Analysis of the effect of equal-channel angular pressing on the strength and electrical conductivity of low-alloyed alloys of the Cu-Cr-Zr system

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Abstract. The effect of equal-channel angular pressing (ECAP) on the strength and electrical conductivity of low-alloyed Cu-Cr-Zr alloys to identify conditions for the formation of states with high strength and electrical conductivity is considered. The increase in the content of alloying elements does not increase the strength of the alloys in the initial quenched state. After ECAP, their strength is increased by dislocations. It is shown that after ECAP of quenched samples, their specific resistances remain almost unchanged due to the increase in the length of the grain boundaries, the volume fraction of small particles of secondary phases and the segregation of alloying atoms from the matrix.

1. Introduction
Copper is a good current conductor and is widely used in electronics, electrical engineering, instrumentation and other industries. However, conductors are often required to have high strength properties [1]. Severe plastic deformation (SPD) methods, for example, ECAP, can increase the true yield strength of Cu by 3–5 times due to the refinement of the structure to nanometric dimensions. In ultrafine-grained (UFG) materials obtained by methods of SPD, the length of grain boundaries (GBs) is significantly higher than in their coarse-grained (CG) counterparts. Moreover, GBs are mainly high-angle and are characterized by a high level of internal stresses [2]. Such structural changes, in turn, are reflected in the physical and mechanical properties of materials [3, 4]. The addition of alloying elements also improves the mechanical properties of copper. The presence of Zr significantly increases the dispersion of the chromium phase released during aging. Zr atoms and the high dispersion of the hardening Cr phase contribute to hardening and increase the heat resistance of alloys of the Cu – Cr – Zr system [5]. This paper presents the results of an analysis of the effect of ECAP on the strength and electrical conductivity of alloys of the Cu-Cr-Zr system using Cu-0.5 wt.% Cr-0.2 wt.% Zr and Cu-1.8 wt.% Cr-0.8 wt.% Zr alloys as an example.

2. Experimental
Samples of alloys Cu-0.5 wt.% Cr-0.2 wt.% Zr and Cu-1.8 wt.% Cr-0.8 wt.% Zr in the initial CG states with an average grain size of d and predominantly high misorientation angles between grains
were obtained as a result of high-temperature heat treatment at a temperature of 1000 °C for 0.5 h, followed by quenching in a 5% NaCl solution. Against the background of the obtained α - solid solution, spherical inclusions of several microns in size D were revealed, which are Cr particles and Cu-Zr compounds [4]. The solubility of Cr in Cu at 1000 °C is 0.4 wt% (0.488 at%), the solubility of Zr in copper is 0.15 wt% (0.104 at%) [5]. Since the content of alloying elements exceeds their solubility in Cu at the quenching temperature, particles of undissolved phases appear in the structure of the alloys. Experimental values of the lattice parameter a, the average particle size D, the grain size d, the average distance between the particles L are presented in table 1 [3]. It was assumed that the values of the lattice parameters after quenching were identical (table 1). The dislocation density q was 6.91·10^{13} \text{and} 2.19·10^{13} in the case of the first and second alloys, respectively.

| Alloy         | a (Å)             | D (nm)                  | L (nm)                  | d (nm)            |
|--------------|-------------------|-------------------------|-------------------------|-------------------|
| Cu-0.5Cr-0.2Zr | 3.62167±0.00005   | (4.3±0.1)·10^3           | 34·10^3                | (140±8)·10^3     |
| Cu-1.8Cr-0.8Zr | 3.62167±0.00005   | (2.6±0.2)·10^3           | 20·10^3                | (110±4)·10^3     |

Samples of the alloy in the CG state were deformed using the ECAP method along route A at room temperature. After ECAP, small particles 7–11 nm in size were found in the alloy structure. In the process of deformation, partial dissolution of the particles of Cr and Cu-Zr formed during quenching occurred, and a supersaturated solid solution formed. An UFG structure was formed with high misorientation angles between the grains. Experimental values of the lattice parameter a, the average particle size D, the grain size d, the average distance between the particles L, the size of coherent scattering regions D_{KRO}, the magnitude of the mean-square lattice elastic microdistortions \( \langle \varepsilon^2 \rangle^{1/2} \) after ECAP are presented in table 2 [3].

