Microstructure and Properties of Rapidly Solidified Cu–0.81Cr–0.12Zr Alloy

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Cu–0.81 mass%Cr–0.12 mass%Zr alloy was spun into ribbon and then aged at different temperatures for different time. The microstructure, microhardness and electrical conductivity were investigated. It is found that the mother alloy ingot solidified under conventional conditions consists of three phases: Cu matrix, Cr and Cu5Zr. Rapid quenching makes Cr and Zr fully dissolve into the copper matrix. As the aging proceeds, Cr and Cu5Zr phases precipitate again from the matrix. The ribbon aged at 773 K for 15 min possesses the best property: a microhardness of 212 HV and an electrical conductivity of 78.9% IACS. Compared with the conventional process (homogenization treatment of a bulk alloy ingot followed by aging), the use of rapid quenching doubles the microhardness while only slightly decreasing the electrical conductivity.

1. Introduction

Copper and copper alloys are widely used in industry because of their high strength, excellent conductivity, outstanding resistance to corrosion, fatigue resistance and so on.1-4 Among them, Cu–Cr–Zr alloys have long been known as appropriate materials for the products such as electrodes for resistance welding, lead frames, trolley wires and many other electrical parts.

Cu–Cr–Zr alloys are the precipitation strengthening materials. Their strength and hardness increase during the initial stage of aging. In recent years, extensive literature has been available on their microstructure,5-8 precipitation kinetics,5-8 physical11,12 and mechanical13 properties, but controversies still remain on the phase constitution and strengthening mechanisms. Batra and Qi14,15 found three phases CrCu5(Zr), Cr and Cu4Zr in the aged Cu–0.8Cr–0.08Zr alloy (weight percent, the same in the following). The intermetallic compound CrCu5(Zr) known as Hesuler phase has a large unit cell containing 8 Cu, 4 Cr and 4 Zr atoms. It will be decomposed into Cr and Zr-rich phases when the aging temperature is above 673 K. Tang et al.5 identified the precipitates in a Cu–Cr–Zr–Mg alloy to be Cu4Zr and CrCu5(Zr, Mg), as has been found by Liu et al.16 at the grain boundary of the rapid solidification structure. Huang and Ma17 argued that the precipitate of Cu–0.31Cr–0.21Zr alloy should be Cu8(3Zr14).

Under the conventional processing conditions, the precipitation strengthening of Cu–Cr–Zr alloys is limited by the solubilities of Cr and Zr in copper matrix. The excessive Cr and Zr can not be redissoved into Cu during the homogenization treatment, and can not play a role in the strengthening. In contrast, the solubilities can be considerably extended by rapid solidification. After proper heat treatment, fine and dense particles are expected to precipitate in the matrix, which can enhance the mechanical properties greatly without doing significant harm to the electrical conductivity of the Cu–Cr–Zr alloy. Rapid solidification therefore has become one of the most effective methods to produce high strength and high conductivity copper alloys. In this work, the Cu–0.81Cr–0.12Zr alloy was rapidly solidified and subsequently aged at different temperatures. The precipitation process and strengthening mechanism were studied.

2. Experimental Procedure

The Cu–0.81Cr–0.12Zr alloy ingots were produced by induction melting the pure copper (99.99 mass%), chromium (99.999 mass%) and zirconium (99.9 mass%) placed in a quartz tube in a vacuum furnace under the protection of high purity argon. To prevent the reaction of Zr with the crucible, the Zr lumps were added at the last. The ingot weighing about 12 g was then jetted under the pressure of pure Ar to a copper roller rotating at a speed of 2500 r/min. The gained ribbon was 2 mm wide and 30–40 µm thick. It was cut into small pieces for aging in a vacuum annealing furnace with a temperature accuracy of ±1 K. The aging temperature ranged from 673 to 873 K, and the aging time ranged from 0 to 180 min. The precipitation kinetics was analyzed by a differential scanning calorimeter (DSC, Perkin-Elmer Pyris Diamond type) at a heating rate of 20 K/min from 323 to 873 K.

The microhardness was measured in a HVS-1000 type hardness tester under a 10 g load and 10 s holding time. Each sample was tested five times. The electrical resistance was measured using the sample of 40 mm length in the four-probe method.

The microstructures of the alloy ingot and the ribbon sample were observed using a JSM-7600 scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDXS). The precipitated phase was examined by a JEM2100 transmission electron microscope (TEM). The TEM foils were cut from the ribbons and thinned by twin-jet polishing in a solution of HNO3 : C2H5OH = 1 : 9 at about 243 K. The operating voltage for TEM observation was 200 kV.
3. Results and Discussion

3.1 Microstructure

Figure 1 shows the backscattered electron image of the microstructure of the Cu–0.81Cr–0.12Zr alloy ingot solidified at conventional conditions. It can be seen that there are lots of bright particles distributing at the grain boundaries along with eutectic structure, and a few bright particles inside the grains.

