Strength and electroconductivity of bulk nanostructured copper alloys

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Abstract. The results of a study of the strength and conductivity of electrotechnical bulk nanostructured copper alloys obtained by methods of severe plastic deformation is presented. The contribution of the microstructure parameters to the formation of high strength while maintaining sufficient electrical conductivity is discussed.

1. Introduction
Modern progress is impossible without the use of electrical materials. To transfer electric energy from the manufacturer to the consumer, to create electric motors and generators, devices and circuits for micro- and nanoelectronics, etc., metal materials are widely used, including copper alloys. The choice in favor of copper alloys as conductors of electric current is due to their inherent high electrical conductivity, strength and ductility. At the same time, the requirements for electrical materials are constantly growing due to changes in their operating conditions. As an example, it is requisite for particularly high-strength copper alloys in high-speed rail transport, heat exchangers, welding electrodes, etc. (figure 1).

Figure 1. Tensile strength vs. electrical conductivity of some commercial Cu-based alloys. KLF-125 corresponds to the Cu-3.2Ni-0.7Si-1.25Sn-0.3Zn alloy, C194 to the Cu-2.3Fe-0.1Zn-0.03P alloy, and OMCL to the Cu-0.3Cr-0.1Zr-0.005Mg-0.02Si alloy [8].
Promising from this point of view are dispersion hardened alloys of the Cu-Cr-Zr system with a Cr content from 0.5 to 1.5 wt.% and Zr from 0.02 to 0.20 wt.% [1,2]. As a result of applying traditional methods of thermo-mechanical treatment, including hardening with high temperature and subsequent aging, for these alloys it is possible to achieve combinations of strength and electrical conductivity of 450 MPa and 80% IACS or 590 MPa and 75% IACS, respectively [3-6]. Moreover, it is characteristic that the increase in strength is accompanied by a decrease in electrical conductivity.

The use of severe plastic deformation (SPD) methods allows the formation of dispersion-hardened copper alloys with high strength bulk nanostructured states with grain sizes of tens to hundreds of nanometers and nanodispersed particles. In this case, the increase in the electrical conductivity of these states is promoted either by aging following SPD [7–9], or by increased SPD temperatures that activate dynamic aging [10–12] or continuous dynamic recrystallization [13], or by high speeds and low SPD temperatures, leading to the formation of deformation nanotwins, in addition to grains of the nanoscale range, [14]. As a result of the above effects on the microstructure of the alloys of the Cu-Cr-Zr system, bulk nanostructured states can be formed, which are characterized by the simultaneous manifestation of high strength and electrical conductivity.

This article presents the results of an analysis of the influence of microstructure parameters on the strength and electrical conductivity of electrotechnical bulk nanostructured copper alloys obtained by SPD methods.

2. SPD and subsequent aging
It is well known that deformation processing by traditional methods leads to an increase in the strength of copper alloys. However, the electrical conductivity decreases significantly. In this state, copper alloys are of no interest from the point of view of industrial applications. The high strength is caused by the small grain size, subgrain structure inside them, deformation twins, a high dislocation density in the grain body, elastic microdistortions of the crystal lattice, etc. These changes in the microstructure during plastic deformation can also affect the electrical conductivity, significantly reducing it. At the same time, subsequent aging, which is a traditional method of heat treatment, can significantly affect both strength and electrical conductivity, significantly increasing the latter. The reason for this is the precipitation of dispersed particles of the second phases from the supersaturated solid solution. In this case, the content of atoms of the alloying elements in the solid solution will decrease, as a result, the elastic stresses in the crystal lattice of the matrix will also decrease, and the scattering of conduction electrons by the atoms of the alloying elements dissolved in the matrix will become less significant.

The degree of influence on the strength and electrical conductivity of the formed microstructure is determined to one degree or another by the nature of the wrought alloys (chemical and phase composition), the nature of the deformation effect (stress-strain state diagram, degree, speed and temperature of deformation), temperature and time of subsequent aging. Thus, it is possible to influence the indicated properties of copper alloys in order to achieve their optimal combination, inter alia, by choosing the optimal combination of parameters of plastic deformation and subsequent aging.

The microstructure of bulk nanostructured copper alloy obtained by SPD methods is significantly different from the microstructure of metals and alloys deformed by traditional methods. Bulk nanostructured states are characterized by a very small grain size with large-angle grain boundaries, a low density of dislocations in the grain body, however, a very high density of extrinsic grain-boundary dislocations, long-range elastic stress fields created by these dislocations, a crystal lattice with a changed parameter, a high concentration of twins, and increased solubility of alloying elements, specific crystallographic texture. Aging of bulk nanostructured alloys obtained by SPD methods, due to the characteristics of the formed ultrafine-grained (UFG) structure, can have certain features.

