Contribution of structural parameters to the strength and electrical conductivity of Cu-0.5%Cr alloy subjected to ECAP and cold rolling

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Abstract. The effect of cold rolling with a reduction rate of 95% at room temperature and subsequent aging on the evolution of the microstructure, strength properties and electrical conductivity of the Cu-0.5Cr alloy (wt.%), which is widely used in the electrical industry in the form of strips and ribbons, has been studied. The cold rolling and aging of the alloy was carried out in coarse-grained and ultrafine-grained states after equal-channel angular pressing. The regularities found were used to assess the contribution of various structural parameters to the level of strength properties as well as the electrical conductivity of the alloy in the obtained states.

1. Introduction
Chrome bronzes are precipitation-hardening alloys and have an optimal combination of physical, mechanical and operational properties after thermal and thermomechanical treatment. In recent years, a new approach has been developed that makes it possible to achieve a significant increase in the strength of alloys of the Cu-Cr system while maintaining high electrical conductivity and ensuring the creation of new generation conductors [1, 2]. This approach is based on replacing traditional machining with methods of severe plastic deformation (SPD). SPD, in particular, equal-channel angular pressing (ECAP), makes it possible to control the mechanisms of hardening and electrical conductivity by refinement of the copper matrix to submicron sizes. The subsequent breakdown of solid solution is accompanied by the formation of nanosized particles of secondary phases, which makes an additional contribution to the strengthening and increase in the electrical conductivity of the formed ultrafine-grained (UFG) states. ECAP makes it possible to obtain bulk billets, as a rule, in the form of rods, however, the issue of obtaining thin strips from ultrafine-grained materials for subsequent use, including in electrical engineering [3], is urgent. Flat rolling of copper, titanium, etc. makes it possible to give massive UFG blanks obtained by ECAP the form of strips [4-6]. In this case, a combined deformation scheme is realized. Changing the deformation mode from ECAP to flat rolling affects the mechanisms of microstructure evolution and physical and mechanical properties. To further improve the functional properties of UFG alloys of the Cu-Cr system, it is necessary to understand the physical nature of increasing the strength and electrical conductivity of these materials.

This paper presents the results of a study on the microstructure and physico-mechanical properties of the Cu-0.5Cr alloy subjected to ECAP, subsequent cold rolling and aging. The regularities obtained were used to assess the contribution of various structural parameters to the level of strength properties, as well as the electrical conductivity of the alloy in the obtained states.
2. Method of experimental research

In this work, studies were carried out on an electrical alloy Cu-0.5Cr (wt%). At the first stage, the samples were exposed at a temperature of 1000 °C for 1 hour, followed by quenching in water to create a supersaturated solid solution of alloying elements in a copper matrix. Thus the initial coarse crystalline state (the IS state) was formed. ECAP was carried out in a die with an internal angle \( \psi = 90^\circ \) along route \( \text{B} \rightarrow \text{C} \) (turning the workpiece 90° clockwise along the longitudinal axis after each pass) at room temperature at a speed of 0.2 mm/s. The number of passes is 8 (the ECAP8 state). Subsequently, cold rolling (CR) was carried out at room temperature with a total reduction ratio of 95% (the ECAP8+CR state). In one pass during rolling, the reduction in thickness was approximately 5%. Between the passes, billets were cooled in air to minimize the effect of deformation heating on the microstructure. The rolling direction was parallel to the direction of extrusion. The equivalent deformation in one pass of ECAP was 1.15, and after rolling by 95% - 3.5. Aging was carried out in air in an oven SUOL 45 at 425 °C for 40 minutes. At all stages of the study, the microstructure was investigated by optical, scanning and transmission electron microscopy (TEM). Studies of the microstructure and properties were carried out in the rolling plane. X-ray structural analysis (XRD) of the samples was performed by diffractometer Rigaku Ultima IV (Bragg-Brentano geometry) using CuK\(_{\alpha}\) monochromatic radiation at the reflected beam (parabolic graphite monochromator). The measurements were conducted along the area of \(2\times2\) mm\(^2\) situated in the center of the samples. The values of the lattice parameter \(a\), the size of the coherent scattering regions (CSR) \(D_{\text{XRD}}\), and the level of elastic microdistortions \(\langle e^2 \rangle\) were calculated by the Rietveld refinement method using the MAUD program. The dislocation density \(\rho_L\) was estimated by the formula (1)

\[
\rho_L = \frac{2(\langle e^2 \rangle)^{\frac{1}{2}}}{D_{\text{XRD}}b},
\]

where \(b\) is Burgers vector.

Tensile tests were performed at a strain rate of \(10^{-3}\) s\(^{-1}\). Samples were cut parallel to the direction of deformation from the central part of the ECAP blanks and sheets after rolling. Uniaxial tensile tests were carried using small specimen on an Instron 8801 tester at room temperature. Conductivity studies were carried out at a temperature \(T = 23^\circ\text{C}\) by the eddy current method. The measurement error was ± 2%.