| Alloy         | \( D_{KRO} \) (nm) | \( \langle \varepsilon^2 \rangle^{1/2} \) (%) | a (Å)             | D (nm)                  | t (nm)                  | L (nm)            |
|--------------|---------------------|---------------------------------------------|-------------------|-------------------------|-------------------------|-------------------|
| Cu-0.5Cr-0.2Zr | 32±3                | 0.24±0.02                                    | 3.6203±0.0002     | (2.5±0.2)·10^4         | 160±7                  | 21.0·10^3         |
| Cu-1.8Cr-0.8Zr | 34±4                | 0.20±0.02                                    | 3.6203±0.0002     | (1.9±0.1)·10^4         | 155±10                 | 21.0·10^3         |

3. Results and discussion

3.1. Strength of alloys in the initial quenched state

Peierls stress, dislocation hardening, solid solution hardening, and hardening by particles of secondary phases contribute to the strength of alloys in the initial state. The Peierls stress \( \sigma_P \) was estimated according to the simplified formula \( \sigma_P = M G \exp \left( 2 \pi / (1-\nu) \right) / (1-\nu) \) [6], where M is the Taylor factor, \( M=3.06 \), \( G=42.1 \) GPa, \( b=0.256 \) nm, \( \nu=0.343 \). The dislocation hardening \( \sigma_{\text{disl}} \) [6] was estimated according to the formula \( \sigma_{\text{disl}} = M a G b \sqrt{q} \) [7]. The parameter \( \alpha \) was taken equal to 0.39, based on the known value of the true yield strength \( \sigma_0 \) of the Cu-1.8 wt.% Cr-0.8 wt.% Zr alloy in the initial quenched state, \( \sigma_0=77.9 \) MPa. When calculating the solid solution hardening \( \sigma_s \approx M G a^{3/2} C_{sa} \) / 760 [6, 8], we used the parameter \( \epsilon \) equal to 0.6 and 2.3 for Cr and Zr, characteristic of Ni and Sn, respectively, as being closer in terms of atomic sizes. In this case, the linear dependence of the solid solution hardening \( \sigma_s \) on the atomic fraction of atoms in a solid solution \( C_{sa} \), \( n=1 \) was adopted. The atomic fractions \( C_{sa} \) of Cr and Zr atoms in the solution, corresponding to their weight fractions of \( W_{sa} \) in the solution, were calculated according to the formula

\[
C_{sa} = W_{sa} \frac{\mu_m}{\mu_a} \frac{W_a}{1-W_a-W_b} + \frac{W_b}{1-W_a-W_b} + 1 \left( \frac{W_a}{1-W_a-W_b} \frac{\mu_m}{\mu_a} + \frac{W_b}{1-W_a-W_b} \frac{\mu_m}{\mu_b} + 1 \right)^{-1}, \tag{1}
\]
where $W_a, W_b$ are mass fractions, $\mu_a, \mu_b$ are the relative atomic masses of substances a and b dissolved in the matrix, $\mu_m$ is the relative atomic mass of the matrix substance. The atomic fractions of dissolved Cr and Zr atoms corresponding to their mass fractions of $W_{sCr}=0.4$ wt% and $W_{sZr}=0.15$ wt%, respectively, as well as the volume fractions of the released large particles, calculated according to the formula $f_{sec} = V_p N_p / V_s$, where $N_p$ is the number of particles in the sample, $V_s$ is the volume of the sample, $V_p$ is particle volume are presented in table 3.

