High strength and good electrical conductivity in Cu–Cr alloys processed by severe plastic deformation

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ABSTRACT

Ultrafine-grained (UFG) microstructures in Cu–Cr alloys were processed by high pressure torsion (HPT). The improved hardness was accompanied by a reduced electrical conductivity due to the large amount of grain boundaries. The effect of heat-treatment after HPT-processing on the hardness and the electrical conductivity was studied for different chromium contents (0.75, 9.85 and 27 wt%). For low Cr concentration (0.75%) the electrical conductivity increased considerably above 250 °C, however the hardness decreased concomitantly. At the same time, for high Cr content (9.85% and 27%) the hardness was only slightly reduced even at 500 °C, while the electrical conductivity increased to a similar level as before HPT due to grain boundary relaxation and decomposition of Cu–Cr solid solution. Our study demonstrates the capability of SPD-processing and subsequent heat-treatment to achieve a combination of high strength and good electrical conductivity.

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1. Introduction

Grain refinement via severe plastic deformation (SPD) is an effective tool for improving the mechanical performance of chromium, zirconium and hafnium bronzes [1–8]. The formation of ultrafine-grained (UFG) microstructures in copper–chromium alloys resulted in an improvement in durability, wear resistance and fatigue strength [2,9] which are important service properties in their applications for resistance welding electrodes and switching devices [10]. One of the most effective SPD method in grain refinement is high pressure torsion (HPT) [1]. Former papers [11,12] have shown that the application of HPT can reduce the grain size down to 10 nm, thereby achieving significant hardening in high-chromium alloys. At the same time, SPD-processing usually yields the reduction of electrical conductivity due to the high density of lattice defects, such as grain boundaries. Tailoring the microstructure by an additional heat-treatment after SPD may yield an improvement of electrical conductivity while preserving the high strength. Most probably, chromium content in Cu has a considerable influence on the effectiveness of these procedures in the achievement of the optimal properties. In this work, we demonstrate the capability of HPT-processing and subsequent heat treatment in obtaining a combination of high strength and good electrical conductivity in chromium bronzes with different chromium contents of 0.7%, 9.85% and 27%.

2. Materials and methods

Copper alloys containing 0.75%, 9.85% and 27% chromium (in wt %) were chosen for the study. Before deformation Cu–0.75%Cr and Cu–9.85%Cr samples were subjected to hot forging at 800 °C, then the forged specimens were heat-treated by two different ways: (i) annealing at 1000 °C for 2 h and cooling in air to room temperature (RT), and (ii) annealing at 1000 °C for 2 h and water quenching to RT. The samples processed by the first and second routes are referred to as “annealed” and “quenched” specimens, respectively. The Cu–27%Cr alloy was studied in the as-cast state. All the samples with 10 mm in diameter and 0.6 mm in thickness were severely deformed by HPT at RT and a rate of 1 rpm under a pressure of 4 GPa. The deformation was performed in a “groove” with the depth of 0.2 mm. The final sample thickness was 0.3 mm. The number of turns was 5 which corresponds to a true strain of ε = 4.8 at the half-radius of the disks. The HPT-processed samples were heat-treated at temperatures ranging from 50 to 600 °C with a step of 50 °C and a holding time of 1 h at each temperature. The microhardness was measured using a 402 MVD Instron Wolpert Wilson Instruments tester. The measurements were made at a distance of 2.5 mm from the sample center (i.e. at the
half-radius of the disks). The resistivity was measured using a BSZ-010-2 micro-ohmmeter at RT. The resistivity was calculated and transformed into electrical conductivity according to International Annealed Copper Standards (IACS). The microstructure was observed using JEM-2100 transmission electron microscope. Thin foils for electron microscopy were prepared by ion polishing with a GATAN 600 unit. The crystallite size, the dislocation density and the twin-fault probability were obtained by X-ray line profiles using a high-resolution rotating anode diffractometer (Nonius, FR591) with CuKα radiation (wavelength: λ = 0.15406 nm). The line profiles were evaluated by the Convolutional Multiple Whole Profile (CMWP) fitting method [13].

3. Results and discussion

Fig. 1 shows that HPT-processing yields significant hardening in all alloys and the hardness increases with increasing Cr content. This effect can be explained by the higher dislocation density and the smaller grain size due to the pinning effect of chromium on lattice defects, either these atoms are in solid solution or they are in precipitates. The grain structure in some selected specimens is shown in Fig. 2 and the grain size values are listed in Table 1. The effect of the initial treatment before HPT on the grain size was marginal. In quenched Cu–0.75%Cr, Cu–9.85%Cr and Cu–27%Cr alloys processed by HPT the average grain size values were ~209, 143 and

![Graphs showing the temperature dependence of microhardness and electrical conductivity for Cu–0.7%Cr, Cu–9.85%Cr, and Cu–27%Cr alloys.]

**Fig. 1.** Temperature dependence of microhardness (a,c,e) and electrical conductivity (b, d, f) of Cu–0.7%Cr (a,b), Cu–9.85%Cr (c,d) and Cu–27%Cr (e,f) alloys.
40 nm, respectively. X-ray line profile analysis also revealed that the lattice defect structure only slightly depends on the initial state (annealed or quenched), while it is very sensitive on the alloying element concentration (see Table 1). With increasing Cr content from 0.75% to 27% the crystallite (subgrain) size decreased from about 60 nm to 36 nm, while the dislocation density and the twin-fault probability increased from $38 \times 10^{14} \text{m}^{-2}$ to $163 \times 10^{14} \text{m}^{-2}$ and 0% to 1.2%, respectively.

