Microstructural Subsequence and Phase Equilibria in an Age-Hardenable Cu-Ni-Si Alloy

Satoshi Semboshi^{1,*}, Mikio Ishikuro¹, Akihiro Iwase² and Takayuki Takasugi²

¹Institute for Materials Research, Tohoku University, Sendai 980–8577, Japan

²Department of Materials Science, Osaka Prefecture University, Sakai 599–8531, Japan

We investigated the microstructural subsequence and phase equilibrium of Cu-4.3 at% Ni-2.2 at% Si alloy specimens during isothermal aging over a temperature range of 698 K to 873 K. During aging in this temperature range, the microstructure of the specimens evolved in the following sequence; continuous precipitation of fine disk-shaped δ -Ni₂Si in the matrix, discontinuous precipitation of cellular components containing coarse fiber-shaped δ -Ni₂Si at grain boundaries, and then occupation of the specimen with cellular components. By analyzing the variations in the hardness and electrical conductivity with aging time as well as temperature, we described the kinetics of the highest number density of fine δ -Ni₂Si continuous precipitates. Based on the chemical analyses of the specimen in a phase equilibrium state using an extraction procedure, we proposed a revised solvus of solutes Ni and Si in the Cu solid solution phase, as well as Cu in the δ -Ni₂Si intermetallic phase in a Cu– δ -Ni₂Si pseudo-binary system. [doi:10.2320/matertrans.MC201706]

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1. Introduction

Among various Cu-based systems, age-hardenable Cu-Ni-Si Corson-type alloys are widely used for electrical connectors and lead frames because of their superior balance of strength and electrical conductivity. Alloys with a typical composition of less than 5 at% Ni and 2.5 at% Si at an Ni/Si ratio of around 2.0 have been commercially fabricated by solid-solutioning at around 1173 K followed by aging over a temperature range of 673 K–773 K. Optimal thermomechanical processing in combination with working and aging can produce tensile strengths of more than 1000 MPa and an electrical conductivity in excess of 30% IACS. Here, “% IACS” represents the percentage based on the conductivity defined in the International Annealed Copper Standard at 298 K, that is, $5.8 \times 10^7 \Omega^{-1}\text{m}^{-1}$. The balance of their hardness and electrical conductivity is competitive with that of the widely used Cu-Be based alloys^{1,2)}. Therefore, a number of fundamental and practical research efforts addressing Cu-Ni-Si alloys have been attempted to understand the mechanisms affecting age-induced microstructural evolution and to further improve their superior properties^{3–9)}.

It is generally recognized that the strengths and electrical conductivities of Cu-Ni-Si alloys are closely dependent on their microstructure; at an early stage of aging, the strength of the alloys increases owing to the continuous nucleation and growth of the nano-scaled δ -Ni₂Si precipitates (i.e., continuous precipitates (CPs)) in the matrix of Cu solid-solution phase^{10–17)}. Here, δ -Ni₂Si has an orthorhombic structure (Space group: *Pnma*, lattice parameter: $a = 0.504$ nm, $b = 0.364$ nm, $c = 0.708$ nm)^{14,17,18)}. At a later stage of a prolonged aging, the strength decreases, which is primarily caused by the development of coarse cellular components consisting of the Cu solid-solution and fiber-shaped δ -Ni₂Ni phase (i.e., discontinuous precipitates (DPs)), accompanied by the consumption of the fine δ -Ni₂Ni hardening species^{17,19–21)}. Meanwhile, the electrical conductivity of the al-

loys increases monotonically during aging, because the amount of solute Ni and Si elements in the matrix decreases as a result of the formation of fine CPs and fiber DPs of δ -Ni₂Si. Thus, to control the mechanical and electrical properties of the alloys, it is important to understand the precipitation behavior in association with the microstructures. The purpose of the present study is, therefore, to investigate the microstructural subsequence and phase equilibrium of commercial Cu-4.3 at% Ni-2.2 at% Si alloy during isothermal aging over a wide temperature range of 698 K–873 K. As a particular feature of this study, a chemical extraction technique was used to quantitatively analyze the microstructure of the aged-specimens^{17,22,23)}. The adopted chemical extraction procedure allowed direct and reliable examination of the structure, volume fraction, and compositions of the constituent phases. Based on the obtained results, the kinetics and phase equilibrium of the aged microstructure are discussed.

