Effects of Small Addition of Ti on Strength and Microstructure of a Cu-Ni-Si Alloy

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Abstract

The effect of addition 0.04 mass% or 0.2 mass% Ti on the mechanical properties of a Cu-2.0 mass%Ni-0.5 mass%Si alloy has been investigated. The addition of 0.04 mass%Ti enhances the strength of the Cu-Ni-Si alloy without reducing its electrical conductivity. This increase in strength is caused by the decrease in inter-precipitate spacing of δ-Ni_2Si precipitates. The addition of trace Ti reduces the equilibrium concentration of Ni and Si atoms in the alloy bearing the δ precipitates, resulting in an increase the volume fraction of δ precipitates and decrease in the inter-precipitate spacing. However, the addition of 0.2 mass%Ti to the Cu-Ni-Si alloy decreases the strength of the alloy. The reduction in strength is attributed to the decrease in the volume fraction of δ precipitates caused by the reduction in Ni and Si atoms in the Cu matrix resulting from the formation of $Ni_{16}Si_7Ti_6$ particles.

Keywords: Cu-Ni-Si alloy; Ti addition; δ-Ni_2Si precipitates; $Ni_{16}Si_7Ti_6$ phase; inter-precipitate spacing.

I. Introduction

Cu-Ni-Si alloys with compositions corresponding to approximately Cu-2 mass%(2 at%)Ni-0.5 mass%(1 at%)Si exhibit a significant age-hardening effect [1, 2]. Typically such alloys are aged at about 450ºC after quenching from a given solution treatment temperature, and tensile strengths of 600 to 800MPa are achieved, depending on the aging time and whether the alloy is cold worked before the aging treatment. The precipitates responsible for the strengthening effect have been identified as δ-Ni$_2$Si [1, 2]. The Cu-Ni-Si system alloys are widely used in applications, such as semiconductor lead-frames, because of their high strength and good electrical conductivity. The requirement of high strength has become increasingly important with the automation of the semiconductor packaging process. One straightforward method of increasing the strength of Cu-Ni-Si alloys is to increase the their Ni and Si contents. Several attempts have been made to improve the strength of Cu-Ni-Si alloys by increasing their Ni and Si contents and/or adding alloying elements such as Mn, Mg and Sn [1, 3-5]. However, these measures generally reduce the electrical conductivity of the alloys.

Recently, Lee *et al* employed thermodynamic calculations to demonstrate that the addition of small amount of Ti to Cu-Ni-Si alloys enhanced the precipitation of the δ precipitates and considerably accelerated the aging response [6]. According to their calculated Cu-Ni$_2$Si quasi binary phase diagram, the addition of Ti is expected to improve both the strength and electrical conductivity of the alloy. However, the expected improvement in strength has not been experimentally achieved with the addition of 0.12Ti (all compositions in this paper are expressed in mass%) to a Cu-3Ni-1Si alloy or 0.24Ti to a Cu-6Ni-1.29Si alloy, because adding Ti to the alloys

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leads to the agglomeration of coarse δ precipitates as well as the accelerated formation of discontinuous precipitation cells upon aging [6].

In this study, the effect of small addition of Ti on the strength of a Cu-2Ni-0.5Si alloy was investigated metallographically. We have found that the addition of 0.04Ti to the alloy enhances the strength of the alloy without decreasing its electrical conductivity. In addtion, the origin of the improvement of strength is also discussed.

II. Experimental

Ingots of Cu-2Ni-0.5Si, Cu-2Ni-0.5Si-0.04Ti and Cu-2Ni-0.5Si-0.2Ti alloys were prepared by melting under an argon atmosphere. The chemical compositions of the alloys are shown in Table 1. The cast ingots were subsequently cut into pieces, homogenized at 1000 ^{o}C for 24 h in a vacuum and cold-rolled to a 50 % reduction. Hereafter, the Cu-2Ni-0.5Si, Cu-2Ni-0.5Si-0.04Ti and Cu-2Ni-0.5Si-0.2Ti alloys are referred to as the base, 0.04Ti and 0.2Ti alloys, respectively. The rolled sheets of the alloys were solution-treated at 1000 ^{o}C for 2h or at 730 ^{o}C for 5 min in a vacuum and then quenched into cold water. The solution treatments resulted in the complete recrystallization of the sheets. The average grain sizes of the alloys were obtained from approximately 100 separate measurements via the liner intercept method. The base alloy sheets solutionized at 1000 and 730 ^{o}C had grain sizes of about 500 and 10 μm, respectively. The adding of 0.04% or 0.2%Ti caused no significant change in the grain sizes. The solution-treated sheets were cold-rolled to a 20% reduction and then aged at 450 ^{o}C for various times in a salt bath.

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Microhardness tests were conducted using the Vickers method. The indentations were made with a diamond square-based pyramid under a load of 0.3kg for a period of 20 s on well-polished surfaces of the specimen pieces. The hardness measurement of each specimen was repeated 10 times and an average value was obtained. Quasi-static tensile tests were performed using an Instron-type testing machine (Shimazu Autograph AG-X) with an initial nominal strain rate of 3×10^{-4} s^{-1} at room temperature. Electrical conductivity was measured at 61 kHz and 20 ^{o}C with an eddy current apparatus (Hocking Autosigma 3000DL). The average conductivity was calculated from 10 independent measurements for each investigated alloy condition.

The microstructure of each specimen was examined by transmission electron microscopy (TEM). Thin foils for TEM observations were prepared by twin-jet polishing at 273 K and 5 V using a solution of 75vol% methanol and 25vol% nitric acid. TEM foils were examined with a JOEL 2000EX or 2010FEF microscope at an operation voltage of 200kV. To obtain the composition of precipitated phases, TEM foils were examined in the JEOL 2010FEF microscope equipped with an energy-dispersive X-ray spectroscopy system. The electron beam diameter used was 0.5 nm.