The results of identifying the phases in the alloy ingot by EDXS are shown in Fig. 2 and Table 1. The dark phase at the grain boundary (Fig. 2(a)) contains 77.75 at% Cr and 22.25 at% Cu. Considering that the solid solubility of Cr in Cu is very small at room temperature and it cannot form into compounds with Cu when there is not other element involved, the dark phase should be pure Cr. The Cu signal in the EDXS spectrum results from the copper matrix. The bright phase shown in Fig. 2(c) contains 83.56 at% Cu, 14.90 at% Zr and 1.54 at% Cr. The ratio of Cu to Zr (Cr) atoms is 5.61, indicating that the bright phase should be Cu5Zr(Cr).

Figure 3 shows the DSC curve of the as-cast ribbon at a heating rate of 20 K/min. Exothermic reactions associated with annihilation of crystal defects and coarsening of grains take place in the annealing process, leading to a concave curve. The small sharp exothermic peak with an onset temperature of 653 K results from the precipitation reaction.

Figure 4(a) shows the microstructure of the section of the as-cast ribbon parallel to the free surface. It consists of equiaxed grains of 5–10 µm in diameter. The grain is significantly refined due to rapid solidification, and meantime there is not any other phase beside the matrix, meaning that solutes Cr and Zr have been completely dissolved in the Cu matrix. The microstructure of the ribbon annealed at 823 K

![Fig. 1 Backscattered electron image of the microstructure of the Cu–0.81Cr–0.12Zr alloy ingot.](image1)

![Table 1 Results of the EDXS qualitative analysis of the dark and bright phases in Fig. 2.](table1)

<table>
<thead>
<tr>
<th>Objective</th>
<th>Cu K (at%)</th>
<th>Cr K (at%)</th>
<th>Zr L (at%)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dark phase</td>
<td>22.25</td>
<td>77.75</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Bright phase</td>
<td>83.56</td>
<td>1.54</td>
<td>14.90</td>
<td>100</td>
</tr>
</tbody>
</table>

![Fig. 2 Morphologies of the detected dark (a) and bright (c) phases in the alloy ingot and the corresponding EDXS spectrum (b) and (d).](image2)

![Fig. 3 DSC curve of the ribbon heated at 20 K/min.](image3)
for 1 h is shown in Fig. 4(b). After aging, the grain size of the copper matrix has increased to 10–20 µm, with precipitates homogeneously distributing in the matrix.

The microstructure on the transverse section of the ribbon is showed in Fig. 5. Columnar grains stretch from the wheel-side to the free-side in the as-cast ribbon [Fig. 5(a)]. After annealing, the grains of Cu become equiaxed and coarsened, and meanwhile numerous particulates of new phases are precipitated from the matrix and distribute uniformly in the microstructure [Fig. 5(b)].

3.2 Properties

Rapid quenching is an effective way to extend the solubility limit of the solute elements, but meanwhile will create a large number of point defects and severe lattice distortion in the solid. In order to get high quality Cu–Cr–Zr alloys, these crystal defects must be diminished through an aging treatment as many as possible.18,19)

Figure 6 shows the microhardness variation of the Cu–0.81Cr–0.12Zr ribbon with the aging proceeding. At the aging temperature of 673 K, the microhardness increases first quickly and then slowly with increasing the aging time. When the aging temperature is raised to 743 K, the microhardness increases more quickly at the initial stage of aging, but then decreases, i.e., overaging occurs. At the aging temperature of 773 K, the microhardness gets to the maximum value of 212 HV within a shorter time (15 min). This is because the higher the aging temperature, the faster the solute diffusion speed and the shorter the time to reach the microhardness peak will be, as also found at the other aging temperature. However, the peak microhardness decreases with further raising the aging temperature. In the experiment, another Cu–0.81Cr–0.12Zr alloy ingot was ever reheated up to 1223 K and then quenched into water. After it was aged at 773 K for 15 min, the microhardness was measured to be only 107 HV. Obviously, rapid solidification can evidently enhance the aging precipitation hardening.

The electrical conductivity of the as-cast ribbon is very low, being only 20.4% IACS. The reason is that rapid
solidification has made all the solute atoms supersaturated in the copper matrix. They act as obstacles to the movement of electrons and increase the probability of electron scattering. The electrical conductivity after aging is shown in Fig. 7. At the initial stage of aging, the electrical conductivity increases quickly due to the dissolution of solute atoms from the supersaturated matrix on a large scale and the reductions of other point defects and the lattice distortion. The slope of the curve becomes steeper with the increasing aging temperature as a result of the accelerating kinetics of precipitation.