3. Results and discussion

The results of detailed studies of the microstructure and properties of the Cu-0.5Cr alloy obtained by optical scanning and transmission electron microscopy, as well as by XRD, are presented in table 1.

In the initial state, the lattice parameter is 3.6184 Å, which indicates the maximum dissolution of alloying elements in the copper matrix among all the studied states. In all states after deformation (CR, ECAP8, ECAP8+CR), the lattice parameter decreases, which indicates a decrease in the concentration of alloying elements in the solid solution. These results are in agreement with the results obtained by TEM. In these states a small number of dispersed particles with a size of about 6 nm are observed in the microstructure, which are distributed inhomogeneously. Subsequent aging leads to a further decrease in the lattice parameter, which approaches the lattice parameter of pure copper 3.6150 Å.

Cold rolling of the coarse-grained state leads to an increase in the dislocation density up to \(2.54 \times 10^{14}\) m\(^{-2}\). Conducting ECAP8 increases the dislocation density to values of \(1.24 \times 10^{14}\) m\(^{-2}\). In this case, the subsequent rolling of ECAP8 increases the dislocation density to \(2.19 \times 10^{14}\) m\(^{-2}\), which is slightly lower than in the case of the CR state. Probably, this is due to the formation of a mixed microstructure with two types of grains/subgrains characterized by two mean sizes after cold rolling of the UFG state obtained by ECAP. The first type of grains/subgrains are small with an average size of 320 ± 20 nm and a high dislocation density. The second type of the observed grains, the fraction of which is 0.25 of the total volume, is characterized by large dislocation-free grains with an average size of 620 ± 30 nm. Most likely, they are created by mechanisms of dynamic recovery, leading to annihilation of dislocations, which reduces the total density of dislocations. Also, in the ECAP8+CR state there is a significantly higher proportion of high-angle boundaries, which is consistent with the results obtained for pure copper [8, 9].

Cold rolling of the initial state increased the strength up to 490 MPa. As a result of ECAP, the strength reached 470 MPa. The highest strength 605 MPa was demonstrated by samples after complex
deformation ECAP8+CR (table 1). Strength growth is accompanied by a slight change in electrical conductivity. In IS it was 37% IACS, after CR - 39% IACS, after ECAP8 - 36% IACS and ECAP8+CR - 37% IACS. Post-deformation aging leads to a 2-fold increase of electrical conductivity for all states. In this case, the strength for the rolled CG state and the ECAP8 state change within the error limits. In the rolled UFG state, it decreases up to 470 MPa.

Table 1. Microstructure parameters, mechanical properties and electrical conductivity.

| State     | $D_{av}$, nm [7] | $d_{av}$, nm [7] | $L_{av}$, nm [7] | $\langle \epsilon^2 \rangle^1$, % | $D_{XRD}$, nm | $\rho_{\perp}$, $10^{14}$ m$^{-2}$ | $\sigma_{UTS}$, MPa | $\sigma_{YS}$, MPa | $\varepsilon$, % | IACS, % |
|-----------|------------------|-----------------|-----------------|---------------------------------|---------------|-------------------------------|----------------|----------------|--------------|---------|
| IS        | 260000           | -               | 3,6184(4)       | 0.015                           | 188           | 0.011                         | 160             | 60             | 42           | 37      |
| CR        | 190±10           | 6               | 3,6163(4)       | 0.12                            | 62            | 2.54                          | 490             | 480            | 8            | 39      |
| ECAP8     | 250±15           | 6               | 3,6159(4)       | 0.11                            | 120           | 1.24                          | 475             | 450            | 17           | 36      |
| ECAP8+CR  | 160±10           | 6               | 3,6159(4)       | 0.10                            | 59            | 2.19                          | 605             | 565            | 13           | 37      |
| CR+A      | 270±30           | 8               | 3,6153(5)       | 0.02                            | 104           | 0.23                          | 495             | 480            | 20           | 74      |
| ECAP8+A   | 300±20           | 10              | 3,6154(4)       | 0.02                            | 117           | 0.19                          | 460             | 430            | 24           | 72      |
| ECAP8+CR+A| 320±20           | 12              | 3,6152(4)       | 0.07                            | 125           | 0.77                          | 470             | 430            | 20           | 74      |

The strength characteristics of metals and alloys are determined by a number of mechanisms. Based on the obtained microstructural parameters, the main strengthening mechanisms were assessed. The superposition of each of the strengthening mechanisms with the lattice friction stress is often linearly additive, i.e. the yield strength of a strain-hardened material is the sum:

$$
\sigma_{0.2} = \sigma_0 + \Delta \sigma_{ss} + \Delta \sigma_{dis} + \Delta \sigma_{GB} + \Delta \sigma_{ph}
$$

(2)

where $\sigma_0$ — strengthening due to friction in the crystal lattice, $\Delta \sigma_{ss}$ an increase in the yield strength due to solid solution hardening, $\Delta \sigma_{dis}$ an increase in the yield strength due to dislocation (strain) hardening, $\Delta \sigma_{GB}$ the grain boundary strengthening associated with a decrease in the grain size, and $\Delta \sigma_{ph}$ increase in the yield strength due to precipitation hardening [6, 10, 11].

