SAXS and XAFS Characterization of Nano-Scale Precipitates in Copper-Base Alloys

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Analyses of small-angle X-ray scattering (SAXS) and extended X-ray absorption fine structure (EXAFS) were performed for characterizing precipitates formed in a Cu-Ni-Si alloy without and with a small amount of Fe, the strength and electrical conductivity of which were improved by aging process. These alloy samples were aged at 720 K after a solution treatment. The SAXS profiles of the samples were measured to investigate the size of precipitates. The results of SAXS measurements showed that nanometer-size precipitates formed in the alloy samples during isothermal aging. The precipitates in the Cu-alloy sample without Fe appeared to be coarsened in a multi-modal size distribution by the aging process. In contrast, the precipitates with homogeneous size were formed for the Cu-alloy sample with Fe. The environmental structure of Ni and Fe of these alloys evaluated by EXAFS measurements revealed that the precipitates of these alloys have the structure of $\delta$-Ni$_2$Si, and Fe substitutes Ni in $\delta$-Ni$_2$Si. It is presumed that the precipitates of homogeneous size in the Fe-added Cu alloy were formed because highly dispersed Fe atoms serve as nucleation sites of Ni$_2$Si.

Keywords: Small angle X-ray scattering; Extended X-ray absorption fine structure (EXAFS); Precipitates

I. INTRODUCTION

Copper-base alloys are extensively utilized for electrical parts such as lead frames and connectors, owing to their high electrical conductivity. In order to prepare for the miniaturization of electronic devices, it is necessary to develop a copper alloy with the higher characteristic. For that reason, various copper-base alloys have been developed [1, 2]. They show excellent properties as a result of controlling the processing conditions. The high performance of copper-base alloys is achieved by forming fine precipitates in the copper matrix during aging. The alloy composition, aging conditions and pretreatment techniques are important parameters for the formation of precipitates bringing high performance of copper-base alloys.

In order to control precipitates, it is essential to characterize their state accurately. Generally, the precipitates in the Cu matrix have been studied by transmission electron microscopy (TEM) observation to evaluate their morphology, size and atomic structures. However, since the information obtained by the TEM is based on limited local area of samples, it is not necessarily adequate in evaluating size distribution of precipitates. Furthermore, the recent copper-base alloys have a trend to contain trace elements. In order to reveal the role of the trace element, different analytical techniques should be applied for characterizing environmental structure of the trace elements. Therefore, the size and atomic-scale structure of precipitates should be characterized with other methods, in order to examine the effects of precipitates on the properties of copper-base alloys. Based on this situation, we have demonstrated that the small-angle X-ray scattering (SAXS) measurements and extended X-ray absorption fine structure (EXAFS) measurements can be promising methods for characterizing the precipitates in the Cu alloys in the previous study [3].

In the present study, the copper-base Cu-Ni-Si and its Fe-added alloys were focused, because the Cu-Ni-Si alloy exhibits better electrical conductivity by addition of small amount of Fe. In order to understand the roll of Fe in the formation of precipitates for the alloy, the precipitates formed in aging processes were investigated in detail. SAXS measurements were carried out to characterize the size distribution of precipitates in the alloys. EXAFS measurements were carried out to identify the compound of precipitates and to specify the characteristic of the local atomic structure around Fe in the alloy. With these structural data, the correlation between precipitates induced by Fe addition and electrical conductivity will be discussed.

II. EXPERIMENTAL

A. Sample preparation

The alloys evaluated in this work were high-purity Cu-3.1at%Ni-1.4at%Si and Cu-3.0at%Ni-1.3at%Si-0.2at%Fe alloys. In the following discussion, the samples that do not contain Fe will be denoted as CuNiSi and those that contain Fe will be denoted as CuNiSi+Fe. The detailed preparation method of these alloys is described elsewhere [2]. Alloy samples were prepared by a hydrogen plasma arc melting method. Solution treatment at 1173 K and subsequently cold rolling by 50% were made for the alloy samples. These alloy samples were isothermally aged.
at 720 K. Although both CuNiSi and CuNiSi+Fe samples showed fundamentally similar electrical conductivity before aging, the electrical conductivity of the CuNiSi+Fe sample was higher than that of the CuNiSi sample aged for 10000 s. Thus, we selected the samples aged for 0 and 10000 s for SAXS and EXAFS analyses in the present work.

B. Measurements

SAXS measurements were carried out using the BL15XU beam line at SPring-8 in Japan. The profiles were measured in the scattering vector $q$ ($q = 4\pi E \sin(2\theta/2)/hc$) range from 0.2 to 3.0 nm$^{-1}$, where $E$ is the X-ray energy, $2\theta$ is the scattering angle, $h$ is Planck’s constant, and $c$ is light velocity. Since the atomic number of Ni is next to that of Cu, the difference of atomic scattering factors of these elements at the X-ray energy far from absorption edge is about only 1, resulting in difficulty in distinguishing Ni compounds in Cu matrix. Therefore, the anomalous dispersion effect around X-ray absorption edge was applied in the present SAXS measurements. The X-ray of 8.313 keV, which is 20 eV below the Ni-K absorption edge, was applied to increase the difference of the atomic scattering factors of Ni and Cu to be about 4.4.

EXAFS measurements were carried out at Ni K-edge and Fe K-edge using the BL01 beam line at SPring-8 in Japan. The EXAFS spectra were obtained using a Si(111) double crystal monochromator in the transmission mode at room temperature. The EXAFS spectra were analyzed using REX2000 software (Rigaku Co.). Moreover, a simulation of the EXAFS function $k^2\chi(k)$ was performed using the FEFF 8.2 code [4].

