Microstructure and Properties of Age Hardenable 
Cu-2.55Ni-0.55Si Alloy

Abstract

Among the age hardenable, non-toxic and lead free copper alloys, Cu-Ni-Si alloys are widely used in electrical industry because of their high strength and moderate conductivity. In order to enhance their mechanical properties, the alloy matrix is strengthened by addition of elements and their microstructures are designed to have very fine δ-Ni$_2$Si particles within α-Cu matrix depending on the applied conventional thermal routes. In this study, Cu-2.55Ni-0.55Si alloy was modified by the addition of 0.25 Zr and 0.25 Cr (wt-%) and the variation of microstructure and properties (hardness and electrical conductivity) was investigated depending on thermo-mechanical routes. The alloy was subjected to solid solution annealing at 950°C for 1h, quenching and aging at 450°C for 2-10h. In order to reveal out the effect of cold deformation ratio on the properties, quenched alloys were rolled by a ratio of 20 and 40% before aging. The results showed that (i) conventionally heat treated alloy had highest hardness value (156 HV) and electrical conductivity (22.5 MS/m) by aging at 450°C for 10h, (ii) thermo-mechanical treated (40% deformed and aged at 450°C for 8h) alloys exhibited 30% higher hardness (200 HV) without a significant loss in conductivity (23.8 MS/m) compared to the conventionally heat treated alloy.

1. Introduction

Precipitation hardenable copper alloys are commonly used in several electrical and electronic applications due to their high strength and electrical conductivity. The physical metallurgical approaches play an important role in designing a matrix to enhance simultaneously these contradicting properties. Therefore, it is desired to form a solid solution having nano-meter sized precipitates by alloying and heat treatment routes. Precipitation can be accelerated by introducing defects (i.e dislocations) using new processing techniques like thermo-mechanical routes and severe plastic deformation methods [1-5].

Among the precipitation hardenable copper alloys, there is great interest to study the microstructure of Cu-Ni-Si alloy since, its microstructure provides super high strength and high conductivity. Its superior properties come from finely dispersed precipitates (δ-Ni$_2$Si) in α-Cu matrix due to applied thermal routes [6-10]. Recently, several researches focused on the alloying elements and new processing techniques to observe their effects on the properties of Cu-Ni-Si alloys. Their results revealed enhancement of both strength and electrical conductivity compared to earlier findings [11-20].

In this study, it is aimed (i) to modify the Cu-2.55Ni-0.55Si alloy by the addition of 0.25 Zr and 0.25 Cr (wt-%), (ii) to examine the microstructural features affecting the properties during thermo-mechanical treatments, (iii) to evaluate the effect of deformation ratio on the aging kinetics calculated according to suggested reports [9, 21, 22].

2. Experimental Procedure

The studied alloy is a member of the Corson alloy family and it contains 2.55 Ni, 0.55 Si, 0.25 Zr, 0.25 Cr (wt-%). The alloy was produced as billet material, hot forged at 880 °C and then cooled in air. Its several properties (hardness, yield and tensile strength, fatigue limit etc.) were studied earlier [23]. In this study, the variation of both hardness and electrical conductivity was studied after conventional heat treatment (solid solution annealing, quenching and aging) and cold deformation before aging. In the first stage, the alloy was solution annealed at 950°C for 1h, quenched and then aged at 450°C for 2-12h. In the second stage, the alloy was cold deformed by rolling with a ratio of 20 and 40% before aging.

In microstructural characterization, alloy surfaces were prepared by grinding with SiC papers, polished with 3 μm diamond paste and etched by a chemical solution including 50 ml HCl + 10 ml HNO$_3$ + 10 g FeCl$_3$ + 100 ml H$_2$O. The etched samples were investigated using Olympus BX41M-LED model light microscope (LM) and Jeol JSM 6060 model scanning electron microscope (SEM).

In order to determine the mechanical and physical properties, the hardness values were measured using a macro Vickers hardness tester (Future Tech FV-700) and the electrical conductivity of the samples was measured using a Climate chamber.
measured using an eddy current apparatus (GE Auto Sigma 3000) with a frequency of 60 kHz.

