Analysis of precipitation in a Cu–Cr–Zr alloy

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Abstract: Precipitates in Cu–0.42%Cr–0.21%Zr alloy were analyzed by using scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDXS) and transmission electron microscope (TEM). After the solid solution was performed at 980 °C for 2 h, water-quenched and aged at 450 °C for 20 h, the precipitate had a bimodal distribution of precipitate size. The coarse precipitates are pure Cr and Cu+Zr, the dispersed fine precipitate is CrCu(S,Zr,Mg) and pure Cr ranging from 1 to 50 nm. The coarse phases formed during solidification and were left undissolved during solid solution. The fine precipitates are the hardening precipitates that form due to decomposition of the supersaturated solid solution during aging.

Key words: Cu–Cr–Zr alloy; microstructure; precipitate; energy dispersive X-ray spectroscopy

Copper and copper alloys are widely used because of their excellent thermal conductivity, outstanding resistance to corrosion, ease of fabrication as well as good strength and fatigue resistance [¹]. Cu–Cr–Zr alloy has attracted considerable interest recently because of its superior combination of high electrical conductivity and high strength. It has been used for many areas such as trolley wire, electrode for resistance welding and lead frame materials [²³]. Many experiments on the mechanical and electrical properties and microstructure have been carried out for the alloy.

The high electrical conductivity is due to the very low solubility of Cr and Zr in Cu, whereas the excellent strength is attributed to precipitation and particle-dispersion strengthening mechanisms. In order to control the microstructure, improve the properties of such alloys and optimize the production techniques, identifying the composition of the phases in the Cu–Cr–Zr alloy is of great value. However, there has been no unanimous agreement on the precipitation of the alloy.

Glazov et al. [⁴⁻⁵] studied the phase equilibrium at the Cu-rich corner of the phase diagram in the ternary Cu–Cr–Zr system within the composition range up to 3.5wt.% Cr and 3.5wt.% Zr at temperatures between 873 K and 1,313 K. According to their results, at 1,213 K, the Cu phase is in equilibrium with the Cr, Cr–Zr, Cu–Zr and liquid (L) phases, and thus Cu+Cr+Cr–Zr, Cu+Cr–Zr+L and Cu+L+Cu–Zr three-phase triangles appear in the isothermal section. On the other hand, Kawasaki et al. [⁶], Fedorov et al. [⁷] and Kuznetsov et al. [⁸] studied the phase equilibrium at the Cu-rich corner of the phase diagram in the ternary Cu–Cr–Zr system within the composition range up to 3.7wt.% Cr and 26wt.% Zr. They found no Cr2Zr phase in their samples, the pseudobinary Cu–Cr–Zr system does not seem to exist. Thus, the Cu + Cr + Cu2Zr phase should exist. However, different stoichiometries were suggested by various investigators for the most Cu-rich intermetallic compound in the binary Cu–Zr system. This causes confusing interpretations on the microstructure observations for Cu–Cr–Zr alloys. Tang et al. [⁹] have identified that the precipitates in a Cu–Cr–Zr–Mg alloy are Cu3Zr and CrCu2(Zr,Mg). Zeng and Hamalainen conducted theoretical and experimental investigations [¹⁰⁻¹¹], showing that three phases Cr, Cu3Zr and Cu exist in this system.

The above experimental investigations were however performed on alloys with much higher zirconium and chromium content. This study deals with the microstructure and precipitation of aged Cu-0.42Cr-0.21Zr, in order to get a better understanding of the strength mechanism and the composition of the precipitates.

1 Experimental procedure

A ternary alloy, Cu–Cr–Zr (Cu–0.42Cr–0.21Zr by wt.%) was prepared in a vacuum induction furnace with electrolytic copper, pure chromium and pure zirconium as charge materials. The specimens were 20 mm × 120 mm and were solution-treated at 980 °C for 2 h, water-quenched, and then aged at 450 °C for 20 h. The electrical resistance was determined by measuring the resistance of a sample with 3 mm × 120 mm using the HEITHLEY-type standard direct-current four-probe technique. The strength was measured for a sample with 5 mm standard pattern using a CMT electronic tensile testing machine.