III. Results

A. *Microhardness*

Figure 1(a) shows the change in the microhardness of the base, 0.04Ti and 0.2Ti alloys during aging at 450 ^{o}C after solutionizing at 1000 ^{o}C and subsequent cold-rolling to a 20% reduction. The microhardness of the three alloys after

solutionizing and subsequent rolling becomes slightly increased with increasing amounts of Ti. The three alloys exhibited maximum hardnesses at 9 h, and the hardness of the 0.04Ti alloy at 9 h was the highest among the investigated samples. The addition of 0.04Ti to the base alloy enhanced the hardness of the alloy. However, but the addition of 0.2Ti lowered it. This latter result is in agreement with the results of Lee *et al.*, who reported that the addition of 0.12Ti or 0.24Ti to Cu-Ni-Si alloys was detrimental to the strength of the alloys [4].

The age-hardening behavior of the three alloys solutionized at 730 ^{o}C for 5min and subsequently cold-rolled to a 20% reduction were also investigated on aging at 450 ^{o}C. The obtained age-hardening curves of the alloys are shown in Fig. 1(b). The aging responses of the three alloys solutionized at 730 ^{o}C are similar to those of the alloys solutionized at 1000 ^{o}C. That is, the microhardness of the three alloys after solutionization and rolling slightly increased with increasing amount of Ti. Moreover, the peak hardnesses of the three alloys occurred after aging for 9 h, and the 0.04Ti alloy exhibited the highest hardness among the three alloys. The hardnesses of the three alloys during aging at 450 ^{o}C for up to 244 h (8.78 x 10^5 s) were approximately 15 to 20 Hv higher than those of the alloys during aging at 450 ^{o}C after solutionizing at 1000 ^{o}C and subsequent cold-rolling (Fig. 1(a)). The higher hardnesses of the three alloys solutionized at 730 ^{o}C compared to those of the alloys solutionized at 1000 ^{o}C is explained by spherical δ-Ni_2Si precipitates remaining in samples even after solutionizing at 730 ^{o}C, which led to a smaller grain size of these alloys compare to that of the alloys solutionized at 1000 ^{o}C, as will be discussed in the next section.

B. *Microstructure*

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TEM observations of the three alloys solutionized at 1000 ^{o}C revealed that there the base and 0.04Ti alloys contained no precipitates, however, coarse particles with a diameter of approximately 500 nm were observed in the 0.2Ti alloy. The lack of precipitates in the base and 0.04 Ti alloys indicates that Ni, Si and Ti atoms were dissolved in the Cu matrix during solutionization at 1000 ^{o}C. Fig. 2(a) depicts the coarse particles in the 0.2Ti alloy. Figs. 2(b) and (c) show the selected-area diffraction pattern (SADP) of the right particle in (a) and a schematic of the SADP in (b), respectively. The zone axis is parallel to $[110]_m$ of the Cu matrix. Analyses of the SADPs of several regions containing coarse particles revealed that the particles had a cubic structure with $a \approx 1.13$ nm. Moreover, the particles exhibited no specific crystallographic relationship with the Cu matrix. This result indicates that the coarse particles formed during casting or homogenization, and remain in the sample even after solutionization.

Energy-dispersive X-ray (EDX) analysis was performed to obtain the chemical composition of the coarse particles in the 0.2Ti alloy. Cu, Ni, Si and Ti atoms were detected when the incident electron beam was directed at the coarse particles. The EDX analysis results are presented in Fig. 3, where the relative atomic ratio of Ni, Si and Ti is plotted against the Cu concentration. The obtained ratio of Ni, Si and Ti is almost constant at approximately 3 : 1 : 1, irrespective of the Cu concentration. On the basis of this result, together with SADP analysis results, the particles were determined to be a $Ni_{16}Si_7Ti_6$ phase with an fcc $Mn_{23}Th_6$ (D8a) type structure with a lattice constant of $a = 1.122$ nm [7].

In the 0.2Ti alloy solutionized at 730 ^{o}C for 5 min, in addition to the coarse $Ni_{16}Si_7Ti_6$ particles, spherical precipitates with a diameter of approximately 50 nm were

observed. Fig. 4 shows an example of these spherical precipitates. Analyses of the SADPs revealed that the precipitates exhibited a structure corresponding to δ-Ni$_2$Si [1, 2]. These spherical δ precipitates exhibited no specific orientation relationship to the Cu matrix. In addition, spherical δ precipitates also observed in the base and 0.04Ti alloys solutionized at 730 ^{o}C. These δ precipitates may effectively suppress the grain growth during solutionization. Consequently, the grain sizes (approximately 10 μm) of the three alloys solutionized at 730 ^{o}C decreased substantially compared to those of the alloys solutionized at 1000 ^{o}C (approximately 500 μm).

Similar to the findings of previous studies [1, 2], it was observed that fine δ-Ni$_2$Si precipitates formed during aging at 450 ^{o}C. Fig. 5 shows a high-resolution TEM image of a precipitate in the base alloy peak-aged at 450 ^{o}C after solution treatment at 1000 ^{o}C followed by 20% cold-rolling. This image was taken using an incident beam parallel to the matrix $[001]_m$. The fine δ-Ni$_2$Si precipitates formed as disks on $\{110\}_m$ with an aspect ratio of approximately 3. An EDX analysis of these δ-precipitates indicated that they did not contain Ti atoms.

