall and modified Warren-Averbach procedures yielded a variation in the dislocation density of the alloy as a function of the aging time. The dislocation density of the alloy before the aging treatment was estimated to be $1.7 \times 10^{15}$ m$^{-2}$, and its high value was held up to the peak-aging time. With the onset of the over aging, however, the dislocation density distinctly decreased by about one order, indicating that a large amount of the dislocation rearranged to release the alloy from the high dislocation-density state. It may be concluded that the massive rearrangement of dislocations was accompanied with coarsening of the precipitates.

INTRODUCTION

Copper matrix alloys have been extensively used for electronic parts because of their high performance of electrical conductivity and mechanical strength. The highly-dispersed nano-scale precipitates, which are formed by an adequate aging treatment, give the alloy a high mechanical performance. On the other hand, the strength is decreased by an over-aging treatment where precipitates are coarsened. It has been reported that the peak-aging time, when the maximum strength is obtained, is shortened by a cold-rolling treatment prior to the aging treatment: (Huang et al., 2003; Markandeya et al., 2005). The cold rolling treatment is essential to introduce crystal defects as a nucleation site of the precipitates. However, the shortened aging time is not necessarily favorable for obtaining a high electrical property because dissolved elements in the alloy, which generally decrease the electrical conductivity of the alloys, should be precipitated in the copper matrix. Thus, the knowledge on the correlation between the growth behavior of precipitates and crystal defects, in particular dislocations, in the copper matrix is indispensable.

A small angle X-ray scattering (SAXS) method can be a powerful tool for quantitative characterization of the growth behavior of the precipitates in the copper alloys. Our previous study using the SAXS method has suggested that a cold-rolling treatment prior to the aging treatment can stimulate coarsening of the precipitates: (Takahashi et al., 2007). This result indicates a high dislocation density induced by the cold-rolling treatment could have effects on...
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the growth behavior of the precipitates. In order to validate this correlation between the growth behavior of precipitates and the dislocation of the copper matrix, the dislocation density must be estimated quantitatively. Dislocations in a crystal are generally observed with an electron microscope and the characters of dislocations are discussed on the basis of the results. However, it becomes difficult to characterize dislocations under the existence of highly-populated precipitates using the direct observation method, which prompts us to apply the X-ray diffraction (XRD) line-profile analysis for characterizing dislocations. The dislocation density can be estimated by careful analysis of diffraction profiles by the modified Williamson-Hall and modified Warren-Averbach methods: (Ungar. and Borbely, 1996).

In this study, the microstructural evolution of a Cu-Ni-Si alloy with the aging time is investigated by the SAXS method and the XRD line profile analysis. On the basis of the structural data, the correlation between the growth behavior of the precipitates and changes of the dislocation density are characterized.

EXPERIMENTAL

The alloy used in this study was a high-purity Cu–Ni (2.47wt%–Si (0.58wt%). The detailed preparation method of these alloys was reported elsewhere: (Suzuki et al., 2006). The alloy was prepared from high purity 6N (99.9999%) copper, 4N nickel and 6N silicon with a plasma arc melting method. A solution treatment at 1173 K for 10^4 s and a subsequent cold rolling by 50% were made, and the alloy was then isothermally aged at 720 K. Figure 1 shows the Vickers hardness of this alloy as a function of the aging time. The hardness rose up to about 5 ks and kept until 10 ks, and then dropped at the aging time of 20 ks. Thus, the peak age condition of this alloy lies around the aging times from 5 ks to 10 ks.

The SAXS measurement was performed using a commercial apparatus (NanoStar, Bruker AXS) equipped with a two-dimensional position sensitive proportional counter. The incident X-ray of Cu Kα was monochromated with a cross-coupled Gōbel mirror and subsequently collimated by three pin holes. The distance between a sample to the counter was 870 mm to cover the range of the scattering vector \( q = 4\pi \sin(\theta/2)/\lambda \) up to 3.0 nm\(^{-1}\), where \( \lambda \) is the wavelength of the X-ray, \( 2\theta \) the scattering angle. Since the background scattering derived from surface imperfections and crystal defects overlaps with the SAXS profile from precipitates, their background contribution was subtracted from the measured scattering profiles using a non-aged sample. The size distribution of precipitates formed in the alloy was obtained from a distance distribution function (DDF), which was calculated from a SAXS profile using the indirect Fourier transform method: (Popela and Glatter, 1997). A DDF gives a relative number of distances of two points inside a particle as a function of the distance \( r \).