Strength due to friction in the crystal lattice ($\sigma_0$) is determined by the Paierls-Nabarro stress, which for copper is equal to $\sigma_0 = 25$ MPa [10].

The variety of possible mechanisms of solid solution hardening greatly complicates the exact quantitative description of these processes. To calculate the solid-solution hardening [11], we used the expression (3):

$$
\Delta \sigma_{ss} = \frac{MG \xi^3}{8 \varepsilon_s^{1/2}}
$$

(3)

where $M$ is the orientation factor, for FCC crystals $M = 3.06$ [12], $G$ shear modulus of the matrix, $G = 42.1$ GPa [13], $\xi$ the concentration of the dissolved element, and $\varepsilon_s$ dimensional mismatch parameter. The solubility of Cr in the copper matrix at 1000 °C is 0.4 wt.% (0.49 at.%) [3] In general, the effect of solid solution hardening in the alloy is small and amounts to 0.045 Pa. Therefore, it can be considered ineffective.

Dislocation hardening caused by an increase in the density of dislocations can be described by the formula proposed by Taylor [14-15]

$$
\Delta \sigma_{dis} = \alpha MG b \sqrt{\rho_{\perp}}
$$

(4)

where $\alpha$ is a coefficient depending on the nature of the interaction of dislocations during strain hardening, which can vary from 0.089 to 0.5, and $b = 0.256$ nm the magnitude of Burgers vector [10].

Dispersion strengthening is of a particular interest. The interaction of dislocations with particles can be realized through various mechanisms depending on the distribution density of particles, their size,
the difference between the shear modulus of the particle and the matrix, and the type of interphase boundaries. After deformation, the contribution of dispersed particles can be neglected, since their distribution is nonuniform, and also because the density of precipitates is rather low. After aging, the size of the strengthening particles was 8-12 nm (table 1), then, according to [16], the strengthening proceeds according to the Orowan mechanism:

\[
\Delta \sigma_{DS} = Q M \frac{G b}{2 \pi (L - d)} \Phi \ln \left(\frac{L - d}{4b}\right),
\]

where \(Q\) is a parameter equal to 0.81-0.85, that takes into account the uneven distribution of particles in the matrix, \(\Phi\) a factor taking into account the type of dislocation, \(\Phi = 1\) in the case of a screw dislocation, \(\Phi = (1 - \theta)^{-1}\) – for edge dislocation, \(\Phi = 0.5(1 + \frac{1}{1 - \theta}) = 1.25\) – for mixed deployment, \(L\) the average distance between particles, and \(d\) the average particle size.

The contribution of grain-boundary strengthening was estimated as

\[
\Delta \sigma_{GB} = k d^{-\frac{1}{2}},
\]

where \(k\) is the coefficient of grain boundary strengthening, which characterizes the material and the state of the boundaries. In this work, the value of the coefficient \(k\) is chosen as 0.21 for IS and 0.11 for UFG states, which corresponds to the calculations presented in [13]. Since after aging of the rolled UFG state large grains are observed, the proportion of which is 0.25 of the total volume, while the UFG microstructure is preserved, the contribution of grain boundaries to grain boundary strengthening was estimated due to the equivalent average grain size \(d_{eq}\), calculated as follows:

\[
d_{eq} = \left(\sum f_i d_i^2 / \sum f_i d_i^2\right)^{-\frac{1}{2}},
\]

where \(f_i\) is the proportion of grains with an average size \(d_i\).

The calculation results are shown in figure 1.

Figure 1. Contributions to the strengthening of various mechanisms.

Figure 1 shows that the dominant mechanism of strengthening after deformation in all states is grain boundary strengthening by the Hall-Petch mechanism. The dislocation mechanism ranks second in terms of contributions. It should be noted that in a rolled coarse-grained sample (CR), the dislocation strengthening numerically approaches the grain-boundary strengthening. In specimens after ECAP8 and ECAP8+CR, grain-boundary strengthening dominates over dispersion strengthening.