C. *Mechanical properties*

Figure 6 presents the stress-strain curves of the base, 0.04Ti and 0.2Ti alloys peak-aged at 450 ^{o}C for 9 h after solutionizing at 730 ^{o}C for 5min and then cold-rolling to a 20% reduction. Hereafter, these samples are referred to as the base-A, 0.04Ti-A and 0.2Ti-A alloys. Table 2 lists the 0.2% proof stress $\sigma_{0.2}$, tensile strength σ_{UTS}, total elongation ε_t, and electrical conductivity E of the base-A, 0.04Ti-A and 0.2Ti-A alloys. The 0.04Ti-A alloy exhibited a larger value of $\sigma_{0.2}$ (= 670 MPa) compared with that of

the base-A alloy, whereas the 0.2Ti-A alloy exhibited a smaller value of $\sigma_{0.2}$ (= 560 MPa). The electrical conductivity of the alloys slightly decreased with increasing Ti content. The values of ε_t were nearly identical for the three alloys.

IV. Discussion

A. *Distribution of Ni, Si and Ti atoms*

On the basis of the microstructural observations and the electrical conductivity measurements, the distributions of Ni, Si and Ti atoms in the δ-Ni_2Si phase, $Ni_{16}Si_7Ti_6$ phase and Cu matrix were estimated for the three alloys that were peak-aged at 450 ^{o}C after solution treatment at 1000 ^{o}C and subsequently rolled to a 20% reduction. The obtained results are shown in Fig. 7. The distributions of Ni, Si and Ti atoms were determined as follows.

The change in the resistivity $\Delta\rho$ of the alloys on aging at 450 ^{o}C for 9 h after solution treatment at 1000 ^{o}C can be expressed as $\Delta\rho = \Delta\rho_{G.B.} + \Delta\rho_{DIS} + \Delta\rho_{SOL}$ [10, 11, 12, 13], where $\Delta\rho_{G.B.}$, $\Delta\rho_{DIS}$ and $\Delta\rho_{SOL}$ are the resistivity contributions from the changes in grain boundary density, dislocation density, and solute atom concentration in the alloys, respectively. Since no change in the grain sizes of the alloys was detected after the aging treatment, $\Delta\rho_{G.B.}$ was considered to be negligibly small. Although the change in dislocation density ΔN of the alloys on the aging was not measured, $\Delta\rho_{DIS}$ will also be small because of the significantly smaller the contribution to resistivity by specific dislocation, $\Delta\rho_{DIS} / \Delta N \approx 0.8$ to 2.3×10^{-16} nΩm^3 [12, 13] than the resistivity contribution of solute atoms of Ni, Si and Ti. Therefore, the main contributor to the measured $\Delta\rho$ was

$\Delta\rho_{SOL}$.

First, the conductivities of the three alloys before and after peak-aging at 450 ^{o}C for 9 h following solutionization at 1000 ^{o}C and cold-rolled to a 20% reduction were measured. Table 3 lists the conductivity data used to estimate the atomic distributions in the three alloys. The electrical conductivity calculated under the assumption that Ni, Si and Ti atoms in the 0.2Ti alloy were completely dissolved in the Cu matrix is also shown in Table 3. The electrical conductivity E was converted into electrical resistivity ρ according to the relation $\rho = \rho_0$ x 100 / E. Here, ρ_0 (= 17.24 nΩm) corresponds to an IACS value of 100 % when expressed in terms of resistivity [6]. Because the increase in resistivity due to the existence of second-phase particles has been reported to be negligibly small [14], experimental data for the dependence of electrical resistivity of the Cu matrix on the Ni, Si and Ti concentrations ($\Delta\rho_{Ni}$ = 12.2 nΩm / at%, $\Delta\rho_{Si}$ = 39.5 nΩm / at% and $\Delta\rho_{Ti}$ = 113.3 nΩm / at%) reported in the literature [9] were used to estimate the atomic distributions. In the case of the 0.2Ti alloy, the difference between the resistivity calculated under the assumption that all Ni, Si and Ti atoms were dissolved in the matrix, and the resistivity experimentally obtained after solutionization at 1000 ^{o}C were used to calculate the distribution of Ni, Si and Ti atoms in the coarse $Ni_{16}Si_7Ti_6$ particles. The calculation results show that approximately 0.15Ti of the added 0.2Ti was consumed to form the $Ni_{16}Si_7Ti_6$ phase and remaining 0.05Ti dissolved into the matrix. This result corresponds well with the result that no $Ni_{16}Si_7Ti_6$ particles were observed in the solutionized 0.04Ti alloy; that is, added 0.04%Ti was completely dissolved into the matrix.

No Ti atoms were detected in the δ precipitates, as mentioned in section III-B, the increase in resistivity induced by the solute Ti was removed from the values of the

resistivity of the 0.04Ti and 0.2Ti alloys before and after aging at 450 $^{\circ}$C using $\Delta\rho_{Ti}$. The amounts of Ni and Si atoms constituting the δ precipitates were subsequently estimated using $\Delta\rho_{Ni}$ and $\Delta\rho_{Si}$.

As shown in Fig. 7, the amounts of Ni and Si atoms constituting the δ precipitates in the alloys increased in the order 0.2Ti < base < 0.04Ti. This trend corresponds to the observation that the peak hardness increased in the same order (Fig. 1). Since portion of the Ni and Si atoms in the 0.2Ti alloy was used to form the $Ni_{16}Si_7Ti_6$ phase, the amount of δ precipitates in the 0.2Ti alloy was smaller than that in the base or 0.04%Ti alloy, and thus the peak hardness of the 0.2Ti alloy was the lowest among the three alloys.