The XRD measurement was made by a conventional X-ray diffractometer system.
Diffraction profiles were measured with a Cu Kα radiation in Bragg-Brentano geometry. After eliminating the Kα2 component and subtracting the background from the measured profiles, the treated profiles were fitted to the pseudo-Voight function. The resulting profile was extracted from this fitted function by the Stokes-deconvolution method: (Stokes, 1948) using a diffraction profile of a standard reference material LaB₆ marketed by NIST. The Fourier coefficient was obtained from this estimation.

RESULTS AND DISCUSSION

Figure 2 shows SAXS profiles, which were corrected by subtracting the SAXS profile of the non-aged sample, at various aging times. The humps appearing in the SAXS profiles shifted to low-q values with an increase in the aging time, suggesting the growth of the precipitates. The calculation fit to the experimental data gave the DDF of the precipitates, and the average radius of the precipitates was estimated from the DDF as shown in Fig. 3 to represent the average size of the precipitates. The precipitates grew gradually to a few nanometers in radius up to an aging time of 10 ks, which roughly corresponds to the peak aged condition. After the aging time of 10 ks, the radius of the precipitates markedly increased from an aging time of 20 ks. This significant coarsening of the precipitates is likely to be due to the Ostwald ripening, inducing the decrease in the number density of the precipitates. Therefore, the drop of the Vickers hardness at the aging time of 20 ks can be ascribed to this drastic coarsening of the precipitates.

In order to investigate the effect of the dislocation in the copper matrix on the growth behavior of the precipitates, the diffraction line profiles of the copper matrix were evaluated. Williamson and
Hall suggested that the FWHM ($\Delta 2\theta$) of a line profile can be expressed as the sum of the two broadening effects: (Williamson and Hall, 1953):

$$\Delta K = 0.9/D + 2\varepsilon \sin(2\theta/2)/\lambda, \quad (1)$$

where $D$ and $\varepsilon$ is an apparent crystallite size and strain, respectively. $\Delta K$ is experimentally determined:

$$\Delta K = \Delta 2\theta \cos(2\theta/2)/\lambda. \quad (2)$$

According to Eqs. (1) and (2), the strain contribution becomes larger for diffraction at higher diffraction angles. Therefore, it is expected that 111 and 420 diffractions of copper can be differently influenced by the strain in the copper lattice. Figure 4 shows variations in the FWHM of the 111 and 420 diffraction lines as a function of the aging time, which were observed at about 43.3° and 144.8°, respectively. The values of the FWHM are estimated from the experimental diffraction peaks which were corrected by subtracting the $K\alpha_2$ component. The FWHM of the 111 diffraction, which is less influenced by the lattice strain, decreased immediately from the start of the aging treatment, indicating the increase of the crystallite size of the copper crystal. On the other hand, the FWHM of the 420 diffraction showed only a slight decrease up to an aging time of 10 ks, and decreased from an aging time of 20 ks. These results imply that the strain in the copper crystal was reserved up to the peak aged condition (10 ks) and relaxed with the progress of the over-aging.

