



Correlations between microstructures and properties of Cu-Ni-Si-Cr alloy

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ABSTRACT

A commercial Cu-Ni-Si-Cr alloy used as a model material was annealed and then peak-aged. The detailed microstructure and property analyses were performed to determine the correlations between the microstructure characteristics and properties. Theoretical calculations, which gave results in good agreement with experimental results, demonstrated that solid-solution scattering and Orowan bypass of precipitate strengthening were the key mechanisms for electrical and mechanical properties, respectively. Furthermore, the effects of composition on the aging behaviors and then electrical and mechanical properties for Cu-Ni-Si series alloys were systematically investigated, showing that both the precipitation extent and mechanical properties improved simultaneously with nominal or effective concentration of the precipitates. Quick estimation on the basis of the present analysis procedure indicates that our work is applicable with high accuracy in real cases.

1. Introduction

Cu-Ni-Si alloys are some of the most widely used materials in electrical and electronic industries for applications such as lead frames, contactors and electrical connectors where a combination of good electrical and mechanical properties are required [1]. In Cu-Ni-Si alloys, there are mainly two kinds of precipitates, that is, β -Ni₃Si and δ -Ni₂Si. These finely-distributed nanostructured precipitates formed during aging cause strong hardening of the alloys and return the electrical conductivity by depleting the matrix from solute atoms [1]. In recent decades, attempts have been made to further improve the electrical and mechanical properties of Cu-Ni-Si alloys and addition of other third alloying elements has proved to be an effective way [2–5]. Addition of Zr refines the microstructure and increases the electrical conductivity but deteriorates the mechanical strength of the alloy [3]. Alloying with Ti reduces the grain size and accelerates the aging response but promotes the agglomeration of the precipitates and inevitably lowers the strength [5]. Among these alloying elements, Cr is a very effective element for improving the mechanical strength without impairing the electrical conductivity because of the precipitation and very low solubility of Cr in the matrix [1,3,6,7]. Moreover, it can significantly refine the structure by the formation of Cr and more stable Cr₃Si particles during the solidification and solution processes [6], which is very beneficial to the production of large heavy structural parts through the conventional melting & casting method. Particularly, the Cr₃Si phase affects primarily the temperature stability of microstructures and properties especially at temperatures higher than that at

which the nickel silicides are dissolved [6]. Considering all these benefits, Cr was chosen to be added to a Cu-Ni-Si alloy in this study for the sake of further use of these series alloys in the structural parts.

Except the composition manipulation, other variables like processing methods that affect the macro- and microscopic properties have also been researched intensively [1,8–10]. However, there are few complete studies that provide quantitative information regarding the individual contributions of various mechanisms to the electrical and mechanical properties [11–13], and the detailed practical relationships between the composition, microstructure and properties have also been lacking. This has led to low efficiency in alloy design, impeding further applications of Cu-Ni-Si alloys; hence it is highly urgent to elucidate quantitative correlations between the composition, microstructure and properties for Cu-Ni-Si series alloys to promote their development and application.

Understanding the respective contributions of the different mechanism can be very useful for achieving desirable properties through optimal balance among the different mechanisms. Therefore, the present work has three basic objectives: first, to characterize all microstructural characteristics of the model Cu-Ni-Si-Cr alloy in detail; second, to quantify the individual mechanisms that affect the electrical and mechanical properties; third, to expand the present discussion into the full composition range to systematically investigate the effects of Cu-Ni-Si alloys' composition on the properties and build up the specific correlations between the composition and properties for direct use in practice.

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2. Experimental procedures

Commercial Cu-2.69Ni-1.14Si-0.45Cr at% alloys were annealed at 930 °C for 1 h and then quenched in water. The annealed alloys were aged at 510 °C for 3 h to obtain a good combination of strength and electrical conductivity [14]. Metallographic observations were conducted on Nikon EclipsMa200 optical microscope (OM) and scanning electron microscopy (SEM, VEGA II-XMU, TESCAN, Czech Republic). Microstructure and precipitate morphology were examined using a high-resolution transmission electron microscope (HRTEM, JEOL Ltd. JEM-2100F). X-ray diffraction (XRD) tests were performed using an X'Pert Pro diffractometer with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) with the step size of approximately 0.016° and the scanning velocity of approximately $1^\circ/\text{min}$. The standard sample of alumina was tested and the data was imported into the program to evaluate the instrumental broadening. Electrical conductivity was measured by a D60k eddy current conductivity meter at room temperature. Tensile specimens were machined into the dog-bone geometry and the gauge dimensions of the samples were 16 mm in length, 7 mm in width and 2.5 mm in thickness. The uniaxial tensile tests were conducted using a computer-controlled MTS 858 testing machine with the nominal strain rate of $5.0 \times 10^{-4} \text{ s}^{-1}$ at room temperature.

3. Results

First, the metallographic examination and the typical tensile true stress-true strain curve of the commercial alloys before annealing are given as a reference in Fig. 1. As can be seen from Fig. 1a, the grains are severely textured which is caused by forging. The average spacing in the direction perpendicular to the elongated direction (the forging direction) is mostly around 30–70 μm . There are a number of regions where particles in light blue aggregate (as indicated by the red dashed circles) with many other isolated but still large ones distributing in the matrix too, indicating the alloy is overaged to some extent. The yield strength is about 600 MPa and the strain to failure lies typically around 0.04, not stable in the tests. Since the alloys will be of limited use with the poor plasticity and are not ideal as a model material, they are annealed again in the laboratory and the later investigation will mainly focus on the annealed and peak-aged samples.