Moreover, as evident in Fig. 7, the amounts of Ni and Si atoms that formed the δ precipitates in the 0.04Ti alloy were slightly larger than those in the base alloy. To discuss the cause of this difference in the amount of δ precipitates formed in the base and 0.04Ti alloys, the equilibrium solute concentration x_e in the Cu matrix of the alloys was investigated, under the assumption of a Cu–δ-Ni_2Si quasi binary system. A value of x_e was obtained by examining the change in the resistivity of each the alloy as a function of aging time t. Because a reliable solvus curve for the Cu–δ-Ni_2Si quasi binary system has not yet been reported, and because values of x_e have only been reported for a few temperatures above 550 $^{\circ}$C [15], alloys solutionized at 1000 $^{\circ}$C and then cold-rolled to a 90% reduction were aged at 550 $^{\circ}$C to allow a comparison with the reported x_e value. The time-dependent solute content $x(t)$ in the Cu matrix was obtained from the change in measured resistivity during aging. The atomic ratio of Ni/Si = 2 was taken into account. $x(t)$ values for the 0.04Ti alloy were calculated after the resistivity increase due to 0.04Ti was removed. According to the Lifshitz and Slyozov [16] and

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Wagner [17] theory of coarsening modified by Ardell [18], the concentration of a solute in a matrix after coarsening time t is expressed as

$$x(t) - x_e \propto t^{-\frac{1}{3}}. \tag{1}$$

Following eq. (1), $x(t)$ was plotted against $t^{-1/3}$ for the alloys aged at 550 $^{\circ}$C, as shown in Fig. 8. In this figure, $x(t)$ obeys the $t^{-1/3}$ law after a certain aging time. Values of x_e were directly evaluated by extrapolation to $t^{-1/3} = 0$ ($t \to \infty$) using the least-squares method, and were estimated to be 664 ± 4 mol m^{-3} and 602 ± 5 mol m^{-3}, respectively. Fig. 9 shows a plot of the estimated values of x_e. The solubility limit data for a Cu-2Ni-0.5Si alloy reported by Watanabe and Monzen [15] using the same method as the present study is also shown in Fig. 9. The value of x_e at 550 $^{\circ}$C for the base alloy is nearly identical to the reported value of 656 mol m^{-3} [15]. More importantly, the value of x_e for the 0.04Ti alloy is lower than that for the base alloy. Thus, the equilibrium solute concentration of the Cu-Ni-Si alloy was lowered by the presence of solute Ti atoms.

B. *Effect of Ti addition on strength*

Lockyer and Noble [19] have suggested that the yield stress of the Cu-Ni-Si system alloys containing δ precipitates at room temperature is controlled by the Orowan mechanism under peak-aging and over-aging conditions. The Orowan stress is inversely proportional to the inter-precipitate spacing λ [20]. The change in strength due to the addition of Ti can then be discussed by estimating λ, which is considered to be the square lattice spacing in parallel planes and is written as [21]

$$\lambda = \bar{r}\left[\sqrt{\frac{2\pi}{3f}} - 1.63\right], \tag{2}$$

where $\bar{r}$ is the average radius of spherical precipitates and f is the volume fraction of precipitates.

Many bright-field TEM images of fine δ-Ni_2Si precipitates formed as disks parallel to $\{110\}_m$ in the base-A, 0.04Ti-A and 0.2Ti-A alloys were obtained with the incident beam parallel to $<001>_m$, $<1\bar{1}0>_m$ and $<1\bar{1}1>_m$. The volume of the disk-shaped δ precipitate was calculated by measuring its diameter and height. Then the radius r of a sphere having the same volume as the disk-shaped precipitate was calculated. The volume fraction f of the base-A alloy was determined from the electrical conductivity E_0 and E_1 of the alloy before and after aging at 450 ^{o}C for 9 h, as listed in Table 2. The conductivity values were first converted into electrical resistivity. Then, the molar fraction of fine δ-Ni_2Si precipitates formed during aging was determined by applying the difference between E_0 and E_1 to the experimental data regarding the dependence of electrical resistivity on Ni and Si concentration [9], taking into account the atomic ratio Ni/Si = 2. From the obtained molar fraction of the δ phase, f was calculated using the molar volume V_m of the δ phase. Variable V_m was calculated as $V_m = N_a abc / n$ ($=$ 6.59 x 10^{-6} m^3 mol^{-1}) using the lattice parameters of an orthorhombic lattice of the δ phase (a = 0.703 nm, b = 0.499 nm and c = 0.372 nm) [1]. Here N_a and n (=12) are Avogadro's number and the total number of atoms in a unit lattice of the δ phase, respectively. In the case of Ti-added alloys, f was calculated after the increase in resistivity induced by solute Ti atoms in the Cu matrix was removed. As noted in the discussion of the atomic distribution of the alloys in section IV-A, the amounts of solute Ti atoms used in the

calculation of f were 0.05Ti for the 0.2Ti-A alloy and 0.04Ti for the 0.04Ti-A alloy. Table 4 lists the values of $\bar{r}$, f and λ for the base-A, 0.04Ti-A and 0.2Ti-A alloys, together with the values of $\sigma_{0.2}$. Variable λ decreases as f increases. Therefore, it can be concluded that the decrease in λ induced by the addition of 0.04Ti results in a corresponding increase in $\sigma_{0.2}$ due to the Orowan looping mechanism.

V. Conclusions

The effects of the addition of 0.2 mass% or 0.04 mass%Ti on the microstructure and mechanical properties of a Cu-2.0 mass%Ni-0.5 mass%Si alloy aged at 450 $^{\circ}$C were investigated. The obtained results are summarized as follows:

(1) Transmission electron microscopy of the solutionized alloy with 0.2 mass% added Ti revealed that coarse particles of a $Ni_{16}Si_7Ti_6$ phase with a fcc $Mn_{23}Th_6$ (D8a) type structure were present [5]. The addition of 0.2 mass%Ti resulted in a decrease in the strength of the Cu-Ni-Si alloy due to the reduction in the volume fraction of the strengthening phase of δ-Ni_2Si. This decrease in volume fraction of δ was caused by the formation of $Ni_{16}Si_7Ti_6$ particles, which were not formed in the alloy with 0.04 mass%Ti added.

(2) The addition of 0.04mass%Ti to the Cu-Ni-Si alloy effectively enhanced the strength without reducing its resistivity. The increase in the strength was attributed to a decrease in the inter-precipitate spacing of δ-Ni_2Si precipitates caused by an increase in the volume fraction of the δ precipitates.