In alloys containing Cr and Zr, there are Cr-based particles and particles of the intermetallic compound Cu$_5$Zr. In the initial states, their sizes $D$ are larger than the minimum particle radius $r_{max}$, which can be cut by dislocations [6]. $r_{max}=ab/2\xi$, where $\xi$ is the size mismatch factor, $\xi=(r_e-r_m)/r_m r_s$ is the radius of the atoms of the dissolved substance, $r_m$ is the radius of the atoms of the matrix. For Cr atoms in a copper matrix, the size mismatch factor is $\xi=0.0156$. Accordingly, $r_{max}\approx3.2$ nm. Cu$_5$Zr particles are not cut by dislocations. The hardening of the material by incoherent particles of $\sigma_{secnc}$ as a result of their bending by moving dislocations was estimated according to the Orowan model [6]: $\sigma_{secnc} = QMGb\Phi \left[ \ln\left( (L-D)/4b \right) \right] / [2\pi(L-D)]$. It was assumed that the particles are enveloped by screw dislocations, respectively, the parameter $\Phi$ was taken equal to 1. The parameter $Q$, taking into account the uneven distribution of particles in the matrix, was chosen from the interval 0.81–0.85 [6]: $Q=0.83$. The values of the particle size $D$ and the distances between the particles $L$ are presented in table 1. The calculated values of active hardening factors in the initial states of the alloys are presented in figure 1.

3.2. Strength of quenched alloys in UFG states

After ECAP, the lattice parameter decreased (table 2), which indicates the release of particles of the secondary Cr phase and the possible formation of Cu$_5$Zr particles [3]. When the Cu lattice parameter changed to 0.000667 nm, 0.4 wt% Cr dissolved in the initial state. A change in the lattice by 0.000525 nm in the state after ECAP corresponds to the mass fraction of dissolved Cr atoms equal to $W_{sCr}=0.315$ wt.%. At the same time, the fraction of dissolved Zr atoms with a corresponding change in the lattice parameter is $W_{sZr}=0.118$ wt.%. The calculated values of the atomic fraction of dissolved atoms of alloying elements, volume fractions of small ($f_{{secCr},s}$, $f_{{secCr},l}$) and large ($f_{{secZr},s}$, $f_{{secZr},l}$) particles, dislocation densities are presented in table 4.

As the above estimates showed, Cr particles with radii larger than 3.2 nm cannot be cut by sliding dislocations. Therefore, small particles are not cut by dislocations. They, like larger particles, are an
obstacle to the path of sliding dislocations and contribute to their accumulation. Peierls stress, dislocation hardening, and solid solution hardening contribute to the strength of alloys in the UFG state. The obtained values of strengthening factors are presented in figure 2.

Table 4. The calculated values of the strengthening factors of the alloys in the state after ECAP.

| Alloy                | $f_{secZr}$ | $f_{secCr}$ | $f'_{secZr}$ | $f'_{secCr}$ | $C_{Zr}$ (at.%) | $C_{Cr}$ (at.%) | $\rho_{tot}$ (m$^{-2}$) |
|----------------------|-------------|-------------|--------------|--------------|----------------|----------------|-------------------------|
| Cu-0.5Cr-0.2Zr     | 0.477·10\(^{-3}\) | 0.244·10\(^{-3}\) | 3.497·10\(^{-3}\) | 2.047·10\(^{-3}\) | 0.0821          | 0.384           | 1.02·10\(^{15}\)      |
| Cu-1.8Cr-0.8Zr     | 1.219·10\(^{-2}\) | 6.731·10\(^{-3}\) | 2.067·10\(^{-2}\) | 1.156·10\(^{-2}\) | 0.0821          | 0.384           | 7.96·10\(^{14}\)      |

Figure 2. Strengthening factors in conditions after ECAP.