2. Experimental

Alloy blocks measuring 30 mm × 30 mm × 3 mm were used as the starting material. The chemical composition of the alloys was Cu-4.3 Ni-2.2 Si in at% (Cu-4.1 Ni-1.0 Si in mass%). The blocks were cold-rolled down to a thickness of 0.3 mm, and then cut off into strips measuring 75 mm × 5 mm × 0.3 mm. The specimens were solution-treated at 1173 K for 3 h in evacuated quartz capsules, and then immediately quenched in water. The contaminated surface layer on the specimens was removed by mechanical polishing. The specimens were re-capsuled in a vacuum of less than 1.0×10^{-2} Pa, followed by isothermal aging at 698 K, 723 K, 773 K, and 873 K for 0.083 h–530 h.

The microstructure of the specimens was observed using a JEOL JSM7001F field emission-scanning electron microscope (FESEM). For the FESEM observations, the specimens were first mechanically polished and then electrochemically polished with a 40% phosphoric acid water solution at room temperature for 5 to 10 s. The Vickers hard-

*Corresponding author, E-mail: semboshi@imr.tohoku.ac.jp

ness and electrical conductivity at room temperature were measured to monitor the microstructural evolution of the specimens during isothermal aging. The Vickers hardness tests were performed using a MITSUTOYO HM101 Vickers micro-hardness tester with an applied load of 1.96 N, and the hardness values were then determined by averaging the values from more than 10 indentations. The electrical resistance of the specimens was measured using a standard DC four-probe method with an Agilent 34420A micro-ohm meter with an accuracy of $\pm 10 \mu\Omega$, which was then used to calculate the electrical conductivity. The precipitates formed in the aged specimens were separated using the following extraction procedure, the details of which are described in the literature^{17,22}: the surfaces of the aged specimens were mechanically polished again to remove the contaminated surface layer. After the specimens had been thoroughly rinsed in pure ethanol, they were cut into small pieces. These pieces were immersed in a 7-mol/L nitric acid/water solution at 273 K for 0.3 h. As a result, the Cu matrix phase dissolved in the solution, but the Ni and Si-rich precipitate phase remained as insoluble residue. The solution was then passed through a membrane filter with a pore diameter of 50 nm. The filtered precipitates were rinsed well with pure water and then dried in a desiccator. The structure of the separated precipitates was analyzed by X-ray diffraction (XRD) using a PANalytical X'pert Pro diffractometer with $\text{CuK}\alpha$ radiation (wave length, $\lambda = 0.1542 \text{ nm}$) and an applied voltage of 40 kV. The weight fractions of the elemental

Cu, Ni, and Si in the precipitates and matrix were obtained by measuring those in the filtered residue and filtrate, respectively, by inductively coupled plasma-optical emission spectrometry (ICP-OES) using a Thermo Fisher Scientific IRIS Advantage DUO spectrometer. Here, the filtered residue, which was identified as being $\delta\text{-Ni}_2\text{Si}$, described latter, was dissolved in a solution of nitric acid, hydrofluoric acid, and pure water (at a ratio of 2:1:4) at 373 K for 1 h in a closed Teflon container, before the ICP-OES measurements¹⁷.

3. Results and Discussion

3.1 Microstructural subsequence

The solution-treated and quenched Cu-4.3 Ni- 2.2 Si (in at%) alloy specimen exhibited a single-phase microstructure of a supersaturated Cu solid solution with an average grain size of approximately $100 \mu\text{m}$. Figure 1 shows FESEM micrographs of the specimen aged at 723 K. In an early stage of aging for 4 h shown in Fig. 1(a), we can find areas of weak contrast with a size of several nanometers in the solid solution phase (see the right-hand side of the inset image, observed at a high magnification), which must correspond to continuous precipitates (CPs) of $\delta\text{-Ni}_2\text{Si}$ ¹⁷. We can also find some areas of bright contrast as indicated by the dotted circles in Fig. 1(a), which corresponds to the fiber-shaped discontinuous precipitates (DPs) of $\delta\text{-Ni}_2\text{Si}$ with the same orthorhombic structure as the CPs, which is confirmed in a