Aging leads to a partial decrease in the contributions of dislocation and grain-boundary hardening, due to the processes occurring during the recovery of the dislocation structure. The separation of nanosized precipitates rich in Cr leads to an increase in dispersion strengthening. The strength of the obtained states after aging is the result of a combination of grain boundary strengthening and precipitation strengthening.
The contribution of various structural parameters to the level of electrical resistance was estimated based on the Matthiessen - Flemming rule:

\[
\rho = \rho_0 + C_v \Delta \rho_v + L_{dis} \Delta \rho_{dis} + S_{GB} \Delta \rho_{GB} + \sum_i C_{sol}^i \Delta \rho_{sol}
\]  

(8)

where \(\rho_0\) is the electrical resistivity of pure copper. Since the resistivity measurements were carried out at room temperature, we will consider the electrical resistivity of pure Cu at room temperature (\(\rho_0 = 1.72 \cdot 10^{-6} \Omega \cdot \text{cm} \, [3]\)). Here, \(\Delta \rho_v, \Delta \rho_{dis}, \Delta \rho_{GB}, \Delta \rho_{sol}\) are additions that take into account the contribution, respectively, of vacancies, dislocations, grain boundaries, and dissolved elements in the copper matrix. \(C_v\) is the concentration of vacancies, \(P\) dislocation density, \(Q\) grain boundaries per unit volume and \(C_{sol}^i\) concentration of solute \(i\) in the matrix.

In this work, we did not measure the concentration of vacancies. According to [16, 17], the maximum concentration of vacancies in copper subjected to severe plastic deformation reaches \(10^{-5}\) wt.%. However, it is important to note that even if such a high concentration of vacancies is achieved during the deformation of the alloy, this should lead to an increase in the specific electrical resistance by only \(0.0013 \mu\Omega \cdot \text{cm}\), i.e. several orders of magnitude lower than \(\rho_0\). Therefore, the influence of vacancies on electrical conductivity can be neglected.

The deformation of IS leads to a significant increase in the dislocation density, while the electrical conductivity remains practically unchanged (table 1). It is known that the calculated values of the increase in the electrical resistivity per unit density of chaotically distributed dislocations in pure copper are equal to \(\Delta \rho_{dis} = 1.9 \cdot 10^{-19} \mu\Omega \cdot \text{m}^2\) [18]. The maximum value of the dislocation density is attained in the rolled CG state, which is \(2.54 \cdot 10^{14} \, \text{m}^2\). It follows from these data that the contribution of dislocations to the electrical resistivity of the Cu-0.5Cr alloy at room temperature does not exceed 0.28% relative to the electrical resistivity of pure copper. Consequently, the dislocation mechanism has no significant effect on the electrical conductivity, which is consistent with the results obtained in [19].

The grain boundary contribution is much more significant. A decrease in the grain/subgrain size and an increase in the length of the boundaries lead to additional scattering of conduction electrons. The estimate of this contribution is \(\Delta \rho_{GB} = 2.1 \cdot 10^{-16} \Omega \cdot \text{m}\) [18].

According to the literature data, the effect of the solid solution on the electrical resistance is quite large. This is due to the distortion of the lattice of the copper matrix, in connection with which the scattering of conduction electrons increases. The electrical properties of a solid solution are also related to the chemical interaction of components [3]. However, it is rather problematic to determine the exact concentration of alloying elements in the copper matrix required for calculations. Taking all other contributions to the electrical resistivity to be insignificant, one can calculate the contribution of the solid solution as the difference between the experimental values and calculated values. The contribution of the solid solution to the scattering is maximum in IS, when a supersaturated solid solution is formed and the lattice is maximally distorted. After deformation, in all considered states, the lattice parameter decreases. In the structure, a small amount of a dispersed phase is observed, which is distributed inhomogeneously. However, the values of electrical conductivity remain practically unchanged. X-ray diffraction data indirectly indicate that the decomposition of the supersaturated solid solution proceeds is more complete after aging. Aging also leads to the development of recovery processes, which
increases the size of grains/subgrains and, accordingly, reduces the grain boundary contribution to electrical resistance. As a result, the electrical resistance is significantly reduced.

Thus, the change in the electrical resistance in this alloy is controlled by the composition of the solid solution. An estimate of the change in electrical resistance suggests that the dominance of this mechanism is so strong that it exceeds the contributions of dislocation and grain-boundary scattering.

4. Conclusions
As a result of studies on the relationship between microstructural parameters and a combination of strength and electrical conductivity in different states of the Cu-0.5Cr alloy, the following was established:
- an increase in strength (almost 3-4 times) as a result of deformation realized by cold rolling and ECAP is mainly due to dislocation and grain-boundary contributions (in the rolled initial state these contributions are equal to each other, in the rolled UFG state the grain-boundary contribution prevails);
- aging leads to the predominance of the dispersion contribution to the strength of deformed states;
- the electrical conductivity of the deformed states is low and its low level is due to the solid solution contribution;
- aging leads to a significant (approximately twofold) increase in electrical conductivity for all deformed states, due to the decomposition of the solid solution, while the contributions of dislocation and grain-boundary electrons scattering are small.

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