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Figures and Tables
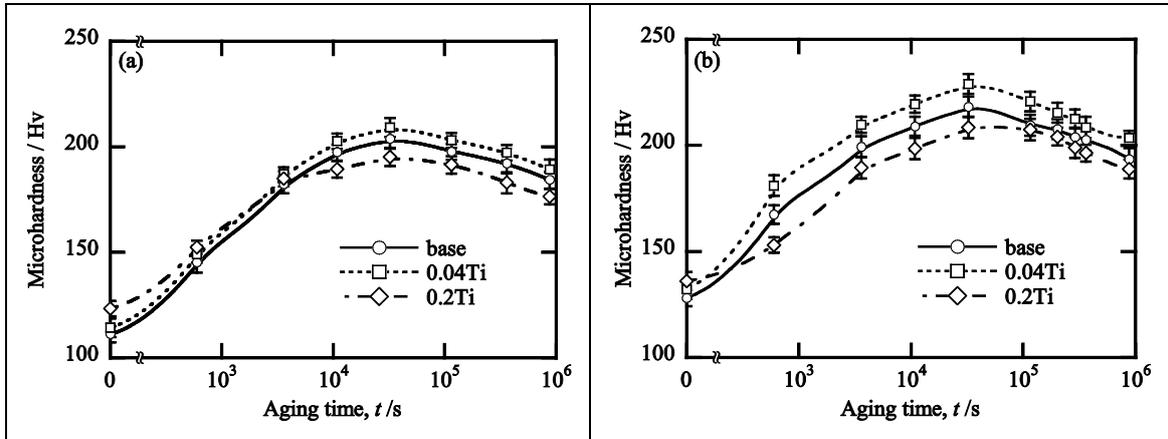
Fig. 1 Change in the microhardness of Cu-Ni-Si (base), Cu-Ni-Si-0.04Ti (0.04Ti) and Cu-Ni-Si-0.2Ti (0.2Ti) alloys during aging at 450 ^{o}C (a) after solutionizing at 1000 ^{o}C for 2 h and then cold-rolling to a 20% reduction, and (b) after solutionizing at 730 ^{o}C for 5 min and then cold-rolling to a 20% reduction. Error bars indicate the standard deviation of 10 replicate measurements.
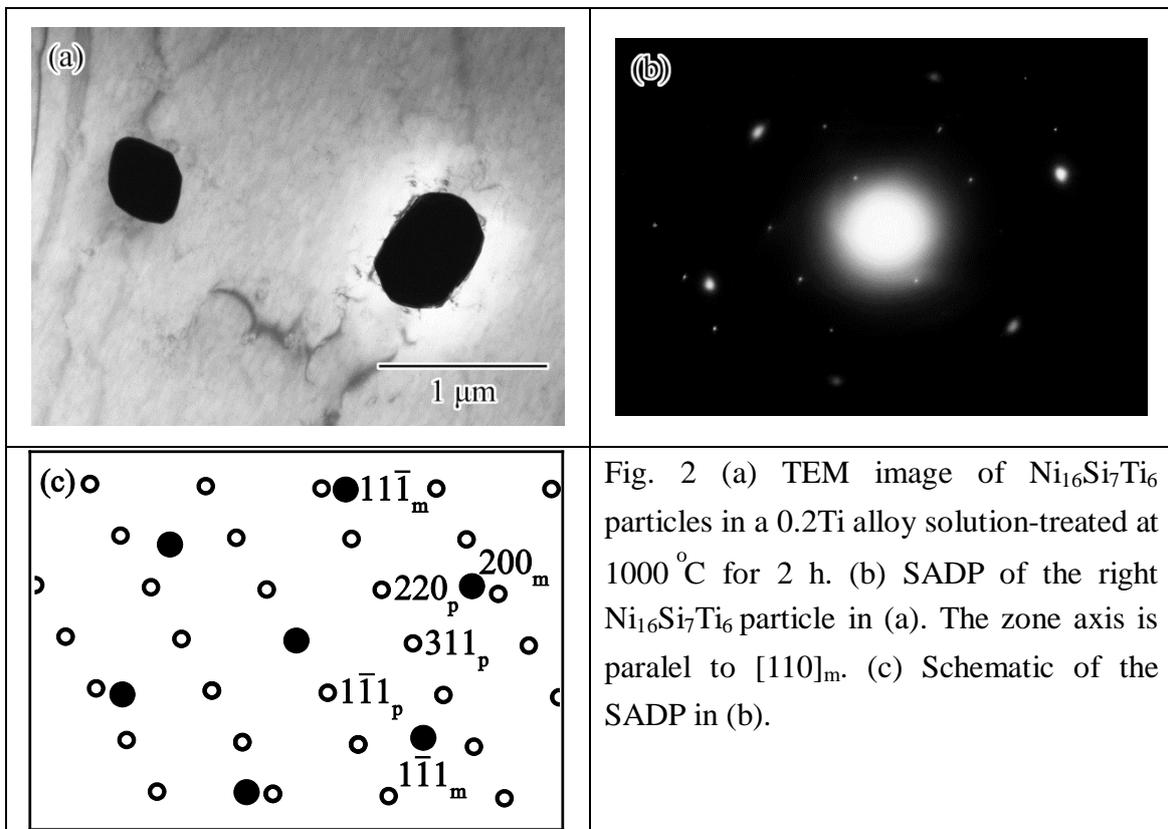

Fig. 2 (a) TEM image of $Ni_{16}Si_7Ti_6$ particles in a 0.2Ti alloy solution-treated at 1000 ^{o}C for 2 h. (b) SADP of the right $Ni_{16}Si_7Ti_6$ particle in (a). The zone axis is paralel to $[110]_m$. (c) Schematic of the SADP in (b).

