Effects of heat treatment and deformation on tensile strength and conductivity of Cu-Cr-Zr alloy doped with lanthanum and yttrium

X Y Ren¹, P Gao¹, H W Zheng¹, W J Yu², S L Wang¹, Y Lei¹, Ch X Yang¹, L Lan¹ and Y F Li¹

¹ Inner Mongolia Metal Material Research Institute, China, Inner Mongolia, BAO Tou 014034;
² BaoTou Ecological Environment Bureau Radiation Office, China, Inner Mongolia, BAO Tou 014034

Email: renxiangyu8717110@163.com

Abstract. Copper chromium zirconium alloy Cu-0.684Cr-0.077Zr-0.012La-0.020Y mixed with lanthanum and yttrium, after treatment at different solid temperatures, through metallographic microstructure and energy spectrum analysis, determine the alloy solid solution temperature is 920°C. After solution treatment at 920°C, the alloy underwent 40%, 60% and 80% deformation after quenching and water cooling, the results showed that after 60% deformation, 520°C and 0.5 hour aging treatment, the alloy could obtain better comprehensive performance, with tensile strength of 527MPa and electrical conductivity of 73%IACS.

1. Introduction
Cu-Cr-Zr alloy is the only high strength and high guide wire frame material that can meet the performance requirements of vlsi (generally containing 0.15% ~ 0.35% Cr, 0.08% ~ 0.25% Zr), thus become the most attractive type with high strength and high conductivity copper alloys, has received extensive attention of both at home and abroad, is the world's industrialized countries to meet the development of large scale integrated circuit racing to the focus of research and development. In the metallurgical industry, rare earth is called "vitamin", in different metal alloy materials system have certain optimum value or proper dosage range, left to the appropriate amount of beneficial to the various performance of alloy, the excessive adverse or detrimental instead, the key to the application of rare earths in copper alloys is to add the right amount, but compared with steel, aluminum, rare earth application in copper and copper alloys are not serious enough widely [1-2]. Therefore, it is necessary to study the properties of rare-earth copper alloys in order to further improve the comprehensive properties of Cu-Cr-Zr alloys.

In this paper, the changes of conductivity and tensile strength of Cu-Cr-Zr alloy with the addition
of trace rare earth elements La and Y in the aging process were studied, and the aging precipitation characteristics of Cu-Cr-Zr-La-Y alloy and the influence of trace rare earth elements La and Y on the properties of Cu-Cr-Zr alloy were discussed in combination with its microstructure.

2. Test materials and methods

The raw materials used in the experiment were Cu-Cr50 (50%(mass fraction)Cr), Cu-Zr40 (40%(mass fraction)Zr), Cu-La50 (50.08%(mass fraction)La) and Cu-Y25 (25.68%(mass fraction)Y). The residual was standard cathode copper with purity of 99.9%(mass fraction). The alloy is smelted by ZG-0.02510kg vacuum medium frequency induction melting furnace, the final composition (%(mass fraction)) of the alloy is Cu-0.684Cr-0.077Zr-0.012La-0.020Y (hereinafter referred to as Cu-Cr-Zr-La-Y). After casting, the alloy ingot was forged into 1cm thick plate after the riser was cut, the skin was removed and the solid solution was treated. Both solution treatment and aging treatment were carried out in SX-5-12 box-type resistance furnace. After solid solution, the conductivity and tensile strength of the alloy samples were measured after aging. The conductivity sample size is 200mm×10mm×15mm. The conductivity was measured by sigma 2008 digital eddy current metal conductometer. CMT5305 microcomputer was used to control the tensile strength of the electronic universal testing machine. The metallographic samples were mechanically polished and impregnated with FeCl₃, anhydrous ethanol and concentrated hydrochloric acid.

