

SAXS and XAFS Characterization of Precipitates in a High-Performance Cu–Ni–Si Alloy

Yohei Takahashi¹, Takashi Sanada¹, Shigeo Sato¹, Toshihiro Okajima², Kozo Shinoda³ and Shigeru Suzuki³

¹NISSAN ARC, LTD., Yokosuka 237-0061, Japan

²Kyushu Synchrotron Light Research Center, Tosu 841-0005, Japan

³Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan

Analyses of small-angle X-ray scattering (SAXS) and X-ray absorption fine structure (XAFS) were performed for characterizing precipitates formed in a Cu-3.1 at%Ni-1.4 at%Si alloy, the strength and electrical conductivity of which were improved by aging. SAXS profiles and XAFS spectra of samples aged at 720 K for different periods of time after a solution treatment were measured. SAXS profiles of samples, which were aged after the solution treatment and subsequently cold rolled, were also measured to investigate the effect of dislocations on precipitation. The results of SAXS measurements showed that nanometer-size precipitates formed in the alloy samples during isothermal aging at 720 K. The precipitates in the samples without cold rolling were coarsened in a single modal size distribution with increasing aging time. In contrast, the precipitates formed in the cold-rolled samples appeared to be coarsened in a multi-modal size distribution with increasing aging time. This aging characteristic of the cold-rolled samples is presumably attributable to their good electrical conductivity. The results of XAFS measurements at the Ni K-edge showed that nickel was substituted for copper in the face-centered cubic (fcc) copper matrix and that the local structure around nickel was changed by isothermal aging. With increasing aging time, extended X-ray absorption fine structure (EXAFS) functions at the Ni K-edge of the samples were found to be changed, which implies that nickel atoms were precipitated as nickel-silicon clusters or intermediate compounds in the fcc copper matrix. In addition, X-ray absorption near edge structure (XANES) spectra at the Ni K-edge indicated that the electronic structure of nickel in the samples was influenced by silicon during aging. [doi:10.2320/matertrans.48.101]

(Received October 13, 2006; Accepted November 13, 2006; Published January 25, 2007)

Keywords: copper base alloy, precipitation, small angle X-ray scattering, X-ray absorption fine structure

1. Introduction

Copper-base alloys are extensively utilized for electrical parts such as lead frames and connectors, owing to their high electrical conductivity. Since high strength is required of copper-base alloys used for small microelectronic devices, copper–beryllium alloys are sometimes applied owing to their high electrical conductivity and high strength. However, because of the toxicity of beryllium, novel metallic materials free of hazardous substances are needed as an alternative to copper–beryllium alloys. For that reason, various copper-base alloys, such as copper–titanium (Cu–Ti) binary alloys^{1–5)} and copper–nickel–silicon (Cu–Ni–Si) alloys,^{6–12)} have been developed. They show excellent properties as a result of controlling the processing conditions. The high performance of copper-base alloys is achieved by the fine precipitates that form in the copper matrix during aging. The alloy composition, aging conditions and pretreatment techniques are important parameters for obtaining high performance in copper-base alloys. For example, the aging characteristics of Cu–Ti alloys have been examined systematically,⁵⁾ and the effect of cold rolling before aging on the properties of Cu–Ni–Si alloys has been also investigated.¹²⁾

In order to control precipitates, it is essential to characterize their state accurately. Precipitates formed by aging have been studied using transmission electron microscopy, but it is difficult to evaluate systematic changes in the size of such precipitates because only local areas are observed. 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.

Small-angle X-ray scattering (SAXS) analysis is a potential method for characterizing compositional fluctuations in alloys.^{13,14)} Since SAXS has been used for analyzing the nano-structure in high-content alloys,^{15,16)} it should be extendable to nano-structural analysis of low-content alloys as well. Analysis of X-ray absorption fine structure (XAFS) may also be useful for analyzing the local atomic structure around a specific element in alloys.¹⁷⁾ This method is applicable to analysis of precipitation in alloys, in which the content of alloying elements dissolved in the matrix is changed by aging. The objective of this work is to characterize the effects of aging and cold rolling on precipitates in a copper alloy, Cu-3.1 at%Ni-1.4 at%Si, using SAXS and XAFS methods.