The specimens were ground, polished, and etched in an aqueous solution of 10% (NH4)2S2O8. The microstructures of
the alloy were examined using an optical microscope and a CSM 950 scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDXS). Thin foils for transmission electron microscope (TEM) examination were sliced from the aged samples and further reduced to 20-30 µm by chemical polishing and ion beam thinning using a Gantan 600 Duo-mill.

The microstructure of Cu-0.42Cr-0.21Zr alloy was investigated using SEM, EDXS, H-800 TEM, and JEM-2010 high resolution transmission electron microscope (HRTEM) operating at 200 kV.

2 Results
2.1 SEM observations

The typical SEM micrography of the coarse phase in the alloy after the heat treatment described above is shown in Fig. 1. The typical EDXS qualitative analysis spectra of these phases are shown in Fig. 2. These results show the distribution of chromium and zirconium. The EDXS quantitative analysis results of these phases are shown in Table 1.

There are three phases in the alloy, copper matrix, chromium-rich phase and zirconium-rich phase. The typical EDXS qualitative analysis spectrum of the chromium-rich phase is shown in Fig. 2(a). There are copper peaks and zirconium peaks besides the chromium peaks in the spectrum. The EDXS qualitative analysis results in Table 1 show that the chromium content of the particle was up to 96.45 wt.%, so we can suppose that the chromium-rich phase is pure chromium. Most of the chromium-rich phase is distributed as little globular particles in a copper matrix, such as particle A in Fig. 1(a), a few distributed as coarse particles, such as particle C in Fig. 1(b). The color of the chromium-rich phase is dark in the backscattered electron imaging (BEI) image.

The typical EDXS qualitative analysis spectrum of...
zirconium-rich phase is shown in Fig. 2(b). There are only copper and zirconium peaks. The zirconium content of the particle was up to 19.55 wt.%. The Cu:Zr atomic ratio is 5.9:1, as shown in Table 1. Considering the contribution of the matrix, we supposed that the zirconium-rich phase could be Cu$_5$Zr. Almost all of the zirconium-rich phase is distributed as coarse particles, as particle B in Fig. 1(a). The color of the zirconium-rich phase is white in the BEI image.

Some chromium is the primary phase embedded in a Cu$_5$Zr matrix, such as particle C in Fig. 1(b). This phenomenon agrees well with experimental examinations of the copper-rich corner of the ternary system Cu-Cr-Zr\cite{12}. From the Zr-rich white particles at the border of many pits and the presence of Zr detected in large Cr-rich pits, we assume that white precipitates and pits are two aspects of the same feature. If the pits, in which pure chromium was detected, once surrounded by the Zr-rich phase, their composition best to Cu$_5$Zr; Stamm postulated that chromium precipitates around a core of Cu$_5$Zr embedded in a pure copper matrix.

### 2.2 TEM observations

To clarify the fine precipitates, the microstructure was analyzed by means of TEM.

Figure 3(a) shows a typical TEM bright field micrography and SADP image of an aged specimen, and Fig. 3(b) shows the dark field. Fine precipitate particles dispersed within the grains in the Cu matrix, having a sizes ranging from 5 – 20 nm. It was found that the electron-diffraction evidence is consistent with the crystal structure of the phase belonging to the space group Fm3m, which is common to the group of inter-metallic compounds known as Hesuler alloys\cite{13}. The composition of the precipitate is likely to be Cr$_2$Cu$_2$(Zr, Mg) which has a similar lattice to Fe$_3$Al. The Hesuler alloys have an fcc crystal structure with a large unit cell that can be thought of as containing 8Cu, 4Cr and 4Zr or Mg atoms. This unit cell can be thought of as containing eight bcc sub-cells with each sub-cell having a Cu atom at its center, and the corner-sites alternately occupied by Cr and either Zr or Mg atoms. It is the sub-lattice that obeys the Nishyama-Wasserman orientation relationship with the matrix\cite{12}:

$$(111)_{\text{fcc}} || (110)_{\text{bcc}}$$

$$(0\bar{1}1)_{\text{fcc}} || (001)_{\text{bcc}}$$

$$(\bar{2}11)_{\text{fcc}} || (\bar{1}10)_{\text{bcc}}$$

In this orientation relationship, the closed-packed planes in the two phases, viz. $\{111\}_{\text{fcc}}$ and $\{110\}_{\text{bcc}}$ are parallel.

