

I. INTRODUCTION

The Cu-Ni-Sn alloys have gathered a considerable amount of interest over the past 20 years because the strength levels of Cu-Ni-Sn alloys with proper thermomechanical processing are equal to those of high-strength, precipitation-hardened Cu-Be alloys.\(^{1-4}\) Furthermore, Cu-Ni-Sn alloys do not present the health hazards or the difficulties in manufacturing associated with Cu-Be alloys. Cu-Ni-Sn alloys are, therefore, possible substitutes for Cu-Be alloys in the manufacture of connectors, spring components, etc., in the electronic industries. The aging response of Cu-Ni-Sn alloys is known to be extremely sensitive to aging temperature, aging time, and/or prior processing history.\(^{1-7}\) When Cu-Ni-Sn alloys are aged below 400 °C after solution heat treatment, for example, the supersaturated solid solution Α is reported to follow the three stages of decomposition. In the first stage, the modulated structure with Sn-rich and Sn-poor regions forms as a result of spinodal decomposition. In the second stage, the metastable γ precipitates with DO\(_{22}\) type structure nucleate from the modulated structure, and the highest strength occurs in this stage. In the final stage of transformation, the γ phases decompose into the cellular structures, consisting of equilibrium Α and γ phases, and the strength ceases to increase or decrease. The effect of cold working prior to aging on tensile properties of Cu-Ni-Sn alloys appears to be significant but is still controversial.\(^{1,2,5,6}\) Helmi and Zsoldos,\(^{[6]}\) for example, studied the aging characteristics of Cu-8Ni-2Sn and Cu-8Ni-5.5Sn alloys, which were 60 pct, cold-rolled, and subsequently solutionized at 800 °C for 30 minutes, and found no evidence of spinodal decomposition. Ray and Narayanan\(^{[2]}\) supported the finding of Helmi and Zsoldos and proposed that high dislocation density introduced in Cu-Ni-Sn alloys by the cold work would accelerate the fine ordered precipitates rather than spinodal decomposition. Lefevre et al.,\(^{[5]}\) on the other hand, advocated the proposition that spinodal decomposition is enhanced in the aged Cu-15Ni-8Sn alloys by severe prior cold working.

In the present study, the aging characteristics of heavily swaged Cu-9Ni-6Sn alloys, the composition of which is known to have the best combination of mechanical and physical properties, were examined. The hardening behaviors of Cu-9Ni-6Sn alloys, either solutionized and aged (S/A) or directly aged (D/A), are discussed with scanning electron microscope (SEM) fractographic studies and transmission electron microscope (TEM) micrographic observations.

II. EXPERIMENTAL PROCEDURE

The 20-mm-diameter bar products of Cu-9Ni-6Sn alloy were prepared with a vertical continuous casting of high purity elemental Cu, Ni, and Sn in air with a casting rate of 280 mm/min. The 20-mm-diameter bar was swaged to 4.5-, 9.6-, and 12-mm-diameter rods, to give a total swaging amount of 95, 77, and 64 pct, respectively. Solution heat treatment was conducted at 850 °C for 1 hour and subsequently water-quenched and aged at 350 °C for 30 seconds to 24 hours. Some specimens were directly aged after swaging without solution heat treatment. Round-bar tensile specimens with a gage length of 25.4 mm were prepared from the center portion of the rod with the loading axis parallel
to the longitudinal direction. Tensile tests were performed at a nominal strain rate of $10^{-4}$/s. After tensile test, the fracture surfaces of selected specimens were examined using a SEM. For optical micrographic examinations, the specimens were etched with 50 mL NH$_4$OH + 25 mL H$_2$O$_2$ + 6 mL HNO$_3$ solution and subsequently cleaned with supersaturated NaOH solution. Transmission electron microscope specimens were prepared using the jet thinning method in 200 mL CH$_3$OH + 100 mL HNO$_3$ solution at −30 °C. X-ray diffraction profiles of selected specimens were recorded with Cu K$_\alpha$ radiation about the {200} reflection with a scan rate of 0.1 deg/min.