3. Results and Discussion

3.1. Initial microstructure

Figure 1a shows the initial structure (non-heat treated) of studied alloy having rough faceted crystals and globular/elongated precipitates within the twinned α-Cu matrix. SEM micrograph given in Figure 1b shows one of the metal silicide phases (Zr_{58}Ni_{28}Si_{14} wt.% ) having a faceted morphology and the elemental Cr phase (visible in light grey contrast) and Cr-rich silicides (Cr_{73}Si_{27} wt-%, visible in dark grey contrast). SEM examinations revealed out a very fine Ni_{2}Si metal silicide phase in the copper matrix (shown by arrow in Figure 1c). Its fine and homogenous distribution in aged α-Cu matrix causes precipitation hardening. Thus, the enhancement of both mechanical and electrical properties in CuNiSi alloys is attributed to this phase [8].

![Image](a)

![Image](b)

![Image](c)

**Figure 1.** LM and SEM micrographs showing the microstructural features of non heat treated alloy.

3.2. Variation of the properties

Figure 2 shows the variation of electrical conductivity of studied alloy as a function of aging time. A supersaturated solid solution forms due to rapid quenching and it has the lowest electrical conductivity due to distorted lattice and high content of impurities. During aging, the distortion of lattice disappears and the impurities have a tendency to leave the lattice causing precipitation and an increase in electrical conductivity. As seen in Figure 2, (i) the electrical conductivity reached a steady state in which there is no significant change with further aging (ii) as the deformation rate increased the electrical conductivity values increased and reached the highest value. Results show that cold deformation makes the matrix more conductive than that of conventional for the same aging times. On the other hand, the recovery and recrystallization phenomena are strictly dependent on the stored energy which is a result of cold deformation and it varies as a function of deformation type and ratio. Continuous increase in electrical conductivity values of deformed alloys for all aging times indicated that the matrix did not undergo recovery and recrystallization.

![Figure 2](Variation of the electrical conductivity of studied alloy as a function of aging time.)

The variation of hardness values of studied alloys are given in Figure 3. The diagram clearly indicates that (i) all aged alloys exhibited higher hardness values compared to supersaturated states, (ii) although no peak value was obtained for conventional alloy, its hardness continuously increased, (iii) as the deformation rate increased the hardness values significantly increased and the peak values were obtained at 450°C for 8h. It is well known that a pre-deformation treatment such as cold-rolling of the Cu-based alloy before aging shortens the peak-aging time for maximum strength. This is believed to be due to deformation-induced defects like dislocations. An increase in the dislocation density leads to new nucleation zones for the precipitates hence the physical properties of Cu-based alloys improve [24]. Solute segregation to dislocations gives rise to the predominant hardening mechanism. The hardening is ascribed to different mechanisms such as hardening by Cottrell and Suzuki locking, solute clusters, ordered
clusters and precipitation hardening [25]. The examination of the microstructures of aged alloys in this study indicates that deformed copper alloys have the superior physical properties due to the increased precipitation of finely dispersed Ni2Si silicides within α-Cu matrix, compared to the conventional alloy (Figure 4).

Figure 3. Variation of the hardness of studied alloys as a function of aging time.

Figure 4. Aged microstructures of (a) conventional and (b) 40 % - deformed alloys.

3.3. Effect of cold deformation on aging kinetics

Several studies reported that aging kinetics can be calculated according to Martitian’s law and Avrami equations using electrical conductivity values for a given aged copper alloy [9, 21, 22]. Kinetic curves are calculated according to this approach and they clearly show the acceleration effect of deformation on the kinetics of modified Cu-2.55Ni-0.55Si alloy (Figure 5).

Figure 5. Kinetic curves of the studied alloys.

4. Conclusion

In this study, a Cu-2.55Ni-0.55Si alloy was modified by the addition of 0.25 Zr and 0.25 Cr (wt-%) and the microstructural features affecting the properties during thermo-mechanical treatments were investigated. The results showed that (i) conventionally heat treated alloy had highest hardness value (156 HV) and electrical conductivity (22.5 MS/m) by aging at 450°C for 10h, (ii) thermo-mechanical treated (40% deformed and aged at 450°C for 8h) alloys exhibited 30% higher hardness (200 HV) without a significant loss in conductivity (23.8 MS/m) compared to the conventionally heat treated alloy, (iii) kinetic curves were calculated according to Martitian’s law and Avrami equations using electrical conductivity values and they clearly showed the acceleration effect of deformation on the kinetics.

Acknowledgement

The authors are grateful to Sağlam Metal Co. for providing the samples used in this study.

References


