Study of rapidly solidified Cu–Cr–RE alloys

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Abstract

Electrical engineering materials of Cu–Cr–RE have been made using the technology of rapid solidification, composite green compacts, extrusion and so on. By means of the analysis of optical metallographs, electron microscopy, physical and mechanical properties as well as electrical properties, and the examining of the hardness, softening temperature, etc. the authors selected Cu–Cr–Y alloy, which has excellent comprehensive properties. The authors have also made a deep study of the chromium and yttrium elements, which affect the structure, the recrystallization temperature, the strength at room and high temperature, the resistivity and contact resistance, and have also compared the properties of the Cu–Cr and Cu–Cr–Y alloy. The results show that rapidly solidified technology and added rare-earth elements not only enhance the fine grain boundary strengthening, but also the second phase strengthening. Cu/Cu–Cr–Y composite material improves the thermal stability and thermal endurance, and also maintains a better electrical conductivity and thermal conductivity. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

With the development of the electrical industry, there is the need to enhance the qualities of conventional electrical materials, including high heat conductivity, high electrical conductivity, high strength and good plasticity. However, it is reported that the detailed study of the electrical materials have been only focused on copper-transition metals and copper-oxide, such as Cu–Zr, Cu–Cr, Cu–Cr–Zr, Cu–Ni–Ti, Cu–Be–Co, Cu–TiN, Cu–Al2O3 and so on. The relevant preparation techniques are casting, mechanical mixing, powder internal oxidizing and mechanical alloying. The strengthening methods include deforming, solid-solution and aging.

Copper–chromium alloys are important electrical materials of high-strength and high-conductivity. The maximum equilibrium solubility of the materials is limited by the conventional solid-solution treatments [1]. In recent years, the rapid solidification technique, has been used to extend the solid solubility of the other elements in copper [2], and it is now possible to reduce segregation, by producing microcrystalline structure, and thus it is possible for many materials to have excellent mechanical and electrical properties.

On the other hand, by adding active rare-earth elements, the copper matrix can be effectively purified and alloyed [3]. This can also lead to reinforced structure, increase in the temperature of recrystallization, and improvement in the thermal stability and, thermal endurance of the alloy.

In addition, by means of the technology of the composite green compact, extrusion is used to process Cu/Cu–Cr–RE compound materials, which not only maintains the mechanical properties, but also effectively improves the electrical conductivity and heat conductivity. In this work, the comprehensive properties of Cu–Cr are compared with those of Cu–Cr–Y alloy.

2. Materials and experimental procedure

Six Cu–Cr–RE alloys were prepared by the vacuum inductive melting pure copper, chromium and rare-earth (purity, $\geq 99.95\%$). Their chemical compositions are Cu–0.5wt%Cr–0.6wt%RE, and Cu–1.1wt%Cr. The powders used in this paper are produced by gas–water centrifugal atomization, using a larger unit capable of producing fine powders [4]. The powder particle size ($D_{50}$) is about 50 μm, and the loose density is 1.95 g/cm³, containing about 0.15wt%O₂.

The technical processes are as follows: atomizing powder → canning → compacting → sintering → extruding → forming → wire of film materials → analyzing chemical composition → testing physical and mechanical properties.
Fig. 1. The hardness of Cu–Cr and Cu–Cr–Y alloys during the process.

Through examining the hardness and soft-temperature, Cu–Cr–Y alloy was found to exhibit the most excellent properties in the six Cu–Cr–RE alloys.

The microstructure of the alloy was examined by optical microscopy (OM) and transmission electron microscopy (TEM). Vickers hardness and strength examinations were made on MVK-C apparatus and ZM-40 tensile equipment. Electrical resistivity was determined by measuring the resistance of wire ($\varnothing$ 0.3 mm) samples with a QJ-36 electrical bridge. The contact electrical resistance was examined using a KWA-OTUJ-52 potentiometer.

3. Results

3.1. Physical and mechanical properties

The hardness characteristics of the forming materials were assessed. Cu–Cr and Cu–Cr–Y alloys hardening curves are presented in Fig. 1. In the deformation range of 50–70%, the hardness of the Cu–Cr–Y alloy is higher than that of the Cu–Cr alloy, and their hardness attains its maximum. After the deformation exceeds 70%, the hardness decreases with increasing deformation.

The tensile strength and elongation of the Cu–Cr and Cu–Cr–Y alloys are shown in Fig. 2. Firstly, in the deformation range of 0–30%, the tensile strength increases with increasing deformation, the tensile strength of Cu–Cr–Y alloy being higher than that of Cu–Cr alloy. Secondly, for deformation over 80%, the tensile strength of the two alloys decreases approximately linearly with increasing deformation. Thirdly, when the deformation ranges from 0 to 40%, the elongation decreases sharply, and then, as the deformation increases, the elongation practically remains the same again. The nature of the elongation charges of the two alloys is similar.