In [7], the Cu-0.5wt.% Cr alloy billets were subjected to SPD by equal channel angular pressing (ECAP). The strength of the state formed as a result of 4 ECAP passes turned out to be equal to 460 MPa and exceeded the strength of the initial solid-solution quenched state equal to ~180 MPa by almost 2.6 times. The ECAP strain rate was 0.2 mm/s. Additional cold rolling of this state was carried out to a compression ratio of 90% at room temperature. At the same time, pancake shaped
microstructure changed to fragmentary one with less sharp boundaries. The formed microstructure can be attributed to UFG structures. The dislocation density as a result of cold rolling increased. Dislocations fragmented the lamella boundaries formed as a result of ECAP. The strength of the condition after 4 passes of ECAP as a result of cold rolling increased to 570 MPa. It was concluded that the high strength of the workpieces subjected to ECAP followed by cold rolling is mainly due to the release of a small grain size, the presence of alloying atoms in a solid solution, a high density of dislocations, and high-angle grain boundaries.

The electrical conductivity of the initial state, equal to 37% with increasing number of ECAP passes and during subsequent rolling, remained almost unchanged, remaining at a low level, and amounted to only 35%. Since the number of ECAP passes and subsequent rolling did not affect the level of electrical conductivity, it was concluded that the dislocation density, which increased as a result of ECAP and subsequent cold rolling, has a smaller effect than alloying atoms in solid solution. An analysis of the obtained experimental results indicated that the indicated regularities in the change in strength and electrical conductivity are associated with depletion of the solid solution by Cr atoms, enlargement of precipitate particles, and annihilation of dislocations of opposite signs. Using this approach, it was possible to achieve a combination of tensile strength of 554 MPa with an electrical conductivity of 84% IACS in samples subjected to ECAP and cold rolling.

In [15], analytical modeling was used to assess the contribution of structural parameters to the strength and electrical conductivity of this alloy. Peierls-Nabarro stress, dislocation hardening, solid solution hardening, and hardening by particles of the secondary phase were considered as possible sources of contributions to the strength characteristics. At the same time, the electron–phonon interaction, the interaction of free electrons with impurity atoms and particles of the secondary phase, and also with dislocations were considered as parameters of the microstructure responsible for the electrical conductivity.

The calculation results showed that the contribution to the strength characteristics of the Cu-0.5wt.%Cr alloy subjected to 4 ECAP passes can be caused, first of all, by dislocation hardening. Its share was estimated at 82%. An assessment of the Peierls-Nabarro stress contribution indicated its contribution of 18%. The contribution of solid solution hardening turned out to be negligible and equal to less than 1%. The contribution of the particles of the secondary phases was estimated to be equal to zero due to their absence in the alloy.

At the same time, in this state, the main contribution to the electrical resistance is due, primarily, to the chromium atoms dissolved in the copper matrix. This contribution exceeded 63%. The second largest was the contribution of thermal vibrations in the crystal lattice, amounting to more than 36%. The contribution of dislocations turned out to be negligible.

Thus, it is possible to affect the strength, first of all, by increasing the density of dislocations, which practically do not affect the electrical conductivity of the alloy. From this it follows that by increasing the density of dislocations due to an increase in the degree of deformation before the start of the processes of recovery and recrystallization or lowering the temperature of deformation, an increase in strength can be achieved. In this case, the conductivity will not fall. Indeed, an increase in the degree of SPD, for example, due to an increase in the number of passes with ECAP, leads to an increase in strength characteristics. In this case, the electrical conductivity does not change. True, at the same time, its value is small and equal to only about 37% of IACS.

As a result of aging following SPD, small particles of chromium were precipitated from the copper matrix in the microstructure of the Cu-0.5wt.%Cr alloy [7]. An increase in the aging temperature up to 450°C with a holding time of 1 hour led to an increase in strength with its subsequent drop at higher temperatures. An increase in aging time in excess of 1 hour led to a drop in microhardness. However, an increase in temperature and duration of aging is accompanied by an increase in electrical conductivity. Thus, experimental studies indicate that up to a certain temperature and exposure time due to the decomposition of the solid solution and the precipitation of fine particles, both strength and electrical conductivity increase.
The resulting increase in strength is due to various multidirectional competitive processes. During aging, the contribution of solid solution hardening decreases, which was negligible anyway. Dislocations annihilate and their density decreases as a result. Accordingly, the role of dislocation hardening decreases. At the same time, the concentration of particles of the secondary phases increases, which resist the slip of dislocations, and accordingly increase their contribution to the strength characteristics. On the other hand, electrical conductivity increases with aging. This is due to the fact that impurity atoms dissolved in the matrix lattice begin to participate in the formation of particles of secondary phases. Thus, the main factor of low electrical conductivity associated with the presence of alloying elements in the matrix of atoms loses its significance. Moreover, the next largest factor, which is the thermal vibrations of atoms in the crystal lattice of the matrix, remains unchanged.