The alloys after HPT have a reduced electrical conductivity, mainly due to the presence of Cr atoms in solid solution (especially for initially quenched states) and increase of the amount of grain boundaries and another lattice defects. Chromium atoms in solid solution reduce the electrical conductivity much more strongly than in the form of precipitates [5]. This effect yields a higher electrical conductivity of the annealed specimens compared to the quenched samples. The solubility limit of Cr in Cu is about 0.75 wt% at the temperature of the initial heat-treatment (1000 °C), therefore in the quenched states the solute Cr concentration cannot exceed this value even if the nominal Cr content is higher (e.g. 9.85%).

Heat-treatments were applied in order to improve the electrical conductivity in the HPT-processed Cu–Cr alloys. The change of the hardness and the electrical conductivity as a function of the heat-treatment temperature is shown in Fig. 1. It can be seen that the hardness decreased or remained at the same level while the electrical conductivity rised with increasing temperature. For both initially annealed and the quenched Cu–0.75%Cr alloys processed by HPT the hardness decrease is marginal up to about 250 °C. This can be explained by the lack of considerable grain growth, as revealed by the comparison of Fig. 2a and b. These images show that in the quenched and HPT-processed Cu-0.75%Cr alloy the grain size increased only...
from \( \sim 209 \) to \( \sim 245 \) nm due to the heat-treatment at 250 °C. Fig. 1b indicates that above 250 °C a significant increment in the electrical conductivity took place through the supersaturated solid solution decomposition (for initially quenched state) and the grain growth (for both initially annealed and the quenched states).

Fig. 1 shows that the thermal stability of the HPT-processed Cu–9.85%Cr alloys is better than that for the Cu–0.7%Cr composition since the higher Cr content has a stronger retarding effect on grain growth. After the heat-treatment at 500 °C the grain size only moderately increased from \( \sim 143 \) nm to \( \sim 229 \) nm (see Fig. 2c and d).

Therefore, the decrease of the hardness is marginal even at high temperatures while the electrical conductivity is considerably increased, as shown in Fig. 1c and d. The strongly improved electrical conductivity (by 38% IACS) in initially quenched alloy after HPT can be explained by chromium precipitation and grain boundary relaxation.

Fig. 2e reveals the appearance of a dispersed Cr particle with the size of about 20 nm. In the annealed and HPT-processed alloy grain boundary relaxation during heat-treatments has a major effect on electrical conductivity, while it has only marginal influence on hardness.

It has been shown that the specific resistance of grain boundaries in Cu decreases from \( 5.5 \times 10^{-16} \, \Omega \, m^2 \) to \( 2 \times 10^{-16} \, \Omega \, m^2 \) due to grain boundary relaxation during annealing [14]. Considering the grain boundary relaxation and the slight grain growth at 500 °C an electrical conductivity increase of about 13% IACS is predicted which is in accordance with the experimental results for annealed and HPT-processed sample. For HPT-processed Cu–27%Cr alloy considerable softening was not observed up to 500 °C (see Fig. 1e) since the grain structure remained very fine. As revealed by the TEM images in Fig. 2f–h the heating up to 500 °C leads to an increase in the grain size from 40 to 96 nm. At the same time, at 500 °C the electrical conductivity increased to the level characteristic for the as-cast state (see Fig. 1f).

Reducing the level of electrical conductivity down to 20% IACS during HPT indicates a possible occurrence of deformation-induced supersaturated solid solution. Thus, a further increase in electrical conductivity upon heating occurs both due to decomposition of solid solution, as well as grain boundary relaxation and moderate grain-growth.

Table 2 summarizes the hardness and the electrical conductivity values in the initial and the HPT-processed states, and after heat-treatments at 250 °C for the Cu–0.7%Cr alloy, and at 500 °C for the Cu–9.85%Cr and Cu–27%Cr alloys. It can be seen that HPT-processing and subsequent heat-treatment at appropriate temperatures in Cu-alloys with high Cr content yields better hardness and electrical conductivity than in the initial states.

4. Conclusions

1. HPT-processing in copper-chromium alloys leads to a significant hardening due to the formation of UFG microstructure. With increasing chromium content the microhardness rises from about 1700 to 2700 MPa due to the reduction in average grain size from \( \sim 209 \) to \( \sim 40 \) nm as well as the increase of the chromium content, the dislocation density and the twin-fault probability. The electrical conductivity is reduced with increasing Cr content due to the higher amount of grain boundaries and Cr alloying atoms.

2. The heat-treatment after HPT results in a gradual decrease of the hardness and an increase in electrical conductivity. For high Cr contents (9.85% and 27%) an appropriate selection of the heat-treatment temperature enables the preservation of the high hardness while the electrical conductivity increased considerably. The significant improvement in the electrical conductivity can be explained by Cr precipitation and grain boundary relaxation. Our study demonstrates the capability of HPT-processing and subsequent heating for obtaining both high hardness and electrical conductivity in Cu–Cr alloys.

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