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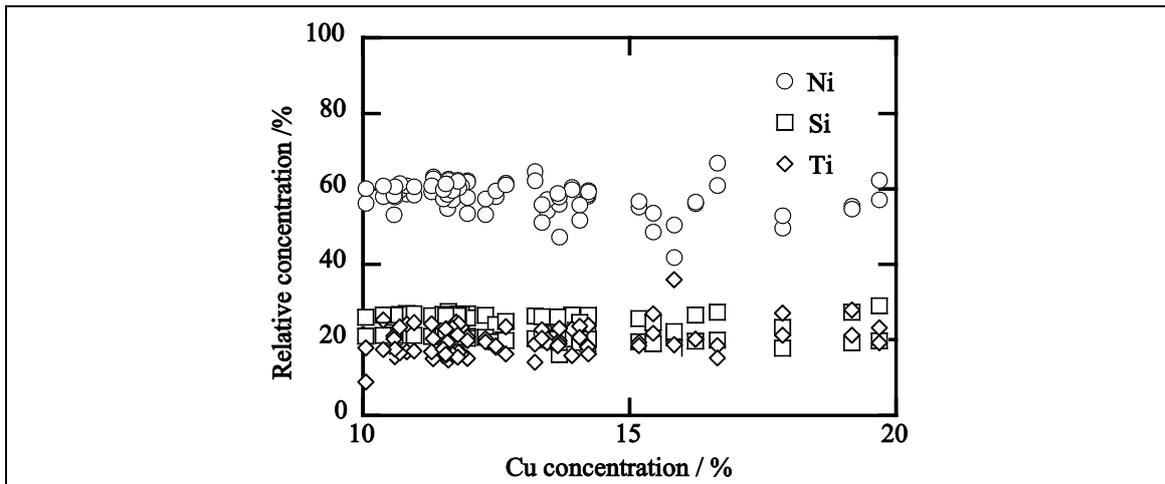
Fig. 3 EDS analysis results obtained from coarse $Ni_{16}Si_7Ti_6$ particles in a 0.2Ti alloy solution-treated at 1000 ^{o}C for 2h.
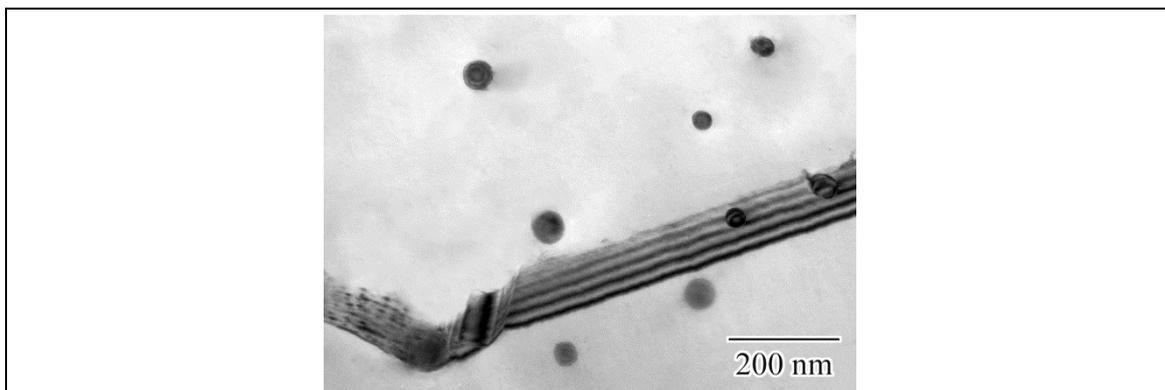

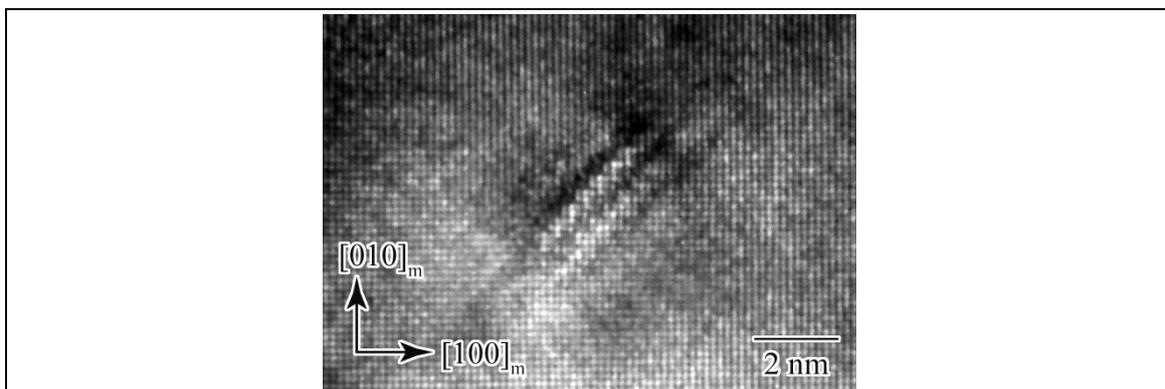Fig. 4 TEM image of spherical δ-Ni_2Si particles in a 0.2Ti alloy solution-treated at 730 ^{o}C for 5 min.

