Enhanced strength and electrical conductivity in ultrafine-grained Cu-Cr alloy processed by severe plastic deformation

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Abstract. The influence of severe plastic deformation on strength and electrical conductivity in the Cu-Cr copper alloy has been studied. Microstructure of ultrafine-grained samples was investigated by transmission electron microscopy and X-ray diffraction with special attention on precipitation of small chromium particles after various thermal treatments. Effect of dynamic precipitation leading to enhancement of strength and electrical conductivity was observed. It is shown that ultrafine-grained samples enable to demonstrate the combination of enhanced thermal stability up to 500°C, high ultimate tensile strength of 790-840 MPa and enhanced electrical conductivity of 81-85% IACS. The contributions of grain boundaries and precipitates to enhanced properties of ultrafine-grained copper alloy are discussed.

1. Introduction
It is known that high strength and enhanced electrical conductivity of the Cu alloys are highly desirable for many wire and cable applications. However, except for very singular nano-twinned copper [1], high strength and high electrical conductivity are as a rule mutually exclusive in metallic materials [2-5]. Here we report a nanostructuring strategy that achieves Cu-Cr-Ag alloys with superior tensile strength and electrical conductivity at room temperature. The new strategy is based on combination of grain refinement down to ultra-fine scale with accelerated formation of nanosized second phase precipitates and purification of the Cu matrix from solute atoms by severe plastic deformation (SPD) processing. This approach can be further adapted to large scale industrial production of cables and wires from nanostructured alloys.

Tensile strength and electrical conductivity are the most important properties of conducting metallic materials used in electrical engineering. Electrical conductivity is very sensitive to the microstructure of metallic materials since it is determined by the scattering of electrons due to disturbances in the crystal structure including thermal vibrations, solutes, and crystal defects. As solute atoms and crystal structure defects lead to increased tensile strength of metals, high electrical conductivity and high strength are usually mutually exclusive. Pure Cu having very high electrical conductivity, but very low tensile strength (100 MPa) is a good example. The alloying of pure Cu, strain hardening, or precipitation strengthening to increase their tensile strength result in a dramatic degradation of its electrical conductivity. The selection of optimum conductors for wire and cable applications is always a compromise between its mechanical and electric properties.

The Cu-Cr alloys are used in numerous applications where an excellent combination of mechanical strength and electrical conductivity is required. For example, they can be important materials for railway contact wires [6] and electrodes for spot welding [7]. These alloys can exhibit the ultimate tensile strength in the range of 450-500 MPa, electrical conductivity between 75 and 85 % of the
conductivity of pure copper (%IACS) and thermal stability up to temperature of 450°C [8] after standard thermal treatments. The enhanced strength is achieved by quenching and aging leading to hardening by Cr precipitates [9], whereas the high conductivity is a result of the extremely low solubility of Cr in Cu at temperatures below 500°C [10]. The Cr precipitates are to prevent also the grain coarsening, whereas 0.1%Ag addition leads to both the slight improving of tensile strength (up to 50 MPa) through solid solution strengthening and decreasing of electrical conductivity by 2-3%IACS [11].

In this work, we propose a new strategy for nanostructural design in the Cu alloys for electrical engineering. This strategy is based on SPD processing of the Cu alloys, which is accompanied with formation of both the ultrafine-grained structure and nanosized second phase precipitates. These structures can show significantly increased mechanical properties due to grain boundary strengthening and precipitation hardening. At the same time a very low content of solute atoms in the Cu matrix may result in enhanced electrical conductivity.

2. Experimental
In the first step the initial Cu-Cr-Ag alloy was coated with liquid glass and solution treated at 1050°C for 1 h with water quenching. Then the disks with a diameter of 20 mm and a thickness of 1.5 mm were subjected to severe plastic deformation by high pressure torsion (HPT) [12] at various temperatures using constrained anvils [13,14].

The microstructure of the Cu alloy was characterized using a JEM-2100 transmission electron microscope (200 kV TEM). The electrical conductivity of the alloy at room temperature was measured using eddy current method. At least 20 measurements were taken and the average values and their standard deviation were calculated. Tensile specimens with dimension 0.5 × 1 × 4 mm³ were machined from the processed bars. Tensile tests were carried out using a specially designed testing machine [15]. Tensile specimens were deformed to failure at room temperature with constant cross-head speed corresponding to the initial strain rate of 10⁻³ s⁻¹. Three tensile specimens were tested and the results thus obtained were found to be reproducible.