2. Experimental Procedure

2.1 Sample preparation

The alloy evaluated in this work was a high-purity Cu-3.1 at%Ni-1.4 at%Si alloy, which showed high strength and low electrical resistivity. The detailed preparation method of the alloy is described elsewhere.¹²⁾ Alloy samples were prepared from 6 N (99.9999%) copper, 4 N nickel, and 6 N silicon using a hydrogen plasma arc melting method. The samples were annealed at about 1173 K, and this process is called the solution treatment. Some of the samples were subsequently cold rolled by 50%. In the following discussion, the samples that were solution treated will be denoted as ST and those that were cold rolled after the solution treatment will be denoted as STCR. The alloy samples were isothermally aged at 720 K for different periods of time.

A previous investigation of aging characteristics revealed

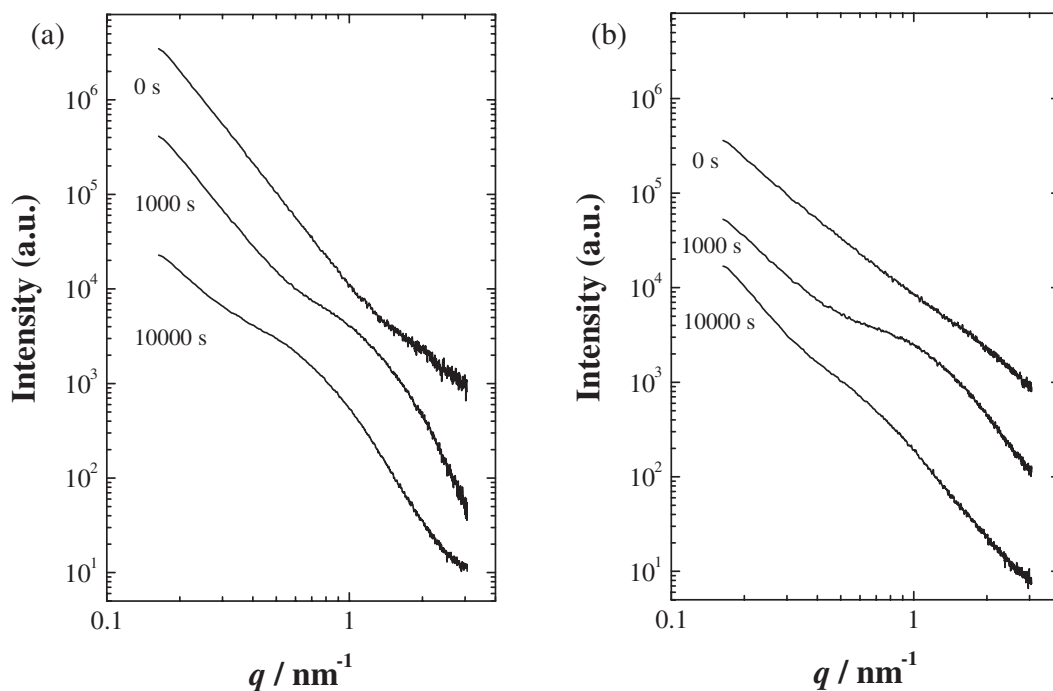


Fig. 1 (a) SAXS profiles of ST samples aged for 0, 1000 and 10000 s and (b) SAXS profiles of STCR samples aged for 0, 1000 and 10000 s.

interesting results.¹²⁾ Although both ST and STCR samples showed fundamentally similar property changes with a longer aging time, some differences were observed between them. After aging for 1000 s, the hardness of ST and STCR samples increased, while their resistivity decreased. Both ST and STCR samples showed nearly their maximum hardness after aging for 10000 s, but the resistivity of the STCR samples was significantly reduced. This suggests that cold rolling may have an additional effect on precipitation in this alloy. Thus, samples aged for 0, 1000 and 10000 s were selected for SAXS and XAFS analyses in the present work.