Fig. 1 FESEM micrographs for Cu-4.3 at% Ni- 2.2 at% Si alloy specimen aged at 723 K for (a) 4 h, (b) 16 h, (c) 48 h and (d) 408 h. In the magnified FESEM micrograph insets (a)–(c), fine continuous precipitates (CPs) appear in the grain. The dotted open circles in (a) and (b) indicate the region of the cellular components containing the fiber-shaped discontinuous precipitates (DPs).

later section. Thus, the fiber-shaped DPs have already been formed at an early stage of aging, together with the formation of fine CPs. During prolonged aging, the fine CPs continuously nucleated and homogeneously dispersed in the matrix of the Cu solid solution, and then grew into disk-shaped particles with a size of several tens of nanometers, as seen in the inset micrographs of Figs. 1(b)–(c). The cellular components composed of the fiber DPs and Cu solid solution phase developed spontaneously, consuming the sound grains containing the fine CPs. Finally, the cellular components occupied almost the entire region of the specimen, as shown in Fig. 1(d). No apparent microstructural evolution could be observed for a prolonged aging period longer than 408 h.

A similar microstructural result, i.e., continuous precipitation of fine disk-shaped δ -Ni₂Si particles, discontinuous precipitation of cellular components containing coarse fiber-shaped δ -Ni₂Si, and the eventual occupation of the specimen with cellular components, was observed for the specimens aged at every temperature between 698 K–873 K. This indicates that, in the investigated temperature range, the equilibrium state for the alloy with a composition of Cu-4.3 at% Ni- 2.2 at% Si consists of two phases, namely, the Cu solid solution and the δ -Ni₂Si formed both continuously and discontinuously.

To investigate the kinetics of the microstructural subsequence during aging, we examined the variations in the Vickers hardness and electrical conductivity for the specimens aged at temperatures of 698 K, 723 K, 773 K, and 873 K as a function of the aging time, as shown in Fig. 2. The Vickers hardness of the quenched specimens was 87 ± 5 HV. During aging at the investigated temperatures, the hardness increased and then reached a maximum, after which it decreased at a rate, as shown in Fig. 2 (a). The maximum values of the hardness decreased with the aging tem-

perature, although the period required to achieve the maximum hardness was reduced. The electrical conductivity of the quenched specimens was 14.5% IACS. The electrical conductivity of the specimen increased with the aging time and then reached saturation at every temperature (Fig. 2(b)). The saturated values of the conductivity decreased as the aging temperature increased, although the period required to reach saturation was shortened.

The hardness of the age-hardened specimen should be affected mainly by structural factors, such as the size and number density of the precipitates, together with the composition and volume fraction of the constituent phases. It is also accepted that the electrical conductivity (and resistivity) of the metallic materials are sensitive to the composition and volume fraction of the constituent phases^{24,25}. Therefore, the saturation of both the hardness and electrical conductivity indicates that the specimens should be virtually in an equilibrium state, at least in terms of microstructural subsequence. Thus, the time required to reach the equilibrium state was roughly obtained, from Fig. 2, as 360 h for the specimen aged at 698 K, 240 h for that aged at 723 K, 168 h for that aged at 773 K, and 144 h for that aged at 873 K.

Figure 3 shows the Arrhenius plots describing the saturation of both the hardness and electrical conductivity during isothermal aging, together with the maximum-hardening condition. The data points are well plotted on a straight line in the temperature range between 698 K–873 K, which were fitted using the following equation:

Condition of maximum-hardening:

$$\ln(t) = -20.9 + 16.8 \times 10^3/T \quad (1)$$

Saturation of electrical conductivity:

$$\ln(t) = 1.47 + 2.96 \times 10^3/T \quad (2)$$

where t is the aging time [h] and T is the aging temperature [K]. Equations (1) and (2) approximately correspond to the

Fig. 2 (a) Vickers hardness and (b) electrical conductivity for Cu-4.3 at% Ni- 2.2 at% Si alloy specimens aged between 698 K–873 K.