The FWHM of a physical profile was theoretically evaluated using the modified Williamson-Hall plot:

$$\Delta K = 0.9/D + \sqrt{\pi M^2 b^2/2 \cdot \rho \cdot \left(K\langle C\rangle^{1/2}\right)^2} + O\left(K\langle C\rangle^{1/2}\right)^2, \quad (3)$$

where $K = 2\sin(2\theta/2)/\lambda$, $\rho$ and $b$ are the dislocation density and the Burgers vector, respectively. $O$ stands for a higher order term in

![Figure 4. Changes of FWHM of (a) 111 and (b) 420 diffractions of copper as a function of the aging time.](image)

![Figure 5. The modified Williamson-Hall plot of the copper alloy at the several aging times.](image)
C is a dislocation contrast factor depending on the relative orientations between the Burgers and line vectors of dislocations and the diffraction vector. 

\[ H^2 = \left( \frac{(h^2k^2 + h^2l^2 + k^2l^2)}{h^2 + k^2 + l^2} \right) \]

where \( H \) is a parameter for \( \{hkl\} \) reflections in a cubic crystal, and \( q \) is an experimentally obtainable parameter depending on the character of dislocations in the crystal. In estimating \( \langle C_{\{h00}\} \rangle \), the three elastic constants, \( c_{11}, c_{12} \) and \( c_{44} \) in the cubic system are required. However, it is not possible to obtain these three elastic constants. On the other hand, it was reported that the value of \( \langle C_{\{h00}\} \rangle \) is around 0.3 from the theoretical consideration and was 0.304 for a pure copper: (Ungar et al., 1999). Therefore, the value of \( \langle C_{\{h00}\} \rangle \) for the present copper alloy including minor-alloyed elements can be approximated by the value for pure copper. Figure 5 shows the modified Williamson-Hall plot at several aging times. As expected from Fig. 4, the slope of the plot changed little up to the aging time of 10 ks and drastically decreased at the aging time of 20 ks. This suggests that a significant decrease in the dislocation density occurred with the onset of the over aging.

In order to estimate the dislocation density in the copper matrix, a further calculation of the line profiles was carried out using the modified Warren-Averbach method:

\[
\ln A(L) \equiv \ln A^5(L) - \left( \pi b^2 / 2 \right) \cdot \rho L^2 \cdot \ln(Rc / L) \left( K^2 \langle C \rangle \right) + O'(K^2 \langle C \rangle)^2,
\]

where \( R_c \) and \( L \) are the effective outer cut-off radius of dislocations and the Fourier length, respectively. \( O' \) stands for a higher order term in \( K^2 \langle C \rangle \). Using the dislocation contrast factors led from the modified Williamson-Hall plot, the modified Warren-Averbach plots were obtained as shown in Fig. 6. (only a couple of representative data sets are shown in the figure.) The plot for the sample aged for 20 ks (an over-aged sample) exhibited much smaller slope than that of the non-aged sample. This implies that the dislocation density for the over-aged sample decreased.
significantly in comparison to the non-aged sample. The dislocation density as a function of the aging time is shown in Fig. 7. Before the aging treatment, the alloy had a high dislocation density of $1.7 \times 10^{15}$ m$^{-2}$, which had been introduced by the cold-rolling treatment. The dislocation density varied with the aging time in accordance with the variation of the growth behavior of precipitates. That is, the dislocation density changed only a little up to the peak-aging time (10 ks) and dropped by one order at the start of the over-aged state (20 ks). This dependence of the dislocation density on the aging time clearly supports the mechanism, which suggested that the coarsening of precipitates is accompanied with the rearrangement of the dislocation in the copper matrix [3]. It should be noted that the dislocation density showed a mild decrease through a prolonged aging time more than 20 ks, implying that dislocations in the copper matrix exhibit stable configuration after the large variation at the aging time of 20 ks.

**Concluding remarks**

1. The SAXS analysis showed that the precipitates formed in the Cu–Ni–Si alloy grew gradually to the radius of a few nanometers by aging at 720 K up to an aging time of 10 ks, where the maximum hardness was obtained. A significant coarsening of the precipitates was caused by aging for more than 20 ks, where the hardness of the alloy started to decrease.

2. The copper alloy after a solution treatment and a subsequent cold rolling treatment had a high dislocation density of $1.7 \times 10^{15}$ m$^{-2}$. The high dislocation density was kept up to the peak-aging time (10 ks). The dislocation density, however, drastically decreased by about one order at the onset of the over aging (20 ks). It can be concluded that this drastic dislocation rearrangement promoted the coarsening of the precipitates.

**REFERENCES**