2.2 Measurements

SAXS measurements were carried out using the NanoStar apparatus (Bruker AXS). A high-flux Cu $K\alpha$ X-ray beam obtained with cross-coupled Göbel mirrors and a subsequent three pinhole collimation system was introduced into the sample chamber. The sample chamber and the beam path to the two-dimensional position-sensitive proportional counter were evacuated to eliminate air scattering. The scattering profiles were obtained by averaging the images in a circular direction. The profiles were measured in the scattering vector q ($q = 4\pi \sin(2\theta/2)/\lambda$) range from 0.2 to 3.0 nm^{-1} , where λ is the X-ray wavelength and 2θ is the scattering angle. The data acquisition time was 3 h for each profile.

Measurements of Ni K-edge XAFS were carried out using the BL15 beam line at the Saga Light Source (SAGA-LS) in Japan. The XAFS spectra at the Ni K-edge were measured using a Si (1 1 1) double crystal monochromator in the transmission mode at room temperature. The XAFS spectra were analyzed using REX2000 XAFS analysis software (Rigaku Co.). In addition, a simulation of the extended X-ray absorption fine structure (EXAFS) function $k^3\chi(k)$ was performed using the FEFF 8.2 code.¹⁸⁾

3. Results and Discussion

3.1 SAXS analysis

Figure 1(a) shows SAXS profiles of ST samples aged at 720 K for 0, 1000 and 10000 s. For the ST samples aged for 0 s, *i.e.*, the solution-treated sample, 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 profiles of the ST sample aged for 1000 s shows a hump at about 1 nm^{-1} . This hump indicates the appearance of small size precipitates. The position of the hump shifts to the lower scattering vector side in the ST sample aged for 10000 s, which implies that the size of the precipitates became larger.

SAXS profiles of STCR samples aged at 720 K for 0, 1000 and 10000 s are shown in Fig. 1(b). The profiles of the samples aged for 0 s and 1000 s are similar to those of the ST samples. However, the hump in the SAXS profile of the sample aged for 10000 s shows lower contrast than the profile of the ST samples. This result indicates that precipitates were not simply coarsened in this sample. It is interesting to note that the aging characteristics of the alloy were significantly influenced by cold rolling after the solution treatment, which implies that precipitation was strongly affected by dislocations formed by cold rolling.

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.¹⁹⁾ Figures 2(a)–(c) show the distance-distribution functions (DDFs) for ST samples aged at 720 K for 0, 1000 and 10000 s, respectively. The DDFs for STCR samples aged at 720 K for 0, 1000 and 10000 s are shown in Figs. 3(d)–(f),

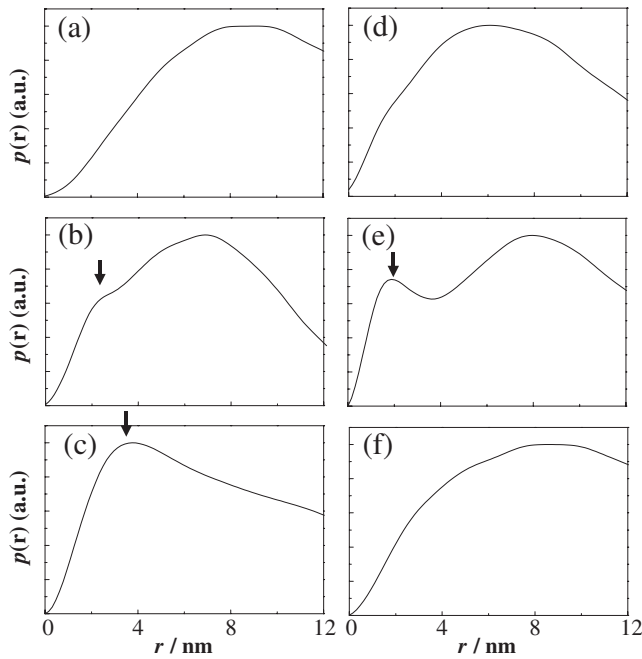


Fig. 2 (a)–(c) DDFs for ST samples aged for 0, 1000 and 10000 s and (d)–(f) DDFs for STCR samples aged for 0, 1000 and 10000 s.