Fig. 5 HRTEM image of a disk-shaped δ-Ni_2Si precipitate in a base alloy aged at 450 ^{o}C for 9h after solutionizing at 1000 ^{o}C for 2h and subsequent cold-rolling to a 20% reduction. The zone axis is parallel to $[001]_m$.
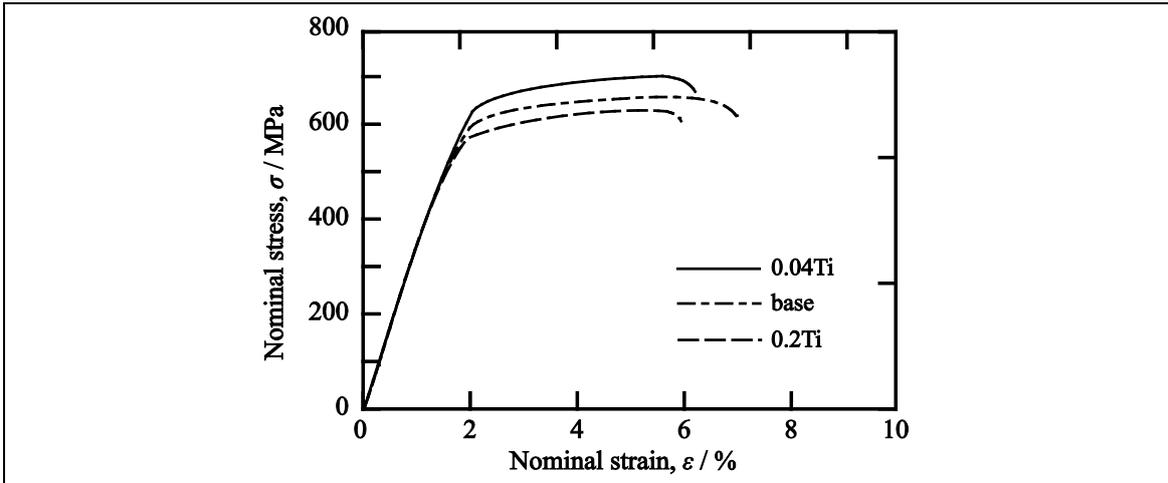
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Fig. 6 Stress-strain curves of base, 0.04Ti and 0.2Ti alloys peak-aged at 450 oC for 9 h after solutionizing at 730 ^{o}C for 5min and subsequent cold-rolling to a 20% reduction.
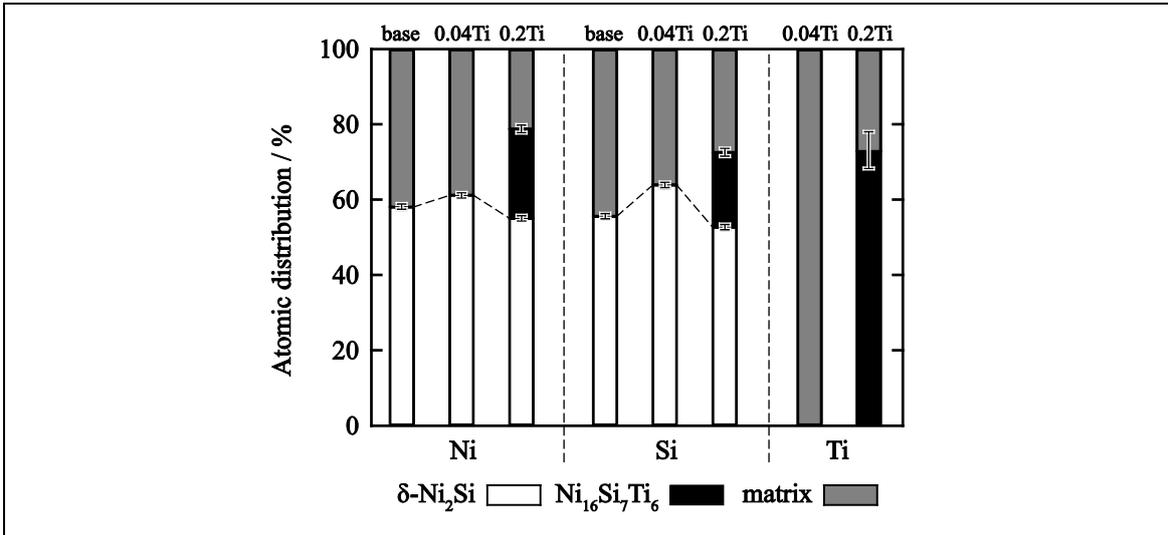