### III. EXPERIMENTAL RESULTS

Figure 1 represents the effect of aging time on the tensile strength of 95 pct swaged Cu-9Ni-6Sn alloys, either solutionized at 850 °C for 1 h and aged or directly aged at 350 °C for 30 s to 24 h. In the S/A specimens, a large number of extremely fine precipitates were observed throughout the matrix, and any other noticeable phases were not found. Previous studies on the transformation behavior of Cu-Ni-Sn alloys suggest that these fine precipitates are metastable γ phases with DO$_{22}$-type structure and a chemical composition of (Cu$_x$Ni$_{1-x}$)$_3$Sn. [3,5] In the D/A specimens, a large number of elongated dislocation substructures were found to gradually decrease with increasing aging time. Unlike the S/A specimens, a considerable amount of sphere- or rod-type precipitates were observed (Figure 4(c)), and the density of such precipitates increased with aging progressed. Fine precipitates of γ phases were hardly found in 95 pct swaged D/A specimens.

Figure 3 shows the SEM fractographs of tensile fractured, 95 pct swaged Cu-9Ni-6Sn alloys, either solutionized and aged for (a) 30 seconds and (b) 3 hours, respectively, or directly aged for (c) 1 hour and (d) 24 hours, respectively. Typical dimpled rupture mode was observed on the fracture surfaces of 95 pct swaged D/A specimens, regardless of aging time. The average size of dimples, however, appeared to decrease slightly with increasing aging time. The average size of dimples, for example, was 4 μm for the D/A specimens aged for 1 hour, while it was 1 to 2 μm for the D/A specimens aged for 24 hours. In 95 pct swaged S/A specimens aged for up to 1 hour, the dominant fracture mode was a dimpled rupture. An intergranular fracture mode began to appear occasionally after aging for 1 hour, and eventually 100 pct intergranular fracture mode was observed in the S/A specimens aged for 3 hours and more (Figure 3(b)).

Figure 4 represents the TEM micrographs of 95 pct swaged Cu-9Ni-6Sn alloys, solutionized and aged for (a) 1 hour and (b) 7 hours, respectively, and directly aged for (c) 1 hour and (d) 7 hours, respectively. In the S/A specimens, a large number of extremely fine precipitates were observed throughout the matrix, and any other noticeable phases were not found. Previous studies on the transformation behavior of Cu-Ni-Sn alloys suggest that these fine precipitates are metastable γ phases with DO$_{22}$-type structure and a chemical composition of (Cu$_x$Ni$_{1-x}$)$_3$Sn. [3,5] In the D/A specimens, a large number of elongated dislocation substructures were found to gradually decrease with increasing aging time. Unlike the S/A specimens, a considerable amount of sphere- or rod-type precipitates were observed (Figure 4(c)), and the density of such precipitates increased with aging progressed. Fine precipitates of γ phases were hardly found in 95 pct swaged D/A specimens.

Figures 5 and 6 represent the change in tensile strength as a function of aging time for Cu-9Ni-6Sn alloys, either solutionized and aged (Figure 5) or directly aged (Figure 6), with different swaging amounts of 95, 77, and 64 pct, respectively. For comparison, the data for the unswaged S/A specimens are also included in Figure 5. The S/A specimens with three different swaging amounts showed a similar aging response with increasing aging time, at least in the first and second stages of aging. The different swaging amounts, however, seemed to affect the aging characteristics in the third stage. In 95 pct swaged S/A specimens, the third stage of the age-insensitive region began after aging for approximately 3 hours. The presence of a plateau region appeared to be delayed in 64 and 77 pct swaged S/A specimens. It was also noted that the unswaged S/A specimens did not show an abrupt increase in tensile strength in the very early stage of aging. After a few tens of seconds, the tensile strength began to increase gradually with aging and reached the peak after aging for 9 hours. The tensile strength of unswaged S/A specimens declined significantly after aging for 24 hours. As demonstrated in Figure 6, 95 pct swaged D/A specimens showed considerably higher tensile strength than 77 and 64 pct D/A swaged specimens in their as-swaged conditions. As aging progressed, the increases in tensile strength of 64 and 77 pct swaged D/A specimens were steeper than that in the 95 pct swaged counterparts. After aging for 7 hours, the difference in tensile strength between