3. Test results and analysis

3.1. Effects of solution at different temperatures and aging at 520°C on microstructure of alloy

![Figure 1. Energy spectrum analysis of Cu-Cr-Zr-La-Y alloy solid solution at 960°C for 1.5 h, ageing at 520°C for 2 h.](image)

As can be seen from the energy spectrum analysis in figure 1, Zr phase is diffusely distributed inside the grain, and Zr phase mainly exists in the form of Cu-Zr compound in the Cu matrix. Because a large number of secondary Cr phases were concentrated in grain boundaries, Cu-Zr phases were mainly precipitated at the Cu matrix. As can be seen from the energy spectrum in figure 1, the atomic ratio of Cu to Zr is close to 7:1. It can be concluded that the Zr-rich phase in the as-cast microstructure of the alloy is mainly composed of Cu-Zr compounds. At present, researchers agree [3-5] that adding a small amount of Zr element can promote the precipitation of the precipitated phase and make the morphology of the precipitated phase fine and diffuse.
Figure 2. Undissolved matter energy spectrum analysis of Cu-Cr-Zr-La-Y alloy solid solution at 960°C for 1.5 h and ageing at 520°C for 2 h.

Energy spectrum analysis of Cu-Cr-Zr-La-Y was performed for the undissolved material at 960°C for 1.5h and aging 520°C for 2h. As shown in figure 2, it is divided into Cr (5.67%) and Cu (the rest). The matrix grains are very coarse and agglomerate, indicating that the solid solution temperature at this time is relatively high and the solid solution temperature should be lowered.

Figure 3. Line scanning analysis of Cu-Cr-Zr-La-Y alloy solution at 960°C for 1.5h.

Figure 4.Cu-Cr-Zr-La-Y alloy was dissolved in solution at 960°C for 1.5h and aged at 520°C for 2h.detect the energy spectrum analysis of rare earth elements.

Surface scanning was performed on Cu-Cr-Zr-La-Y alloy with solid solution at 960°C for 1.5h and aging at 520°C for 2h, as shown in figure3. It could be clearly seen that Cr rich phase was precipitated in large amounts and distributed in the form of strip aggregation. The Cu-Cr-Zr-La-Y alloy, which was dissolved in solution at 960°C for 1.5h and aged at 520°C for 2h, was tested for the energy spectrum analysis of rare earth elements.As shown in figure4, the rare earth elements because of the adding quantity is less, the purifying grain boundary and contribution to the strength of alloy fine-grain strengthening effect is not big, but a small amount of rare earth elements because of its role can help purify the grain boundary secondary Cr rich phase at the grain boundary precipitates, help alloy
precipitation strengthening effect.

![Microstructure Images](image)

**Figure 5.** Microstructure of Cu-Cr-Zr-La-Y alloy with different solid solution temperature and aging.

Figure 5 (a), (b) and (c) show the metallographic microstructure of the Cu-Cr-Zr-La-Y alloy after 1.5 hours of solid solution at 960°C, 940°C and 920°C, quenching and cooling, and aging at 520°C for 2h. The microstructure of Cu-Cr-Zr-La-Y was similar at different temperatures. Due to quenching stress, many quenching twins [6] occur in the alloy in figure 5(a) and figure 5(b), and the grains are relatively small. Most of these grains are distributed at the grain boundary. With the increase of temperature, the grains in figure 5(a) grew further after solution at 960°C. According to the energy spectrum analysis in figure 2, the Cr-rich phase was mainly precipitated along the grain boundary at and near the grain boundary of the alloy. The Cr-rich phase is mainly composed of dispersed Cr particles. With the increase of temperature, the Cr-rich phase is distributed in grain boundary and grain boundary adhesion in the form of strip particles. When studying Cu-Cr-Zr alloy, I.S.Batr [7] et al believed that there were two Cr phases in different forms in Cu-Cr-Zr alloy. One is the thick Cr phase, the other is the Cr phase of B.C.C structure precipitated in the aging process. The precipitation sequence is as follows: supraturated solid solution $\rightarrow$ Cr atom segregation zone $\rightarrow$ metastable f.c.c structure Cr phase $\rightarrow$ b.c.c structure Cr phase. In figure 5(b), the alloy Cu-Cr-Zr-La-Y was dissolved in solution at 940°C for 1.5h, and the particles were distributed in the copper matrix. In figure 5(c), the alloy cu-cr-zr-la-y was dissolved in solution at 920°C, but no undissolved matter was found in the matrix. Therefore, the solution temperature of 920°C for 1.5h is the best solution treatment process.