3. Results and discussion
After HPT processing at 300°C we have observed the combination of enhanced microhardness and electrical conductivity in comparison with the samples processed at 20°C (Fig.1). It should be noted that aging in coarse-grained samples starts usually at 400°C. However the peak of microhardness in ultrafine-grained samples was achieved at 300°C. It means that HPT leads not only to grain refinement, but also to dynamic aging at lower temperatures [16], because the temperature of aging in ultrafine-grained material reduces by 100°C.

Additional annealing does not have significant influence on microhardness and electrical conductivity of samples processed by HPT at 300°C (Fig. 2) because of previous dynamic aging. At the same time after HPT at RT and additional annealing we observed significant increase of microhardness and electrical conductivity. If the observed rise of microhardness is typical for aging, the increase of electrical conductivity can be explained by lowering the concentration of the alloying elements inside grains because of their migration to grain boundaries during aging at temperatures above 300°C.

Careful TEM studies have shown that the alloys HPT processed at RT exhibit a very homogeneous UFG microstructure (Fig. 3a,b) with a mean grain size of about 200 nm. No visible precipitates have been detected after this treatment. At the same time in addition to a grain size of 200 nm we observed the precipitation of the Cr particles with a size of 10 nm directly after HPT processing at 300°C (Fig.3c,d). It should be noted that precipitation of the Cr particles in the Cu-Cr-Ag alloy has been observed also after standard treatment by quenching and aging in [17].
Figure 1. Dependence of microhardness (1) and electrical conductivity (2) on the annealing temperature for 30 min in the HPT samples produced at various temperatures.

Figure 2. Dependence of microhardness (1,2) and electrical conductivity on the annealing temperature (3,4) for the HPT samples: (1,3) HPT at 20°C; (2,4) HPT at 300°C

Dynamic aging!
Figure 3. Microstructure after HPT: (a,b) at RT; (c,d,e) at 300°C; (f) at RT and additional annealing at 500°C, 30 min; (a,c) bright field image; (b,d) dark field image; (e) electron diffraction pattern from the Cr precipitates; (d,f) arrows show precipitates

A very high ultimate tensile strength of 840 MPa with a ductility of 10% has been achieved in the HPT samples after additional aging (Fig. 4). For comparison the strength in the coarse-grained material subjected to standard treatment (quenching and aging at 450°C, 1 h) was equal to 430 MPa (Fig. 4).
Obviously the enhanced strength in the HPT samples can be explained by formation of the UFG structure [18] and dispersion hardening [9], while the decrease in ductility is a result of difficulties in the dislocation storage inside small grains.

Taking into account the results of microstructural investigations, we can clarify the parameters of optimal microstructure for achieving the combination of high strength, good electrical conductivity and enhanced thermal stability in copper alloys. One can see from the results obtained that the best
results are achieved at a mean grain size of 200 nm and a size of precipitates of 10 nm. It should be noted that similar conclusion has been made recently for the Al-Mg-Si alloys processed by SPD [5]. On the ratio between strength and electrical conductivity for Cu alloys (Fig. 5) the area below dark line shows the properties belonging to initial coarse-grained materials, whereas the second area demonstrates the properties which are observed after standard treatments involving quenching, rolling and aging. As demonstrated in this paper there appears the area marked by red, which can be achieved by formation of the ultrafine-grained structure with nanosized precipitates using severe plastic deformation.

4. Conclusions
In summary, one can conclude from the results obtained that the regime of the SPD processing governs the volume fraction of precipitates and segregations, thereby affecting a grain size and dynamic aging influencing on the properties of copper alloys. In particular, the combination of high ultimate tensile strength of 840 MPa, good electrical conductivity of 85% IACS and thermal stability up to 500°C has been achieved in the Cu-Cr-Ag alloys by SPD processing. However, it is important to optimize the parameters of the SPD treatment to fabricate UFG alloys with the optimal microstructure which is characterized by a grain size less than 200 nm and a size of precipitates less than 10 nm. In recent years, the ECAP-Conform [20], as a continuous SPD method, has been developed to fabricate long-length rods and wires, opening the way for practical use of these results.

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