Fig. 3 Arrhenius plots of the aging temperature, $1/T$, versus aging time in hours (represented by $\ln(t)$), which describe the saturation of both the hardness and electrical conductivity (indicated by $\blacksquare$) and the peak-hardened condition (indicated by $\diamond$) for Cu-4.3 at% Ni-2.2 at% Si alloy specimens. The former corresponds to the condition in which the equilibrium state is reached, while the latter corresponds to the fine continuous precipitates of δ -Ni₂Si.

kinetics required to reach the highest density of CP δ -Ni₂Si and the phase equilibrium, respectively.

3.2 Phase equilibrium

We assumed that the specimen aged beyond the period given by eq. (2) should be in an equilibrium state. To confirm the structure of the precipitates in the equilibrium state, the precipitates of the fully aged specimens were separated by the extraction procedure, and were then subjected to XRD analysis. Figure 4 shows the appearance of the precipitates separated from the specimen aged at 723 K for 408 h. We can see fibers measuring several tens of nm in diameter and several μ m in length, and a small number of fine particles with a size of several tens of nm. This morphological feature is consistent with the DPs and CPs, respectively, shown in Fig. 1(d). Figure 5 shows the XRD profile of the precipitates separated from the specimen, which exhibited peaks corresponding to δ -Ni₂Si with an orthorhombic structure having a space group of *Pnma*. Therefore, the precipitates in the aged specimens were identified as δ -Ni₂Si.

The compositions and volume fractions of the constituent matrix and precipitates for the aged specimens can be also evaluated directly by performing ICP-OES analyses on the

filtrate and insoluble residue remaining after the extraction procedure. Table 1 lists the weight fractions of the elements Cu, Ni, and Si in the matrix and the precipitates of the specimens aged up to the final state at 698 K for 530 h, 723 K for 408 h, 773 K for 400 h, and 873 K for 240 h, which are denoted as W^m_{Cu} , W^m_{Ni} , and W^m_{Si} , and W^p_{Cu} , W^p_{Ni} , and W^p_{Si} , respectively. The total weight fractions of the Cu, Ni, and Si in the matrix and precipitates of the aged specimens, i.e., $W^m_{Cu} + W^m_{Ni} + W^m_{Si} + W^p_{Cu} + W^p_{Ni} + W^p_{Si}$, were always very close to 100% ($100 \pm 0.5\%$) for all the specimens, suggesting that the chemical extraction procedure could account for all the constituent elements in the specimens.

The validity of the chemical compositions obtained by an extraction procedure and then ICP-OES measurement is also supported by the saturated electrical conductivity measured for the fully aged alloys. The electrical conductivity of the aged alloys can be estimated from the amount of solutes of Ni and Si in the matrix, ignoring the contribution of the δ -Ni₂Si precipitate phase. Actually, the volume fractions of the δ -Ni₂Si precipitates for the specimens that are fully aged at every temperature were estimated to be only less than 5.1 vol%, using the weight fraction in Table 1 and a calculated density, 7.30 g/cm³ for δ -Ni₂Si and 8.94 g/cm³ for Cu. The electrical conductivity of the Cu matrix containing Ni and Si solutes, σ , was estimated using the following Nordheim's equation:

$$1/\sigma = 1/\sigma_{Cu} + A_{Ni}C_{Ni} + A_{Si}C_{Si} \quad (3)$$

Here, σ_{Cu} is the electrical conductivity of pure copper, A_{Ni} and A_{Si} are the coefficients, and C_{Ni} and C_{Si} are the concentrations of solutes Ni and Si, respectively. The values of A_{Ni} and A_{Si} were reported to be $1.25 \times 10^{-8} \Omega\text{m/at\%}$ and $3.95 \times 10^{-8} \Omega\text{m/at\%}$, respectively²⁶⁾. Thus, the electrical conductivity calculated using eq. (3) was 52% IACS for the specimen aged at 698 K for 530 h, 51% IACS for that aged at 723 K for 408 h, 46% IACS for that aged at 773 K for 400 h, and 39% IACS for that aged at 873 K for 240 h. These values are very close to the measured ones shown in Fig. 2; i.e., 51.4% IACS at 698 K, 50.8% IACS at 723 K, 46.7% IACS at 773 K, and 38.6% IACS at 873 K.