3.3. Specific electrical resistance of alloys in the initial quenched state

Thermal vibrations of atoms at the nodes of the crystal lattice and defects in its structure contribute to the specific electrical resistance of alloys in the initial states. The average value of the electrical resistivity $\rho_T$ due to thermal vibrations of the lattices Cu ($\rho_{TCu}$), Cr ($\rho_{TCr}$) and the compound CuZr ($\rho_{TZr}$) can be calculated according to the formula $\rho_T=(1-f_{secCr}-f_{secZr})\rho_{TCu}+f_{secCr}\rho_{TCr}+f_{secZr}\rho_{TZr}$, where attention to the contribution to the electrical resistivity of the regions occupied by particles of Cr and CuZr. However, in the calculations, the value of $\rho_T$ was calculated without taking into account the contribution of CuZr particles according to the approximate formula $\rho_T=(1-f_{secCr})\rho_{TCu}+f_{secCr}\rho_{TCr}$, where $\rho_{TCr}=2.7·10^{-8}$ Ω m is the electrical resistivity Cr at room temperature. It was assumed that the electrical resistivity $\rho_{TZr}$ of the CuZr compound is on the order of the electrical resistivity of the Cu lattice. In this case, the contribution of CuZr particles to the average value of $\rho_T$ will be three orders of magnitude smaller in the case of Cu-0.5 wt.% Cr-0.2 wt.% Zr and two orders of magnitude smaller in the case of Cu-1.8 wt.% Cr-0.8 wt.% Zr of the contribution of the Cu lattice, since their volume fractions are $f_{secZr}\approx2.422·10^{-3}$ and $f_{secZr}\approx3.131·10^{-2}$, respectively. The values of the volume fraction of Cr particles in the case of the first and second alloy are presented in table 3.

The alloying atoms dissolved in the matrix increase the electrical resistivity by the value of $\rho_a$ ($\rho_{Cu}$ и $\rho_{Zr}$) [10]:

$$\rho_a = \frac{k^2h^3n_eC_{se}}{9e^2\pi l} \left[ 1 - \frac{\sin 2kl}{2kl} \right],$$

where $n_e$ is the volume concentration of the matrix atoms, $k=2\pi\lambda$ is the wave number, $\lambda=h/m^*\nu_e$ is the electron wavelength, $m^*$ is the effective electron mass, $\nu_e$ is the Fermi velocity, $h$ is Planck’s constant, $e$ is the electron charge value, $n_e$ is the density of free electrons, $l$ is the size of the region of interaction of an electron with an alien atom.
The increment in resistivity due to Cr and Zr atoms was calculated for the sizes of the scattering potential action area equal to \( t_{Cr} = 1.35b \) and \( t_{Zr} = 1.73b \), respectively, \( b \) is the value of the Burgers vector.

The particles of the secondary phases contribute to the resistivity of the alloy by \( \rho_{sec} (\rho_{secCr}, \rho_{secZr}) \) \[6\], equal to

\[
\rho_{sec} \approx \frac{m u e f_{sec} \pi}{n e^2 V_{pa}} (R + r)^2 ,
\]

where \( R \) is the radius of the region of interaction of the electron with the particle, which is equal to the radius of the particle, \( r \) is the screening radius, \( r \approx 3 \cdot 0.554 \cdot 10^{-10} \text{ m} \) \[6\], \( V_{pa} \) is the volume of spherical particles of the secondary phase.

Dislocations increase the resistivity of the alloy by \( \rho_{disl} \) \[10\]:

\[
\rho_{disl} = \frac{2 \hbar k l k n e^{2}}{9 n e^2} \left( 1 - \frac{\sin 2kl}{2kl} \right).
\]

The grain boundaries also contribute to the resistivity of the alloy, which depends on the misorientation angle between the grains. In the case of high misorientation angles in CG polycrystals, it is equal to \( \rho_{gb} = 2.5 \cdot 10^{-16} N_{gb} \), where \( N_{gb} = S / \Omega \approx 1 / \delta \), \( S \) is the area of boundaries in the volume \( \Omega \) \[11\].

Let's assume the share of high-angle boundaries is approximately 78%. The contribution of all factors increasing the resistivity of alloys in the initial CG state is presented in figure 3.