3.2. The effect of deformation on the tensile strength and conductivity of the alloy

The alloy Cu-Cr-Zr-La-Y was dissolved in solution at 920°C for 1.5h with different deformation and aging at 520°C. The tensile strength and conductivity of the alloy were shown in figure 6.

![Conductivity and Strength Curves](image)

**Figure 6.** Relationship curves between conductivity(a) and tensile strength(b) of Cu-Cr-Zr-La-Y alloy.
and deformation amount after solid solution at 920°C for 1.5h, quenching and water cooling, dealing with different deformation amount and aging at 520°C.

Figure 6 shows the curve of the relationship between the conductivity, tensile strength and deformation of cu-cr-zr-la-y alloy after solution at 920°C for 1.5h and the deformation of 40%, 60% and 80% after quenching and water cooling respectively. It is generally believed that after the cold deformation of the alloy, the aging phase nucleation point is increased, making the precipitated phase more diffuse and more evenly distributed, reducing the effect of discontinuous precipitates and thus improving the properties of the alloy [8].

Deformation on the influence of the conductivity and the influence law of temperature on conductivity is consistent, namely deformation, the greater the conductivity recovery is faster, as shown in figure6 (a), at less than 60% of deformation degree, the conductivity of the alloy with the increase of the deformation degree rise, this is because when the deformation degree is not big, the cold deformation increases the aging precipitation in nuclear points, have a promoting effect on aging, make it easier for solid solution of particle precipitation, thereby reducing the scattering of the electron, therefore conductivity increases; However, when the deformation is greater than 60%, the conductivity decreases. This is because when the degree of cold deformation is too large, the crystal defects and lattice distortion increase and the effect on electron scattering is strengthened, so that the conductivity of the alloy decreases with the increase of deformation degree after 60% deformation.

According to figure6 (b), the tensile strength of the alloy increases with the increase of deformation degree. This is because the cold deformation in the alloy import a large number of dislocation, form work hardening, namely with the increase of deformation degree, increase of dislocation density, the dislocation reactions and delivery aggravate each other, the result is a fixed jog, dislocation tangles and other obstacles, in order to cause dislocation is difficult to through these obstacles and be limited within a certain range of movement. In order for the metal to continue to deform, additional forces are needed to overcome the strong interaction between the dislocations. Deformation at the same time also increased the inside of the alloy in the number of defects such as dislocations, grain boundaries, interface, the lattice distortion caused by the internal energy increases, for the precipitated phase of nucleation and growth provides a favorable condition [9], the second phase is more diffuse, tiny, promoted the precipitation strengthening, therefore, with the increase of deformation degree of tensile strength is also increasing. The peak value of tensile strength of 80% deformed alloy is lower than that of 60% deformed alloy, although it reaches the peak value of tensile strength in the shortest time. This is because the precipitation process of 80% deformed alloy was quickly completed in the early aging stage, and then it entered the phase growth stage, resulting in the peak tensile strength of the alloy slightly lower than 60% deformed alloy. In general, the alloy was dissolved in solution at 920°C for 1.5h, quenched by water cooling, deformed by 60%, aged at 520°C for 0.5h, with the best conductivity of 73% and tensile strength of 527MPa.

4. Conclusions
(1) When the solid solution temperature at 960°C and 940°C, the alloy grain is relatively large and Cr particles appear clustered and distributed in strips. After the solid solution at 920°C, no undissolved matter is found in the matrix. Solid solution at 920°C for 1.5 hours is the best solid solution treatment
process of Cu-0.684Cr-0.077Zr-0.012La-0.020Y alloy. 

(2) Cu-0.684Cr-0.077Zr-0.012La-0.020Y alloy was dissolved in solution at 920°C for 1.5h, quenched water cooling, 60% deformation, aging at 520°C for 0.5h, the best performance conductivity is 73%, the tensile strength is 527MPa.

Acknowledgment
Natural science foundation of Inner Mongolia autonomous region (No. :2015MS0570)

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