Analytical modeling confirms this conclusion. Estimates made for this alloy in the state after 4 ECAP passes, rolling by 90% and aging at 450 °C with a holding time of 1 hour indicate the following. The main contribution to the strength of this state is made by dispersed chromium particles precipitated from the solid solution. This contribution is about 54%, i.e. it grew from almost zero value, characteristic for the state formed as a result of 4 ECAP passes. At the same time, the contribution of dislocation hardening fell from 82% to ~30%. The Peierls stress contribution has remained unchanged. On the other hand, after aging, the main contribution to the electrical resistance is made by the thermal vibrations of the atoms of the matrix. Its value was about 83%. However, it is not possible to influence the magnitude of this factor. The second largest is the contribution of chromium atoms in the matrix lattice. It amounted to about 12%, i.e. fell three times compared with the state after 4 passes ECAP. The contribution of the released chromium particles was less than 5%. Thus, a change in the balance between the number of atoms of impurity atoms in the matrix and in the composition of the released particles can optimize the electrical conductivity. The contribution of the dislocations turned out to be negligible.

Thus, dispersed particles of secondary phases are the main parameter of the microstructure that can be purposefully controlled. Their concentration and size, as well as the distribution in the body or grain boundaries, should determine the combination of strength properties and electrical conductivity.

It should be noted that the use of SPD in combination with subsequent aging was used by other researchers as well for this and other alloys of the Cu-Cr system, including with the addition of atoms of various kinds of alloying elements. For example, in [16], the properties of the Cu-0.80%Cr-0.080% Zr alloy (wt.) were optimized. As a result of 8 ECAP passes along the Bc route, followed by aging at a temperature of 425 °C for 240 minutes, the microstructure of the initial annealed and quenched coarse-grained state became UFG and predominantly equiaxed, but slightly elongated grains (subgrains) were also observed in it. The ultimate tensile strength of the annealed, hardened and aged state, on the one hand, and the hardened state after ECAP and aging, on the other hand, are 396 and 670 MPa, respectively, and the electrical conductivity reached 75% and 74% IACS, respectively.

Thus, the potential of achieving high bulk electrical conductivity strength corresponding to the initial quenched and aged state in bulk nanostructured materials obtained by SPD and subjected to subsequent aging has been demonstrated.

3. Dynamic aging and dynamic recrystallization in SPD

As shown by experimental studies [10-12], the formation of bulk nanostructured states, characterized by the simultaneous manifestation of high strength and electrical conductivity, can occur as a result of dynamic aging during SPD. The samples of the Cu-0.5wt.%Cr alloy with small additions of Ag, Fe, P, and Si atoms were studied. SPD by means of high pressure torsion (HPT) was implemented at an elevated temperature of 300 °C. As a result of this treatment, an UFG structure with nanodispersed particles was formed. Thus, instead of a two-stage process of deformation with subsequent aging, a one-stage process is proposed that combines both of these processes. The fact of dynamic aging is indicated by the fact that annealing after HPT does not lead to significant changes in microhardness and electrical conductivity. In this case, the samples demonstrate a high ultimate tensile strength of 790-840 MPa and a high electrical conductivity of 81%-85% IACS. Based on the studies, the authors
came to the conclusion that the optimal combination of high strength and electrical conductivity corresponds to a microstructure with an average grain size of about 200 nm and a particle size of 10 nm. Such a microstructure is also characterized by increased thermal stability up to 500 °C. Thus, the particles of the secondary phases released during the dynamic aging process, in this case, determine the optimal combination of strength and ductility.