Different from microhardness, electrical conductivity does not decrease after the initial rapid rise. Raising the aging temperature can make more of the supersaturated solute atoms precipitate from the Cu matrix within a certain time, and therefore results in a larger conductivity. For example, aging the ribbon at 773 K for 30 min affords a conductivity of 79% IACS, while aging at 823 K for 30 min increases the conductivity to 80% IACS. Although overaging occurs as the aging temperature exceeds 773 K, the growth of the precipitates does little harm to the electrical conductivity of the alloy.

A good combination of the mechanical and electrical properties is obtained in the Cu–0.81Cr–0.12Zr ribbon aged at 773 K for 15 min: a microhardness of 212 HV and an electrical conductivity of 78.9% IACS.

3.3 TEM observation

As mentioned above, the Cu–0.81Cr–0.12Zr alloy ribbon has good mechanical and electronic properties after an appropriate aging treatment. In order to get an insight into the precipitation phase, TEM was used to examine the microstructures of the ribbons aged at 743 K for 30 min and 773 K for 15 min to the microhardness peak and that overaged at 823 K for 30 min.

Mechanical and electronic properties of copper alloys depend on the size and distribution of the precipitates. According to a previous investigation, there is a coherent strengthening relationship between the precipitates and the copper matrix at the early stage of aging. Figures 8(a) and 8(c) show the TEM images of the microstructures aged to the microhardness peak at 743 and 773 K, respectively. The spherical precipitates are about 5–10 nm in diameter and homogeneously dispersed in the matrix. If the aging temperature increases to 823 K, and the time extends to 30 min, i.e., into the overaging stage, large spherical precipitates of 10–20 nm in diameter form [Fig. 8(e)]. The peak microhardness of the sample aged at 773 K is higher than that aged at 743 K because more precipitates form, which hinders the movement of dislocations more efficiently. At the overaging stage, the precipitates are coarsened by merging each other [Fig. 8(e)]. Correspondingly the gap between two adjacent precipitates becomes larger and the microhardness declines obviously.

Figures 8(b), 8(d) and 8(f) show the selected area electron diffraction (SAED) patterns taken from the aged ribbons. The indexing result of the diffraction patterns in Figs. 8(b) and 8(d) is shown in Fig. 9. It is clear that the precipitates are bcc Cr and fcc Cu2Zr. Besides, there are no other diffraction spots. The bcc Cr precipitates exhibit the well known Nishiyama-Wassermann orientation relationship with the Cu matrix: (111)_{Cu}//(110)_{Cr}, [011]_{Cu}//[001]_{Cr}, [211]_{Cu}//[110]_{Cr}. The close-packed planes of (111)_{bcc} and (110)_{bcc} are parallel for these two phases. In this case, the increment of the maximum shear stress by the coherent strengthening can be expressed as follows:21,22)

\[
\Delta \tau_{cs max} = 1.84 G f^{1/2}
\] (1)
where $G$ is the shear elastic modulus of the matrix, $\varepsilon$ a function of the mismatch degree $\delta$ and $\gamma$ the fraction volume of the precipitates. At the peak stage of aging treatment, the volume fraction of the precipitates that are coherent with the matrix reaches to the maximum, resulting in the largest increase in $\Delta\tau$ in the matrix. The coherent stress is one of the important factors to strengthen the alloy.

In the overaged state, diffraction rings characterizing Cr nano crystals that are non-coherent with the Cu matrix appear [Fig. 8(f)] besides the diffraction spots reflecting the Nishiyama-Wassermann orientation relationship between precipitates and the matrix. This indicates a sequential transition from coherent to semi-coherent to non-coherent relationship with the aging going on. Correspondingly the microhardness decreases slowly with the aging time increasing after the microhardness peak.

Recently, the Kurdjumov-Sachs relationship between the nano-sized Cr particles and the Cu matrix was revealed in the aged Cu–Cr alloys, in which $\{111\}_{fcc}$ and $\{110\}_{bcc}$ are parallel, and the close-packed direction $\{110\}_{fcc}$ is parallel to the close-packed direction $\{111\}_{bcc}$. From Fig. 9, it is known that such a relationship does not exist in the present study.

4. Conclusions

1) There are three phases, Cu matrix, Cr and Cu$_5$Zr in the Cu–0.81Cr–0.12Zr mother alloy ingot solidified under conventional conditions and the ribbon rapidly quenched and aged.

2) With the increasing aging temperature, the peak microhardness of the ribbon increases first and then decreases, but the electrical conductivity constantly increases.

The best property of Cu–0.81Cr–0.12Zr alloy is obtained in the ribbon aged at 773 K for 15 min: a microhardness of 212 HV and electrical conductivity of 78.9% IACS. This microhardness is significantly larger than the value of the alloy treated following the conventional casting, homogenizing and aging procedure.

Acknowledgements

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REFERENCES