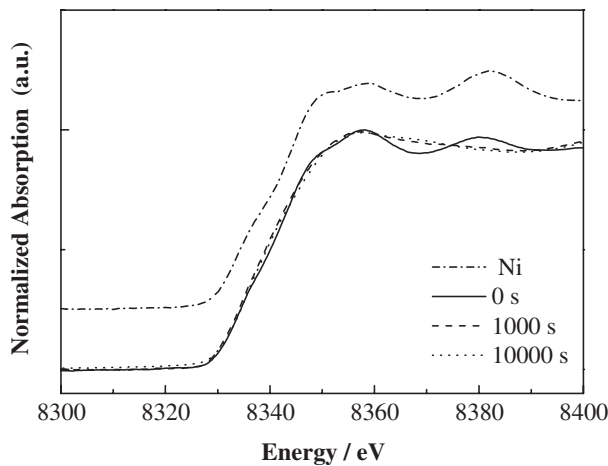


Fig. 3 XANES spectra at the Ni K-edge of ST samples aged for 0, 1000 and 10000 s. XANES spectrum of nickel foil is also shown for reference.

respectively. As the DDFs were calculated from scattering profiles that included background scattering, the functions for the samples before aging do not necessarily represent the real size distribution of precipitates. Nevertheless, aging characteristics are observed in these DDFs for the samples aged for 1000 and 10000 s. In the ST and STCR samples aged for 1000 s, precipitates of 2 nm in radius appear to have formed, although there may have been some difference in the size distribution of precipitates between the two types of samples. The DDF for the ST sample aged for 10000 s shows that precipitates of about 3 nm in radius formed as a result of aging, indicating that the precipitates were coarsened in nearly a single modal distribution. On the other hand, the DDF for the STCR sample aged for 10000 s does not show a clear peak. This indicates that precipitates formed in this

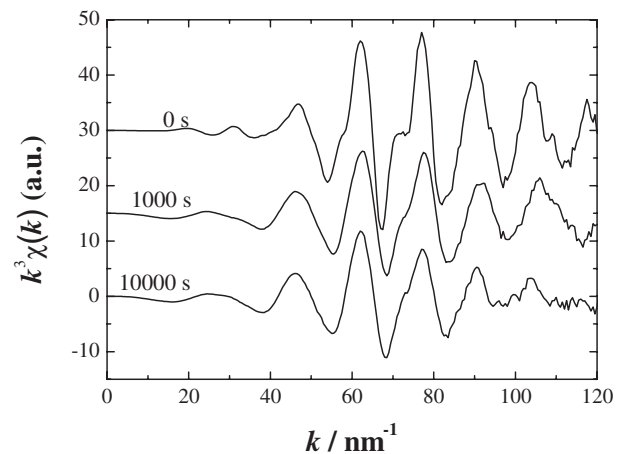


Fig. 4 EXAFS functions $k^3\chi(k)$ at the Ni K-edge for ST samples aged for 0, 1000 and 10000 s.

sample were coarsened not in a single modal size distribution, but in a multi-modal size distribution. Dislocations formed by cold rolling are thought to suppress coarsening of precipitates in the single modal distribution through preferential precipitation on dislocations. Such preferential precipitation in the cold-rolled samples might have significantly decreased the amount of nickel and silicon dissolved in the matrix by aging, resulting in improvement of the electric conductivity of the STCR samples.

3.2 XAFS analysis

X-ray absorption near edge structure (XANES) spectra at the Ni K-edge for the alloy samples without cold rolling (ST samples) aged for 0, 1000 and 10000 s are shown in Fig. 3. The XANES spectra of the ST samples are similar to that of Ni foil with a face-centered cubic (fcc) structure, which implies that nickel was substituted for copper in the fcc copper matrix. The XANES spectrum of the ST sample aged for 1000 s was different from that of the solution-treated sample. This indicates that the electronic structure of nickel was changed by aging, which is thought to result from the interaction of nickel with another element, particularly silicon, during aging. However, no clear difference was observed in XANES spectra between the samples aged for 1000 and 10000 s. Therefore, the average electronic structure of nickel precipitated in the copper matrix was apparently similar in the samples aged over 1000 s, although the amount of nickel dissolved in the copper matrix decreased during aging. These results imply that most of the nickel had already started to interact with silicon after aging for 1000 s.