3.1. Microstructure of Cu-Ni-Si-Cr alloy

Fig. 2 displays the results of the metallographic examination through OM and SEM with the grain diameter distribution obtained by the line intercept method [15], all for the annealed samples. The grains are mostly equiaxed and are relatively coarse after annealing but

without apparent growth as compared with the origin, which is probably due to the presence of the Cr₃Si phase impeding the microstructure from coarsening as mentioned before [6]. From the intercept distribution, it can be deduced that the average grain size is approximately $65 \pm 4 \mu\text{m}$. In addition, some particles in light blue can be found in Fig. 2a as indicated by the red arrows. Further observation on these particles by SEM shows that their diameters vary from sub-micrometers to about ten micrometers. The EDS analysis conducted on the relatively large ones verifies that these particles are Cr/Si compounds. Since the present annealing temperature falls into the proposed temperature range of Ref. [6] where the multi-scaling particles found after super saturation are all confirmed to be Cr₃Si, it is thus rational to take these particles as Cr₃Si phase accordingly. The Cr₃Si precipitates are considered to be produced mainly in the liquid state or introduced into the alloy with the input material, and can have a positive impact on the mechanical properties at high temperatures [1,6].

Fig. 3 shows the TEM micrographs and statistical diameter distribution of the precipitates. As seen from Fig. 3a, a high number density of nano-scaled precipitates with strain field contrast are distributed homogeneously in the matrix, as was also reported in previous studies [1]. There are generally three existing forms for Cr in the present alloy, that is, solute atom, undissolved Cr particles and chromium silicides (Cr₃Si) [6,16]. The contributions from the various existing forms of Cr to the properties will be discussed later and quantitative analyses related only with the precipitates of nickel silicides are considered here.

Even though two major Ni/Si precipitates are present in the Cu-Ni-Si-Cr alloy, namely, β -Ni₃Si and δ -Ni₂Si (as indicated in Figs. 3c through $[0\ 0\ 1]_{\text{Cu}}$), their diameters may lie in the same range in the present aging conditions [1,7,17], and their properties are highly similar, as will be described below. Therefore, it is reasonable to measure and count their diameters as a whole. The result is summarized in Fig. 3d. From the distribution, the average radius of the precipitates can be determined to be approximately $4.5 \pm 1 \text{ nm}$ with the volume fraction of $2.5 \pm 0.5\%$. The ratio of the number of the two kinds of precipitates is roughly assumed to be 1:1 for simplicity. In addition to the nickel silicides, some precipitates different are shown in Fig. 3e and f. As indicated by the red dashed circles in Fig. 3e, the precipitates are mostly spherical and are a little larger than the Ni/Si precipitates, that is, over ten nanometers. From the size and shape, they can be recognized as the newly precipitated Cr particles [1,18–21]. As to the precipitate in Fig. 3f, the diameter is slightly smaller than one micrometer and its appearance is just as same as that of Cr₃Si in Ref. [6]. It may still be attributed to the primary Cr₃Si phase considering its large size.

So far, Ni₂Si particles, Ni₃Si particles and Cr particles have been found except the very fine Cr₃Si particles (formed during aging), which

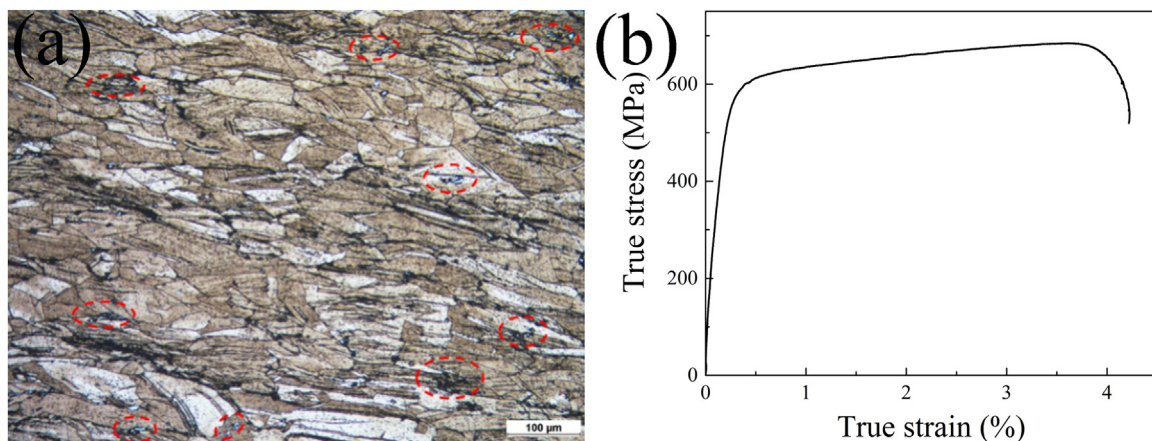


Fig. 1. The microstructure and mechanical properties of the commercial alloys before annealing : a) the metallographic examination; b) the typical tensile true stress-true strain curve. The dashed circles in Fig. 1a indicate some of the particle aggregation regions.

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