Table 1 states that the amount of solute elements of Ni and Si in the matrix of the quenched specimen decreased significantly as a result of aging at every temperature, which is due to the formation of Ni- and Si-enriched precipitates during aging. For the specimens in an equilibrium state, the Ni and Si contents in the matrix phase increased slightly with an increase in the temperature. Meanwhile, the precipitates of δ -Ni₂Si were found to contain a small amount of Cu, and the Cu content increased with the temperature. The measured atomic ratio of Ni/Si was almost constant, being 1.79 ± 0.04 , which is somewhat less than the stoichiometric composition of 2.0. This suggests that the δ -Ni₂Si intermetallic phase has some compositional range caused by containing Cu element, which was reported previously²⁷⁾.

The atomic fractions of Ni and Si in the matrix, and Cu in the precipitates of the specimens in the equilibrium state, which were converted from the data in Table 1 and denoted as C^m_{Ni} , C^m_{Si} , and C^p_{Cu} [at%], can be fitted with linear functions and plotted as shown in Fig. 6, and be expressed by the following equations:

Fig. 4 Micrograph of precipitates separated from Cu-4.3 at% Ni-2.2 at% Si alloy specimen aged at 723 K for 408 h using an extraction procedure.

Fig. 5 X-ray diffraction profile of the precipitates separated from Cu-4.3 at% Ni-2.2 at% Si alloy specimen aged at 723 K for 408 h using an extraction procedure.

Table 1 Elemental contents in Cu solid solution and δ -Ni₂Si precipitates, and atomic ratio of Ni/Si in precipitates for fully aged Cu-4.3 at% Ni-2.2 at% Si alloy specimens, as obtained by extraction procedure and ICP-OES measurement.

Aging Temp., time	Matrix			Precipitates			
	W_{Cu}^m (mass%)	W_{Ni}^m (mass%)	W_{Si}^m (mass%)	W_{Cu}^p (mass%)	W_{Ni}^p (mass%)	W_{Si}^p (mass%)	Atomic ratio of Ni/Si
698 K, 530 h	94.93 ± 0.15	0.604 ± 0.009	0.073 ± 0.021	0.048 ± 0.001	3.363 ± 0.026	0.898 ± 0.010	1.79 ± 0.03
723 K, 408 h	94.96 ± 0.11	0.609 ± 0.010	0.080 ± 0.013	0.045 ± 0.001	3.361 ± 0.006	0.924 ± 0.010	1.74 ± 0.02
773 K, 400 h	94.67 ± 0.55	0.644 ± 0.007	0.117 ± 0.014	0.053 ± 0.001	3.439 ± 0.015	0.897 ± 0.009	1.81 ± 0.02
873 K, 240 h	94.85 ± 0.67	0.712 ± 0.011	0.178 ± 0.011	0.095 ± 0.001	3.231 ± 0.014	0.851 ± 0.009	1.82 ± 0.02
as-quenched (before aging)	94.91 ± 0.13	3.991 ± 0.050	1.004 ± 0.048	---	---	---	---

Fig. 6 (a) Ni, Si, and Ni+Si contents in the Cu solid solution phase and (b) Cu content in the δ -Ni₂Si precipitate phase of the fully aged Cu-4.3 at% Ni-2.2 at% Si alloy specimens.

$$\ln C^m_{Ni} = 0.397 - 545.8/T \quad (4)$$

$$\ln C^m_{Si} = 2.864 - 3240/T \quad (5)$$

$$\ln C^p_{Cu} = 3.648 - 2787/T \quad (6)$$

In addition, the solubility product of δ -Ni₂Si precipitates in the Cu solid-solution matrix, $(C^m_{Ni})^{1.79}(C^m_{Si})$, was given from the eqs. (4) and (5), as following,

$$\ln (C^m_{Ni})^{1.79}(C^m_{Si}) = 3.579 - 4222/T \quad (7)$$

Here the power of 1.79 for C^m_{Ni} is from the Ni/Si ratio for δ -Ni₂Si precipitates based on the result listed in Table 1. The (Ni+Si) content plotted in Fig. 6(a) is fitted by the eq. (7).