III. RESULTS AND DISCUSSIONS

A. Size distribution of precipitates

Figure 1(a) shows SAXS profiles of the CuNiSi samples aged at 720 K for 0 and 10000 s. For the profile of the sample aged for 0 s, the scattering intensity decreases linearly in the log-log plot, which presumably results from the inhomogeneity of the atomic distribution in the alloy and/or from surface roughness. Such scattering may be regarded as background scattering, although it remains in the scattering profiles for the aged samples. The SAXS profile of the CuNiSi sample aged for 10000 s shows an ambiguous hump around 0.4 nm$^{-1}$. This hump indicates the appearance of precipitates.

SAXS profiles of the CuNiSi+Fe samples aged at 720 K for 0 and 10000 s are shown in Fig. 1 (b). The profile of the CuNiSi+Fe sample aged for 0 s is similar to that of the CuNiSi sample aged for 0 s. Clear hump is observed in the profile of the CuNiSi+Fe sample aged for 10000 s. This result indicates that precipitates were coarsened uniformly in this sample. It is interesting to note that the aging characteristics of the alloy were significantly influenced by addition of Fe, which implies that precipitation was strongly affected by additional Fe.

In order to investigate the size distribution of precipitates formed in the samples by aging, the SAXS profiles were analyzed using the indirect Fourier transform method [5]. Figures 2 show the distance-distribution functions (DDFs) for the CuNiSi and CuNiSi+Fe samples aged at 720 K for 0 and 10000 s. Since the DDFs were calculated from scattering profiles that included background scattering, the DDFs for the samples before aging do not represent the real size distribution of precipitates. The DDF for the CuNiSi sample aged for 10000 s does not show a clear peak. Thus, we can understand that there is size distribution of precipitates for the CuNiSi sample aged for 10000 s. On the other hand, the DDF for the CuNiSi+Fe sample aged for 10000 s shows that precipitates of about 3 nm in radius formed as a result of aging. This implies that fine and uniform precipitates formed in the alloy.
FIG. 3: (a) EXAFS functions $k^3 \chi(k)$ at the Ni and Fe K-edge for the CuNiSi+Fe samples aged for 0 s. The calculated curve is led by the model structure that Ni and Fe atoms substitute Cu in the fcc-Cu lattice. (b) EXAFS functions $k^3 \chi(k)$ at the Ni and Fe K-edge for the CuNiSi+Fe samples aged for 10000 s. The calculated curve is led by the model structure of $\delta$-Ni$_2$Si at the Ni K-edge.

B. Local structure of precipitates

Figure 3(a) shows $k^3$-weighted EXAFS functions at the Ni and Fe K-edge for CuNiSi+Fe aged for 0 s. It can be easily seen that the EXAFS functions at Fe K-edge have similar shape of the functions at Ni-K edge. The EXAFS functions of model structures calculated using the FEFF 8.2 code [4], in which Ni and Fe atoms substitute Cu in the fcc-Cu lattice. The calculated functions reproduces fairly well the shape and phase of the observed EXAFS functions at Ni K-edge and Fe K-edge. This clearly suggests that Ni and Fe atoms were dissolved substitutional in the Cu lattice.

Figure 3(b) shows $k^3$-weighted EXAFS functions at the Ni and Fe K-edge for the CuNiSi+Fe aged for 10000 s. Characteristic shoulder peak appeared at about 60 nm$^{-1}$ and 75 nm$^{-1}$ in the functions for the non-aged sample were unclear in the functions for the aged sample. This implies the changes of environmental structure of Ni and Fe originated from the formation of precipitates. It has been reported that a possible precipitate compound in the Cu-Ni-Si system might be nickel silicide [6]. In order to confirm the local structure of precipitates formed in the aged sample, EXAFS functions for several type of nickel silicide compounds were calculated, and it turned out that the calculated EXAFS function led by $\delta$-Ni$_2$Si reproduce the observed function as shown in Fig. 3(b).

Thus, the precipitates can be regarded as $\delta$-Ni$_2$Si. It should be emphasized that the EXAFS functions at Fe K-edge is identical to that at Ni-K edge, suggesting that Fe atoms substitute Ni ones in $\delta$-Ni$_2$Si.

The effect of Fe in forming precipitates for Cu-Ni-Si alloy can be deduced that the highly dispersed Fe atoms is nucleation site of $\delta$-Ni$_2$Si, resulting in the formation of uniform size precipitates. High dispersion of Fe atoms might effectively pull Ni and Si atoms from the Cu matrix, which can achieve better electrical conductivity of the alloy.

IV. CONCLUSIONS

In order to understand the role of Fe in the formation of precipitates for the Cu-Ni-Si alloy, the precipitates formed in aging processes were investigated by SAXS and XAFS analyses. SAXS profiles showed that nanometer-size precipitates were formed during isothermal aging at 720 K. The coarsening of the precipitates in the alloy samples without Fe seemed to occur in a multi-modal size distribution. On the other hand, the precipitates were coarsened in nearly a single modal size distribution with increasing aging time in the samples with Fe. This phenomenon is thought to be caused by preferential precipitation around Fe atoms. EXAFS spectra showed that Ni and Fe atoms substitute in the fcc-copper lattice for the sample before aging. The EXAFS spectra measured for the aged sample reveal that Ni and Fe have the same atomic structure of $\delta$-Ni$_2$Si. Fe is likely to occupy Ni sites in the $\delta$-Ni$_2$Si. It was speculated that highly dispersed Fe atoms could become the nucleation site of the precipitates and pull Ni atoms and Si atoms from the matrix effectively. As a result, the Fe-added Cu-Ni-Si alloy would get higher electrical conductivity than the Cu-Ni-Si alloy.

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