The authors of [13] also used elevated SPD temperatures to control the strength and electrical conductivity of the Cu-0.8%Cr-0.06%Zr (wt.) Alloy. In this case, SPD was implemented by ECAP at various elevated temperatures in the range 473-673 K. The formation of the UFG structure was considered the result of continuous dynamic recrystallization. The increase in strength during SPD from 215 MPa to 480 MPa and 535 MPa at ECAP temperatures of 673 K and 473 K, respectively, was justified by grain refinement and an increase in the dislocation density. Moreover, the contribution of the latter component was assessed as predominant. At the same time, electrical conductivity was 73% IACS and 66% IACS, respectively. Its slight decrease from the 79% IACS characteristic of the initial state was associated with the formation of a structure with a high dislocation density in the grain body during ECAP. However, the authors do not note the role of atoms of alloying elements in solid solution and particles of the secondary phases in the formation of an attractive complex of strength and electrical properties, as is the case in other articles devoted to this subject.

4. Dynamic plastic deformation

High speeds and low temperatures of plastic deformation significantly affect the microstructure of metallic materials. In this case, a significant refinement of the structural elements takes place, additional deformation modes are activated, the dislocation density increases, and deformation twinning processes are activated. At the same time, dynamic recovery processes are difficult. All this helps to increase the strength characteristics. Moreover, the evolution of the electrical conductivity of materials subjected to such influences is of interest.

In [14], as a result of dynamic plastic deformation at a temperature of liquid nitrogen (LNT-DPD) with velocities of 10^3–10^5 s^-1 in the Cu-1 wt.% Cr-0.1% Zr alloy, a nanostructured state was formed, which is characterized by record strength values equal to 700 MPa, and electrical conductivity equal to 78.5% IACS. The formed nanostructured state was characterized by an average nanograin size of about 47±19 nm and an average nanotwin size of about 25±14 nm, with a volume fraction of about 20%. In this case, considered as the annealed state, the strength was slightly less than 400 MPa. Annealing was performed to precipitate Cr particles from the solid solution and increase the electrical conductivity up to 84.2% IACS. For comparison, along with dynamic deformation, the ingots in the initial state were subjected to quasistatic deformation by compression at a rate of 10^3 s^-1 at room temperature (RT-QSC). The authors concluded that the deformation nanotwins characteristic of the nanostructure obtained by the LNT-DPD method are responsible for high strength. Moreover, they have a significantly smaller effect on the drop in electrical conductivity than the boundaries of nanograins. It is noted that the contribution of dispersion hardening in alloys of the Cu-Cr-Zr system subjected to SPD can be reduced due to the strongly deformed microstructure. As a result, the high strength of the alloy subjected to LNT-DPD is mainly due to a mixed type microstructure consisting of nanograins, nanotwins and Cr particles. Moreover, the contribution of these parameters to the increase in strength is difficult to single out.

The authors associated the slight decrease in electrical conductivity with an increase in the degree of deformation during LNT-DPD with the propagation of defects in the crystal structure, including dislocations and boundaries. It is believed that twins have significantly lower electrical resistance than boundaries with different misorientation angles.

An analysis of the obtained experimental results using analytical modeling [17] showed the following. In the initial annealed state, low strength is determined by the low dislocation density, and high electrical conductivity by a small contribution to the resistance of the particles of the secondary phases. This contribution is comparable with the contribution of dislocations. The increase in strength due to RT-QSQ is mainly due to dislocation hardening. The decrease in electrical conductivity is
associated with the scattering of conduction electrons at grain boundaries and vacancies. The contribution of the latter is approximately 13 times less than that of the former. In the state after LNT-DPD, an even greater increase in strength is associated with the formation of twin boundaries. At the same time, a slight decrease in electrical conductivity is due to electron scattering, primarily at grain boundaries. The contribution of electron scattering on deformation vacancies is approximately 4 times smaller, and at the twin boundaries it is still almost 18 times smaller. Thus, the simulation results indicate a significant role of twin boundaries in the formation of a high-strength state as a result of LNT-DPD. At the same time, twins have little effect on electrical conductivity. In this case, the role of electron scattering at numerous grain boundaries of the nanostructured state is significant.

It is clear that a high density of grain boundaries in the nanostructured state cannot be avoided. However, it is possible to form bulk nanostructured states with a high density of nanotwins either by increasing the speed and/or lowering the temperature of the SPD, or by choosing a more alloyed alloy with a lower stacking fault energy, more prone to twin deformation. Furthermore, a new process of ECAP and deep cryogenic treatment (DCT) was proposed to achieve a combination of tensile strength ~423 MPa and electrical conductivity ~97.9% IACS simultaneously [18].

5. Conclusions
The above results of experimental studies and analytical modelling indicate the possibility of simultaneously achieving high strength and electrical conductivity due to the targeted effect on bulk microstructure parameters of bulk nanostructured copper alloys for electrical purposes.

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