Figure 4 shows k^3 -weighted EXAFS functions at the Ni K-edge for ST samples aged for 0, 1000 and 10000 s. The amplitude of the EXAFS functions decreased in the aged samples, especially in the high- k region. Characteristic shapes located at about 55 nm^{-1} and 70 nm^{-1} in the functions for the ST sample aged for 0 s were unclear in the aged samples. The changes in resistivity¹²⁾ due to aging indicated that the amount of nickel dissolved in the matrix of the present alloy samples aged at 720 K for 1000 s and 10000 s was about 70% and 30%, respectively. Nevertheless, the changes in the EXAFS spectra due to aging imply that the

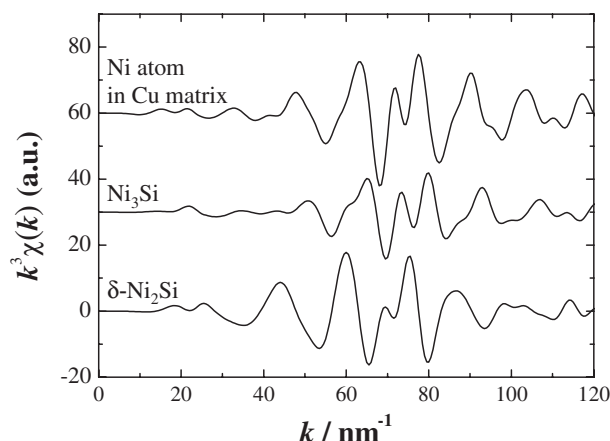


Fig. 5 EXAFS functions $k^3\chi(k)$ at the Ni K-edge for Ni_3Si and $\delta\text{-Ni}_2\text{Si}$ and the model structure in which nickel atoms are substituted in the face-centered cubic copper matrix as calculated with the FEFF 8.2 code.¹⁸⁾

formation of nickel-rich precipitates was accompanied by a change in local structure around nickel in the alloy.

The EXAFS function of a model structure calculated using the FEFF 8.2 code,¹⁸⁾ in which nickel atoms are substituted for copper in the fcc copper matrix, is shown in Fig. 5. The calculated function reproduces fairly well the shape and phase of the experimental EXAFS function for the ST sample aged for 0 s, as shown in Fig. 5. This is because nickel was dissolved in the copper matrix in the solution-treated sample. It has been reported that a possible precipitate compound in the Cu–Ni–Si system might be nickel silicide, such as Ni_3Si and $\delta\text{-Ni}_2\text{Si}$.^{6,8)} In order to characterize the local structure of precipitates formed in the aged samples, EXAFS functions for Ni_3Si and $\delta\text{-Ni}_2\text{Si}$ were calculated as shown in Fig. 4. The calculated functions were dissimilar to the experimental EXAFS functions for the samples aged for 1000 s and 10000 s. This implies that most of the nickel atoms were not precipitated as such ideal compounds in the copper matrix. It is likely that they were precipitated as nickel-rich clusters or intermediate compounds, perhaps containing silicon, although further structural analysis must be carried out to clarify this point.

4. Concluding Remarks

SAXS and XAFS analyses were carried out to characterize precipitates in the Cu-3.1 at%Ni-1.4 at%Si alloy. The main findings obtained in this work are summarized below.

- (1) SAXS profiles showed that nanometer-size precipitates were formed during isothermal aging at 720 K. The precipitates were coarsened in nearly a single modal size distribution with increasing aging time in the samples without cold rolling before aging. On the other hand, the coarsening of the precipitates in the cold-rolled alloy samples seemed to occur in a multi-modal size distribution. This phenomenon is thought to be

caused by preferential precipitation on dislocations formed by cold rolling.

