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Mechanical Properties of Cu-4.0wt%Ni-0.95wt%Si Alloys with and without P and Cr Addition

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Abstract. The effects of P and Cr addition and two-step aging on the microstructure and mechanical properties of a Cu-4wt%Ni-0.95wt%Si alloy have been examined. The addition of 0.02wt%P improves both strength and elongation because it suppresses discontinuous precipitation reaction. The Cr addition to the Cu-Ni-Si-P alloy decreases greatly the grain size, resulting in an increase in elongation. Two-step aging, pre-aging at 300 or 350°C and subsequent second-step aging at 450°C, causes an increase in strength without reducing elongation. The increase in strength is attributable to the decrease in inter-precipitate spacing by the two-step aging. The two-step aged Cu-4wt%Ni-0.95wt%Si-0.02wt%P-0.02wt%Cr alloy attains a tensile strength of 830MPa, an elongation of 13% and an electrical conductivity of 35%IACS.

Introduction

Cu-Ni-Si alloys with compositions corresponding approximately to Cu-2wt%(2at%)Ni-0.5wt%(1at%)Si exhibit a significant age-hardening effect. The precipitates responsible for the age-hardening effect have been identified as δ -Ni₂Si [1]. The Cu-Ni-Si system alloys are widely used in such applications as semiconductor lead-frames owing to their high strength and good electrical conductivity. Recently, the requirement of high strength becomes increasingly important with automation of the semiconductor packaging process. One straightforward method to increase the strength is to increase the contents of Ni and Si in the Cu-Ni-Si system alloys.

In a previous study [2], we have found that, in a Cu-4wt% (4at%)Ni-0.95wt%Si (2at%) alloy containing larger amounts of Ni and Si than conventional Cu-Ni-Si system alloys, both continuous precipitation and discontinuous precipitation (DP) took place simultaneously during aging, and that the addition of a small amount of P to the alloy suppressed the DP. In this study, the effect of adding P on the mechanical properties of the same alloy is examined. In addition, we will show that the Cr addition to the Cu-4wt%Ni-0.95wt%Si-0.02wt%P alloy refines the grain size, resulting in an increase in elongation, and that two-step aging enhances the strength of the P-added alloy.

Experimental Procedure

Cu-4wt%Ni-0.95wt%Si alloys with and without 0.02wt%P and a Cu-4wt%Ni-0.95wt%Si-0.02wt%P-0.02wt%Cr alloy were prepared by melting under an argon atmosphere. The cast alloys were homogenized at 1000°C for 10 h and cold rolled to the reduction of 85% in thickness. Then the alloys were solutionized at 1000°C for 4 h or at 900°C for 5 min and quenched into cold water. Aging treatments were performed at 450°C for various times in a vacuum following 5% cold rolling. Microstructures of the aging alloys were studied by transmission electron microscopy (TEM). Thin

foils for TEM observations were prepared by a standard electropolishing method. TEM foils were examined in a JOEL 2010FEF microscope at an operation voltage of 200kV.

Tensile tests were performed using a static Instron type testing machine with a constant strain rate of 10^{-3}s^{-1} at room temperature. Electrical resistivity was measured by an eddy current apparatus at 20°C .

Results and Discussion

Microhardness and electrical resistivity.

Figure 1 shows the change in the microhardness and electrical resistivity of Cu-Ni-Si, Cu-Ni-Si-P and Cu-Ni-Si-P-Cr alloys during aging at 450°C after solutionizing at 1000°C for 4 h. For the Cu-Ni-Si-P and Cu-Ni-Si-P-Cr alloys, all P atoms were assumed to dissolve in the Cu matrix, and the resistivity increment caused by 0.02wt%P in the matrix was removed using the experimental data on the dependence of electrical resistivity on the P concentration, $\Delta\rho_{\text{P}}=5.1\times 10^{-8}\Omega\text{m/at\%}$. The addition of P to the Cu-Ni-Si alloy caused no change in the grain size after the solution treatment, but the addition of Cr to the Cu-Ni-Si-P alloy changed the grain size from about $100\mu\text{m}$ to $80\mu\text{m}$. For each alloy, the peak hardness effect occurs after aging for about 5 h and the hardness decreases continuously at longer aging times. The addition of P and Cr to the Cu-Ni-Si alloy does not significantly change the microhardness after the solution treatment. The P addition slightly enhances the hardness on aging. The hardness and the electrical resistivity are practically unaffected by the Cr addition to the Cu-Ni-Si-P alloy.