3.2. Elevated temperature properties of alloys

The high temperature tensile strength of the deformed materials are summarized in Table 1. The tensile strength of Cu–Cr–Y alloy is higher than that of Cu–Cr alloy.

3.3. Electrical resistivity and contact resistance

The electrical resistivity curves of alloys with heat treatment are shown in Fig. 3. The electrical resistivity decreases approximately linearly with increasing heat treatment temperature. The values do not significant difference between the Cu–Cr and the Cu–Cr–Y, both with higher thermal stability.

The values of contact resistance are presented in Table 2. The contact resistance goes down with increasing the mechanical contact loads, and the contact resistance values of Cu–Cr–Y alloy are lower than those of the Cu–Cr alloy.

3.4. Physical properties of alloys

The results of comprehensive properties are listed in
Table 2
Contact resistance of deformed alloys

| Alloys   | Contact resistance (mΩ) |
|----------|-------------------------|
| Cu–Cr    | 5.9                     |
| Cu–Cr–Y  | 3.0                     |

Table 3
The synthetic properties of Cu–Cr and Cu–Cr–Y

| Alloys   | Cu–Cr | Cu–Cr–Y |
|----------|-------|---------|
| Melting point (°C) | 1054 | 1079 |
| Density (g/cm³) | 8.7 | 8.81 |
| Resistivity ρ Ω cm (25°C) | 1.901 | 1.915 |
| Resistivity temperature coefficient $\alpha_{500-1000°C} \times 10^3$ | 3.86 | 3.81 |
| Tensile strength MPa |
| Annealing | 367 | 330 |
| Deforming | 504 | 511 |
| Elongation% |
| Annealing | 17 | 27 |
| Deforming | 1.7 | 1.5 |
| Hardness HV |
| Annealing | 59 | 70 |
| Deforming | 114 | 122 |
| Electrical conductivity IACS% | 90.7 | 90.03 |

4. Discussion

The microstructure of Cu–Cr–Y alloy is presented in Figs. 4 and 5 by the optical microscope and transmission electron microscope. The important characteristic of Cu–Cr–Y alloy is that a sub-microscopically fine dispersed second phase exists, and the copper matrix has a fibrous structure, such as dispersed second phase particles in parallel with the processing direction. There is no porosity, shrinkage and impurity in the alloy matrix.

Because of the application of rapidly solidified technique, Cu–Cr–Y alloy micro-structure was found to be without any segregation. For this reason, the new technique improves the strength and plasticity, which obeys the Hall–Petch rule. Because of the high melting point, thermal stability of second phase as well as obstruction of dislocation movement in the matrix, the alloy is strengthened and hardened. This regularity is in accord with the Orowan rule. However, a very fine dispersion of second phase in the matrix with its particle sizes and spacings between them of not more than a few tens of nm is necessary to obtain the desired strengthening effect.

The fine dispersed second phase is generally coherent with the matrix, and dispersed particles in the boundary and intra crystalline prevent grain boundary sliding and the dislocation climbing, restraining the recrystallization, and therefore this improves the strengthening effect.

In the electrical function aspect, the dispersed phase eliminates the volatilization and movement of the copper matrix, which improves the ability of resistivity and wearability in the electric arc. Consequently, the alloy has a long service life and a wide application.

For the extruded Cu/Cu–Cr–Y composite material, the electrical conductivity, thermal conductivity as well as mechanical properties can be improved.

Fig. 4. Microstructure of Cu–Cr–Y alloy: (a) Cu/Cu–Cr–Y surface morphology; (b) cross-sectional structure.

Fig. 5. Transmission electron micrograph of Cu–Cr–Y alloy.
The effective spread of the compound grain boundaries, and the fibrous structure in parallel with the extruding direction formed by second phase and copper matrix, will sharply decrease the surface composite resistivity and the contact resistivity of the alloy. This feature is in accord with the results experiment. (Section 3.3).

Therefore, the Cu–Cr–Y alloy not only has excellent thermal stability and thermal endurance, but also it can replace the current Cu–Cr alloy.

5. Conclusions

1. Rapidly solidified technology and the addition of rare-earth element not only refine the grain, but also form second phase, which can strengthen the alloy.
2. Cu–Cr–Y alloy has a stable structure, high elevated temperature strength and plasticity.
3. The rapid solidification and extrusion technologies improve efficiently the electrical conductivity and heat conductivity of Cu–Cr–Y alloy.
4. The comprehensive properties of Cu–Cr–Y alloy are better than those of Cu–Cr alloy. It can be used for the electrical engineer material, such as resistance welding electrodes, lead wire in incandescent lamps, and lead frame materials.

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