- (2) XANES and EXAFS spectra showed that nickel was substituted in the fcc copper matrix in the solution-treated samples. The XANES spectra also indicated that the electronic structure of nickel was changed during aging, suggesting that nickel interacted with silicon to form precipitates. The EXAFS spectra at the Ni K-edge changed in the aged alloy samples. This spectral change would correspond to an aging-induced change in the local structure around nickel in the samples, which suggests the formation of nickel-rich precipitates.

Acknowledgements

The authors wish to express their thanks to Professor K. Mimura, Professor M. Isshiki and Professor Y. Waseda for their valuable discussions. XAFS measurements were performed with the permission of the SAGA-LS. This work was supported by a grant-in-aid for scientific research from the Japan Society for the Promotion of Science (No. 17310041).

REFERENCES

- 1) S. Nagarjuna, M. Srinivas, K. Balasubramanian and D. S. Sarma: *Scr. Metall. Mater.* **33** (1995) 1455–1460.
- 2) S. Nagarjuna, M. Srinivas, K. Balasubramanian and D. S. Sarma: *Acta Mater.* **44** (1996) 2285–2293.
- 3) S. Nagarjuna, M. Srinivas, K. Balasubramanian and D. S. Sarma: *Mater. Sci. Eng. A* **259** (1999) 34–42.
- 4) S. Nagarjuna, K. Balasubramanian and D. S. Sarma: *Mater. Sci. Eng. A* **225** (2001) 118–124.
- 5) S. Suzuki, K. Hirabayashi, H. Shibata, K. Mimura, M. Isshiki and Y. Waseda: *Scr. Mater.* **48** (2003) 431–435.
- 6) D. Zhao, Q. M. Dong, P. Liu, B. X. Kang, J. L. Huang and Z. H. Jin: *Mater. Sci. Eng. A* **361** (2003) 93–99.
- 7) F. Huang, J. Ma, H. Ning, Y. W. Cao and Z. Geng: *Mater. Lett.* **57** (2003) 2135–2139.
- 8) D. Zhao, Q. M. Dong, P. Liu, B. X. Kang, J. L. Huang and Z. H. Jin: *Mater. Chem. Phys.* **79** (2003) 81–86.
- 9) V. C. Srivastava, A. Schneider, V. Uhlenwinkel, S. N. Ojha and K. Bauckhage: *J. Mater. Process Tech.* **147** (2004) 174–180.
- 10) H. J. Ryu, H. Baik and S. H. Hong: *J. Mater. Sci.* **35** (2000) 3641–3646.
- 11) P. Liu, J. Su, Q. Dong and H. Li: *Mater. Lett.* **59** (2005) 3337–3342.
- 12) S. Suzuki, N. Shibutani, K. Mimura, M. Isshiki and Y. Waseda: *J. Alloy Compounds* **417** (2005) 116–120.
- 13) O. Kratky and O. Glatter: *Small-Angle X-Ray Scattering*, (Academic Press, New York, 1982) pp. 18–51.
- 14) H. Brumberger: *Modern Aspects of Small-Angle Scattering*, (Kluwer Academic Publishers, New York, 1995) pp. 2–56.
- 15) H. Okuda, S. Ochiai, K. Ito, and Y. Amemiya: *Scripta Mater.* **46** (2002) 795–800.
- 16) X. Y. Xiong, M. Ohnuma, T. Ohkubo, D. H. Ping, K. Hono, S. Ohnuma, H. Fujimori and T. Masumoto: *J. Mag. Magnetic Mater.* **265** (2003) 83–90.
- 17) M. Sakurai, M. Matsuura, K. Kita, H. Sasaki, J. Nagahora, T. Kamiyama and E. Matsubara: *Mater. Sci. Eng. A* **375** (2004) 1224–1227.
- 18) A. L. Ankudinov, B. Ravel, J. J. Rehr, and S. D. Conradson: *Phys. Rev. B* **58** (1998) 7565–7576.
- 19) J. B. Popera and O. Glatter: *J. Appl. Cryst.* **30** (1997) 431–442.