The magnitudes of $(C^m_{Ni})^2(C^m_{Si})$ and C^p_{Cu} correspond to the terminal compositions of the matrix and δ -Ni₂Si precipitates phases, respectively. Considering the Cu- δ -Ni₂Si pseudo binary system, we can propose the solvus (solid lines) depicted in the phase diagram of Fig. 7, which was constructed using the phase diagram produced by Sokolovskaya *et al.* from the experimental assessment (dotted lines)²⁸⁾. The terminal composition of the δ -Ni₂Si phase defined by eq. (7) is in good agreement with that reported by Sokolovskaya *et al.*²⁸⁾ with an experimental accuracy, as shown in Fig. 7. Meanwhile, the terminal composition of Cu solid solution phase, defined by eq. (6) was slightly shifted to the left with respect to the magnitude depicted in the reported diagram.

Fig. 7 Solvus obtained in this study (indicated by the solid line), as drawn in the Cu- δ -Ni₂Si pseudo binary phase diagram²⁸⁾. The composition of δ -Ni₂Si, which is located at the right-hand end of the phase diagram, was assumed to be Ni- 35.7 at% Si (i.e., Ni/Si = 1.79) based on the result listed in Table 1.

Strictly describing, it is controversial whether the content in the matrix and δ -Ni₂Si precipitates phases, shown in Fig. 6, corresponds to a true equilibrium composition. The composition measured in this study might be shifted from the true one, arising from contribution of interface energy between the matrix and disk-shaped CPs or fiber-shaped

DPs with a small diameter of several ten nano-meters, according to Gibbs-Thomson effect²⁹). Thus, an influence of precipitation size on the compositional distribution of the constituent phases should be understood to discuss true phase equilibrium. In addition, it should be also important to confirm the solvus at a higher temperature than 873 K, as well as the eutectic and eutectoid points shown in Fig. 7. These can be examined reliably using extraction procedure, which will be reported in a future.

4. Conclusions

The precipitation behavior and phase equilibrium for Cu-4.1 at% Ni- 2.2 at% Si alloy isothermally aged at temperatures of 698 K–873 K were investigated in the present study. On the basis of the results obtained, the kinetics of the microstructural subsequence and the saturated composition of the constituent phases were quantitatively evaluated. The salient findings can be summarized as follows:

- (1) The microstructural subsequence of those specimens aged at a temperature of 698 K–873 K progressed in accordance with the following subsequence; continuous precipitation of fine disk-shaped δ -Ni₂Si particles, discontinuous precipitation of cellular components containing coarse fiber-shaped δ -Ni₂Si, and eventual occupation of the specimen with cellular components. Accordingly, the quenched specimen aged at these temperatures is finally decomposed into a two-phase microstructure consisting of a Cu solid solution and δ -Ni₂Si precipitates.
- (2) The kinetics of the maximum-hardness can be approximated by eq. (1), which must correspond to the highest number density of continuous precipitates of fine δ -Ni₂Si hardening species. The kinetics of the saturated electrical conductivity are described by eq. (2), which corresponds to the phase equilibrium.
- (3) The δ -Ni₂Si precipitates in the fully aged specimens contain a small amount of Cu, the content of which increases slightly with the aging temperature. The solvus of the Cu for the δ -Ni₂Si phase can be provided by eq. (6). The measured Ni/Si ratio was 1.79 ± 0.04 , which is somewhat less than the stoichiometric composition of 2.0. The amount of Ni and Si elements in the Cu solid solution also increases with the aging temperature, as defined by eq. (7). The solvus revised in this study slightly shifted to the Cu-rich side in comparison with the Cu– δ -Ni₂Si pseudo-binary diagram produced by Sokolovskaya *et al.*

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