Fig. 7 Comparison of the distribution of Ni, Si and Ti atoms among the δ-Ni$_2$Si precipitates, Ni$_{16}$Si$_7$Ti$_6$ particles and Cu matrix in base, 0.04Ti and 0.2Ti alloys aged at 450 ^{o}C for 9 h after solutionizing at 1000 ^{o}C and subsequent cold-rolling to a 20% reduction.
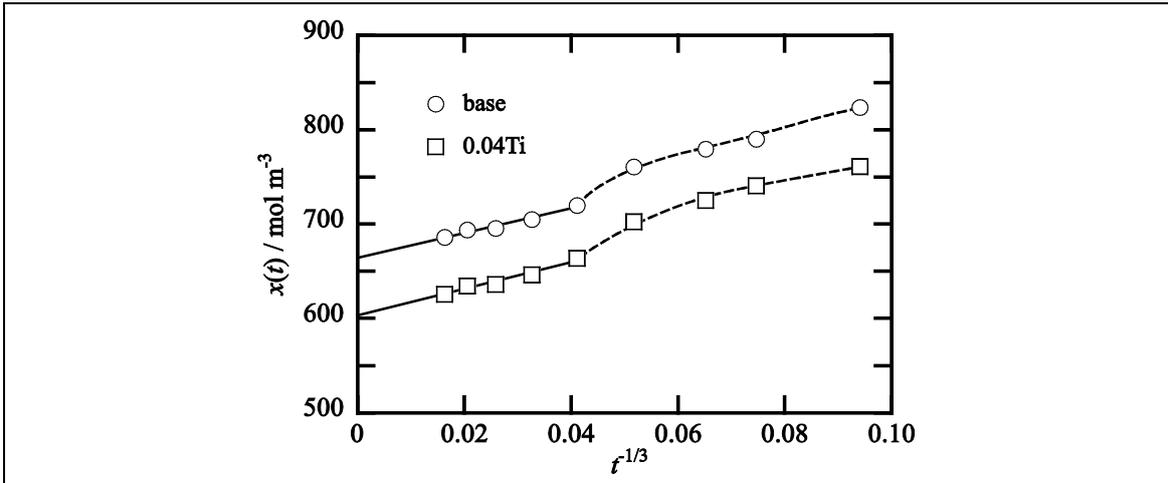
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Fig. 8 Change in the solute concentration $x(t)$ in the matrix of base and 0.04Ti alloys bearing δ-Ni_2Si precipitates during aging at 550 ^{o}C after solutionizing at 1000 ^{o}C for 2 h and subsequent cold-rolling to a 90% reduction.
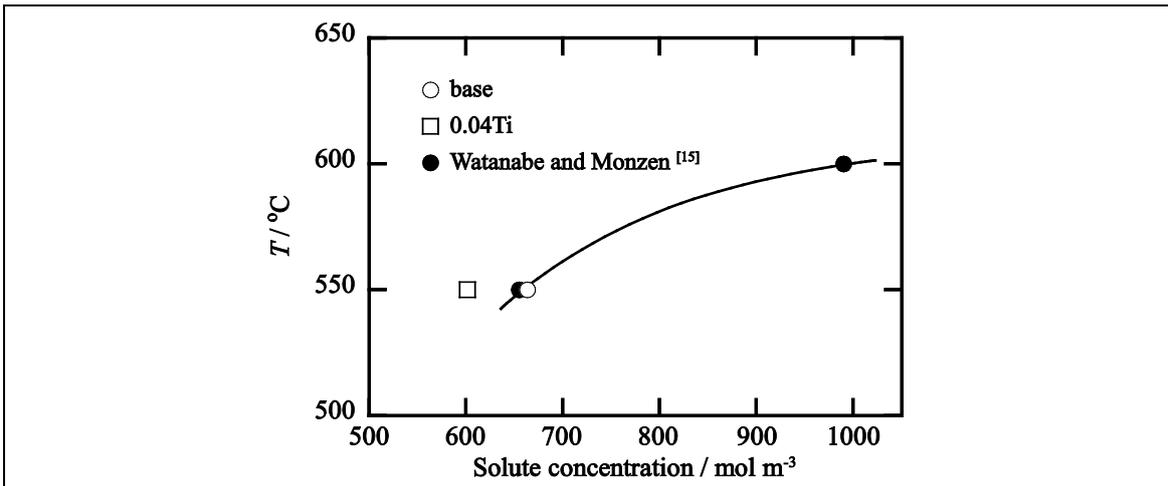

Fig. 9 Plot of the equilibrium solubility at 550 ^{o}C as a function of solute concentration in the matrix of base and 0.04Ti alloys bearing δ-Ni_2Si precipitates. Also shown are data previously reported by Watanabe and Monzen [15].

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Table 1 Chemical composition (mass%) of Cu-2Ni-0.5Si, Cu-2Ni-0.5Si-0.04Ti and Cu-Ni-Si-0.2Ti alloys.

	Ni	Si	Ti	Cu
Cu-2Ni-0.5Si	1.98	0.52	-	bal.
Cu-2Ni-0.5Si-0.04Ti	2.03	0.49	0.04	bal.
Cu-2Ni-0.5Si-0.2Ti	2.08	0.51	0.19	bal.

Table 2 Values of the 0.2% proof stress $\sigma_{0.2}$, tensile strength σ_{UTS}, total elongation ε_t and electrical conductivity E_1 for base (base-A), 0.04Ti (0.04Ti-A) and 0.2Ti (0.2Ti-A) alloys peak-aged at 450 ^{o}C for 9 h after solutionizing at 730 ^{o}C for 5min and subsequent cold-rolling to a 20% reduction. Also shown are the values of the conductivity E_0 of the three alloys solutionized at 730 ^{o}C for 5 min.

specimen	$\sigma_{0.2}$ [MPa]	σ_{UTS} [MPa]	ε_t [%]	E_1 [%IACS]	E_0 [%IACS]
base-A	610	670	7	45.9 ± 0.1	25.2 ± 0.1
0.04Ti-A	670	710	6	45.1 ± 0.1	24.0 ± 0.1
0.2Ti-A	560	630	6	44.2 ± 0.1	25.3 ± 0.1

Table 3 Values of the electrical conductivity E_0 and E_1 for base, 0.04Ti and 0.2Ti alloys before and after peak-aging at 450 ^{o}C for 9 h after solutionizing at 1000 ^{o}C for 2 h and subsequent cold-rolling to a 20% reduction. Also shown is a value of the conductivity E_0' calculated with the assumption that Ni, Si and Ti atoms are completely dissolved in the Cu matrix of the 0.2Ti alloy.

	%IACS		
	E_0	E_1	E_0'
base	21.3 ± 0.2	42.0 ± 0.4	-
0.04Ti	20.1 ± 0.1	41.2 ± 0.3	-
0.2Ti	21.4 ± 0.3	40.3 ± 0.4	14.7

Table 4 Values of the 0.2% proof stress $\sigma_{0.2}$, average radius of δ-Ni$_2$Si precipitates $\bar{r}$, precipitate volume fraction f and inter-precipitate spacing λ for base (base-A), 0.04Ti (0.04Ti-A) and 0.2Ti (0.2Ti-A) alloys peak-aged at 450 $^{\circ}$C after solutionizing at 730 $^{\circ}$C for 5 min and subsequent 20% cold-rolling.

	$\sigma_{0.2}$ [MPa]	$\bar{r}$ [nm]	f [%]	λ [nm]
base-A	610	2.1 ± 0.2	1.36 ± 0.01	22.6 ± 2.2
0.04Ti-A	670	2.1 ± 0.1	1.48 ± 0.01	21.5 ± 1.1
0.2Ti-A	560	2.1 ± 0.2	1.28 ± 0.01	23.4 ± 2.3