### 2.3 HRTEM observations

From the TEM observations, it can be seen that the decomposition product appears to exist in different states of evolution with different structure; namely, solute segregation, nano-domains of precursor and fine ordered bcc precipitates. To further resolve their morphological features, HRTEM was carried out. Figure 4(a) depicts an HRTEM micrograph exhibiting lattice fringes associated with $\{220\}_{\text{fcc}}$. The fringe spacing measured from the micrograph was seen to be approximately 0.13 nm, which agrees well with $d_{220}$ of Cu (0.1278 nm).

![Fig. 3 TEM micrography of the alloy: bright field micrograph and SADP image (a); dark field micrograph (b)](image)

![Fig. 4 HRTEM micrographs of the alloy (a) and the typical EDXS qualitative analysis spectrum of phases (b)](image)
Fine precipitates of the ordered bcc phase, as shown in Fig. 3(b), with a lobe-shape contrast can also be seen in the HRTEM micrography in Fig. 4(a). The typical EDXS qualitative analysis spectrum of the chromium-rich phase is shown in Fig. 4(b). There are copper spectrum peaks and chromium peaks, so we can suppose that the lobe-shape contrast is pure chromium.

3 Discussions

As described above, there are three phases in the alloy, copper matrix, chromium-rich and zirconium-rich phases. No intermetallic phase of chromium or zirconium exists. This result agrees well with recent theoretical studies. The fine precipitates are chromium and the coarse phases mainly consist of Cu_{Zr}.

In our experiment, most of the Zr-rich phase and Cr-rich phase distributed singly, but the two phases could exist together, as shown in Fig. 1(b) that Zr-rich phase and Cr-rich phase exist together and the Cr-rich phase is embedded in a Cu_{Zr} matrix (particle C). There is an obvious interface between the two phases. No intermetallic phase exists. From the size and shape shown in Fig. 1(b), particle C should be formed during the solidification of the alloy. It is assumed that the Cr-rich phase solidified from the melt, and then the Zr-rich phase solidified at the interface between the Cr-rich phase and the melt. The Cr-rich phase acted as nuclei of solidification for the Zr-rich phase. So although chromium and zirconium could form during solidification and were left undissolved during solution treatment as the Cr content of the alloy is in excess of the equilibrium solubility.

The TEM results indicate that the fine precipitate is likely to be CrCu_{Zr}(Zr,Mg), with sizes ranging from 20 to 50 nm and obeying the N-W Orientation relationship with the matrix. HRTEM results suggest that the finer precipitate is pure Cr, which sizes ranging from 1 to 20 nm. The fine and finer precipitation are the ones that form due to decomposition of the supersaturated solid solution during aging.

4 Conclusions

(1) After the solid solution was performed at 980 °C for 2 h and aged at 450 °C for 20 h, the precipitation had a bimodal distribution of precipitate size. The coarse precipitates mainly consist of pure chromium and Cu_{Zr}, no inter-metallic phase of chromium and zirconium exists. The coarse phases formed during solidification and were left undissolved during solution.

(2) The TEM and HRTEM results showed that the dispersed fine precipitate is CrCu_{Zr}(Zr,Mg) and pure Cr, with sizes ranging from 1 to 50 nm. The fine precipitates are the ones that form due to decomposition of the supersaturated solid solution during aging.

(3) The key factor in improvement of the mechanical properties of the alloy is avoiding coarse precipitation during solidification or fragmenting the coarse precipitates and redistributing the alloying content.

References