![Figure 3](Image)

**Figure 3.** The contribution of microstructure elements to the electrical resistivity of alloys in the initial states.

Model values of the true value of the yield strength \( Y_i \), electrical resistivity \( \rho \), electrical conductivity \( \delta \) and available experimental values of the true yield strength \( Y_{expi} \), specific electrical conductivity \( \delta_{expi} \) of Cu-0.5Cr-0.2Zr and Cu-1.8Cr-0.8Zr alloys in the initial CG condition are presented in table 5.

| Alloy         | \( Y_i \) (MPa) | \( Y_{expi} \) (MPa) | \( \rho \) (\( \Omega \cdot \text{m} \)) | \( \delta \) (IACS, %) | \( \delta_{expi} \) (IACS, %) |
|--------------|----------------|----------------------|-------------------------------|----------------------|-----------------------------|
| Cu-0.5Cr-0.2Zr | 123.1          | -                    | 5.763 \cdot 10^{-8}           | 29.9                 | 29.0 \pm 0.6               |
| Cu-1.8Cr-0.8Zr | 77.4           | 77.9                 | 5.775 \cdot 10^{-8}           | 29.9                 | 30.0 \pm 0.6               |

3.4. **Specific electrical resistance of alloys in UFG states**

In the state after ECAP, in addition to the above factors, electron scattering from the released small particles of Cr and CuSzr (\( \rho'_{secCr}, \rho'_{secZr} \)) contributes to the electrical resistivity of the alloys:
\( \rho_t = (1 - f_{secCr} - f_{secCu}) \rho_{Cu} + (f_{secCr} + f_{secCu}) \rho_{Cr} \). The contribution of GB in the case of high misorientation angles is \( \rho_{gb} = 5.6 \cdot 10^{-16} N_{gb} \) [10, 11]. The contribution of all factors increasing the electrical resistivity of alloys in the initial CG state and in the state after ECAP is presented in figures 3 and 4, respectively.

**Figure 4.** The contribution of microstructure elements to the resistivity of alloys in states after ECAP.

Model values of the true value of the yield strength \( Y_t \), electrical resistivity \( \rho \), electrical conductivity \( \delta \) and available experimental values of the true yield strength \( Y_{expi} \), specific electrical conductivity \( \delta_{exp} \) of Cu-0.5Cr-0.2Zr, Cu-1.8Cr-0.8Zr alloys in the initial CG condition are presented in table 6.

**Table 6.** The model values of the true yield stress \( Y_t \), specific electrical resistance \( \rho \), the specific electrical conductivity \( \delta \) and the experimental values of the true yield stress \( Y_{expi} \), specific electrical conductivity \( \delta_{exp} \) of the alloys in the UFG state.

| Alloy         | \( Y_t \) (MPa) | \( Y_{expi} \) (MPa) | \( \rho \) (\( \Omega \cdot \text{m} \)) | \( \delta \) (IACS, \%) | \( \delta_{exp} \) (IACS, \%) |
|---------------|-----------------|----------------------|-----------------|-----------------|-----------------|
| Cu-0.5Cr-0.2Zr | 423.3           | -                    | 5.327 \( \cdot \) 10^{-8} | 32.4            | 30.0 \( \pm \) 0.6 |
| Cu-1.8Cr-0.8Zr | 377.5           | 393.5                | 5.662 \( \cdot \) 10^{-8} | 30.5            | 29.0 \( \pm \) 0.6 |

4. **Conclusions**

An increase in the content of alloying elements slightly reduced the strength of the alloys in the initial states. Their resistivity has not changed. After ECAP, dislocation hardening of an alloy with a high content of alloying elements is lower than that in an alloy with a lower content of Cr and Zr atoms. The values of the resistivity of the alloys after ECAP differ little. In an alloy with a higher content of alloying elements, it is slightly higher due to the higher volume fraction of fine particles. Moreover, the strength of alloys after ECAP increases significantly. At the same time, their resistivity practically does not change, due to the fact that a decrease in the contribution of alloying elements is compensated by an increase in the contribution of grain boundaries and small particles of precipitated phases. To obtain alloys with high strength and electrical conductivity, their subsequent processing is necessary, which promotes the release of foreign atoms from the matrix into particles of the secondary phases, and an increase in the density of dislocations.

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