DP took place in the P-free alloy just before the hardness reached a maximum value, and the regions of DP cells increased with aging time. Similar to the previous study [2], the P addition retarded the DP, which did not form in the Cu-Ni-P and Cu-Ni-P-Cr alloys under aging treatments in this study. The hardness of the DP cells is much lower than that of the grain interior and decreases with aging time, as seen in Fig. 1. Corresponding to the initiation and growth of DP cells, the electrical resistivity of the Cu-Ni-Si alloy sharply decreases.

Fig. 1 Microhardness and electrical resistivity changes of Cu-Ni-Si, Cu-Ni-Si-P and Cu-Ni-Si-P-Cr alloys aged at 450°C after solutionizing at 1000°C for 4 h. DP=discontinuous precipitation, AQ=as quenched.

Fig. 2 (a) HRTEM image of a disk-shaped $\delta\text{-Ni}_2\text{Si}$ precipitate in a Cu-Ni-Si alloy aged at 450°C for 5 h after solutionizing at 1000°C for 4 h. The zone axis is the matrix $[001]_{\text{m}}$ direction. (b) $[001]_{\text{m}}$ SADP corresponding to (a).

Microstructural observations. The TEM observations of the present alloys aged at 450°C for various times of 1 to 160 h following the solution treatment at 1000°C for 4 h revealed that there existed disk-shaped $\delta\text{-Ni}_2\text{Si}$ precipitates alone within the grains. Figure 2(a) shows a high-resolution TEM (HRTEM) image of a $\delta\text{-Ni}_2\text{Si}$ precipitate in the Cu-Ni-Si alloy aged at 450°C for 5 h, taken with

an incident beam parallel to the matrix $[001]_m$. Fig. 2(b) is the $[001]_m$ selected-area diffraction pattern (SADP) corresponding to (a). From an analysis of the SADP, an orientation relationship was found between the Cu matrix and the δ precipitate: $(110)_m // (001)_p$; $[001]_m // [010]_p$. This orientation relationship is in agreement with that previously reported in the literature [3].

Mechanical properties of alloys. The mechanical properties and electrical resistivity of the Cu-Ni-Si, Cu-Ni-Si-P and Cu-Ni-Si-P-Cr alloys after heat treatments were investigated and the results are presented in Fig. 3.

As shown in Fig. 3, 0.2% proof stress $\sigma_{0.2}$ and tensile stress σ_{UTS} of the Cu-Ni-Si alloy (specimen A) are lower than those of the Cu-Ni-Si-P alloy (specimen B), because of the formation of DP cells in the former alloy. After solutionizing at 1000°C for 4 h, aging was carried out at 450°C for 5 h. After the solution treatment, no precipitates were observed in the Cu matrix and thus the grain size became large with $100\mu\text{m}$. On the other hand, the Cu-Ni-Si-P alloy which was solutionized at 900°C for 5 min (specimen C) had spherical precipitates with an average diameter of 50nm . Analyses of SADPs of several regions containing the precipitates revealed that the spherical precipitates were the $\delta\text{-Ni}_2\text{Si}$ phase and exhibited no specific orientation relationship to the Cu matrix. No orientation relationship with the matrix can be understood since complete recrystallization occurred by the solution treatment at 900°C for 5 min. The large precipitates restricted the growth of recrystallized grains, so that the average grain size was refined to $15\mu\text{m}$. The grain refinement brings about an increase in elongation without reducing strength (Fig. 3). The Cu-Ni-Si-P alloy (specimen D), which was cold-rolled by 5% before aging, shows larger values of $\sigma_{0.2}$ and σ_{UTS} than the specimen C.

Recently, it has been reported that the addition of a small amount of Cr to Cu-Ni-Si system alloys produces an intermetallic compound of Cr_3Si , which is formed mainly in the liquid state during the solidification [4]. The dispersed Cr_3Si particles impede grain growth at temperatures higher than that at which the $\delta\text{-Ni}_2\text{Si}$ phase is dissolved. In the present study, 0.02wt%Cr was added to the Cu-Ni-Si-P alloy and the same solution treatment and thermo-mechanical treatment as the specimen D were carried out (specimen E). Owing to the grain refinement to $4\mu\text{m}$, elongation was greatly improved (Fig. 3).

It is well known that the strength of age-hardenable alloys is improved by two-step aging [5, 6]. In this study, A two-step aging treatment, that is, pre-aging at 300°C for 12 h or at 350°C for 1 h and subsequent second aging at 450°C for 5 h, was performed using the Cu-Ni-Si-P-Cr alloy. The specimens pre-aged at 350 and 300°C are termed as specimen F and specimen G. Comparison between the specimens F and G shows that the pre-aging at the lower temperature causes a more increase in strength without decreasing elongation. It may be noted that the specimen G has a tensile strength of 830MPa , an elongation of 13% and an electrical conductivity of 35%IACS.

Fig. 3 Mechanical properties and electrical conductivity of specimens after various heat treatments.

Lockyer and Noble [7] have reported that the yield stress at room temperature of a Cu-Ni-Si system alloy containing δ -Ni₂Si precipitates is controlled by the Orowan mechanism at the peak-age and over-age conditions. The Orowan stress is inversely proportional to the inter-precipitate spacing l . The increase of strength by the two-step aging can then be discussed by estimating l . l is taken as the square lattice spacing in parallel planes and is written as [8]

$$l = r \left[\left(\frac{2\pi}{3f} \right)^{\frac{1}{2}} - 1.63 \right], \quad (2)$$

where r is the average radius of precipitates and f is the volume fraction of precipitates. The radius of a sphere of volume equal to that of disk-shaped δ -Ni₂Si precipitates was calculated. No Cr particles are assumed to precipitate on two-step aging. Then f was determined by applying the values of electrical resistivity before and after two-step aging to the experimental data on the dependence of electrical resistivity on the Ni and Si concentrations in the literature [9]. The number density N of the δ -Ni₂Si precipitates was yielded from r and f . The estimated values of N and l are listed in Table 1 together with the values of $\sigma_{0.2}$. It can be concluded from Table 1 that the increase in N or decrease in l by two-step aging results in the corresponding increase in $\sigma_{0.2}$ due to the Orowan looping mechanism.

Table 1 Values of the radius r of δ -Ni₂Si precipitates, the number density N of δ -Ni₂Si precipitates, the inter-precipitate spacing l , and 0.2% proof stress $\sigma_{0.2}$ for a Cu-Ni-Si-P-Cr alloy under three aging conditions after solutionizing at 900°C for 5 min.

Aging condition	r (nm)	N (10 ²³ m ⁻³)	l (nm)	$\sigma_{0.2}$ (MPa)
450°C×5 h	2.8	3.3	18.4	650
350°C×1 h →450°C×5 h	2.6	4.5	16.5	680
300°C×12 h →450°C×5 h	2.3	6.5	14.7	700

Summary

The improvement of the mechanical properties of a Cu-4wt%Ni-0.95wt%Si alloy has been attempted by the P and Cr addition and two-step aging. The results are summarized as follows:

- (1) Adding 0.02wt%P considerably improves the mechanical properties of the Cu-Ni-Si alloy, owing to the suppression of discontinuous precipitation reaction at boundaries.
- (2) The Cr addition to the Cu-Ni-Si-P alloy significantly reduces the grain size and thus enhances the elongation of the alloy. Application of two-step aging to the Cr-added alloy increases the strength without reducing elongation by effectively decreasing the inter-precipitate spacing.

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