Contribution of structural factors to the specific electrical resistance of nanostructured Cu-Cr-Zr alloy

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Abstract. The specific resistance of the nanostructured Cu-1.8 wt.% Cr-0.8 wt.% Zr alloy has been analyzed by means of analytical modeling. The contribution of different structural parameters to the specific resistance of the material has been estimated.

1. Introduction
The energy industry demands the conductors with high strength and high electrical conductivity [1]. Reducing grain size allows increasing the strength characteristics of such materials. At the same time, this leads to an increase in electrical resistance. In this regard, the issue of the contribution of structural parameters to the formation of a state with optimal strength and electrical conductivity is relevant [2, 3]. In this paper, analytical modeling methods are used to analyze the contribution of different structural parameters into the specific electrical resistance of the Cu-1.8 wt.% Cr-0.8 wt.% Zr alloy in various structural states.

2. Experimental and theoretical approaches
A detailed description of the experiments is presented in [3]. Samples of the Cu-1.8 wt.% Cr-0.8 wt.% Zr alloy, were kindly provided by Prof. Wei Wei in the initial coarse-grained (CG) state and in the state after equal-channel angular pressing (ECAP). The initial state (IS) was formed as a result of high-temperature heat treatment at 1000 °C for 0.5 h, followed by quenching in 5% NaCl solution. Samples of the alloy in the IS were deformed by 4 ECAP passes using route A at room temperature (RT). As a result, a nanostructured (NS) state of the alloy was formed (4ECAP state). The samples of the alloy in the 4ECAP state were subjected to subsequent aging at a temperature of 450 °C for 1 hour, which led to the formation of the 4ECAP+A state. The microstructure was studied using an OLIMBUS GX51 optical microscope, a JEOL JSM-6490LV scanning electron microscope and a JEOL 2100 transmission electron microscope. X-ray diffraction analysis of the samples was carried out on a Rigaku Ultima IV diffractometer. The measurements of the specific electrical resistance were carried out at RT by the eddy current method. The experimental values of the sizes of coherent scattering domains $D_{\text{XRD}}$, the magnitude of the mean-square lattice of elastic microdistortions $(\varepsilon^2)^{1/2}$, lattice parameter $a$, average particle size $d_{\text{av}}$, grain size $d$, and average distance between the particles $L_{\text{av}}$ are presented in table 1.
The analysis of the specific electrical resistance of various structural states was carried out taking into account the contribution of alloying atoms, dislocations, particles of secondary phases, grain boundaries (GBs) and thermal vibrations of the crystal lattice. The contribution of the dissolved atoms of the alloying elements was estimated by the formula presented in [4]:

$$\rho_s = k^2 h l n^2 C_{sa} \left( 1 - \frac{\sin(2kl)}{2kl} \right) \left( 9e^2 n_e \right)$$

(1)

where \(n_s\) is the volume concentration of the matrix atoms, \(k = 2\pi/\lambda\) is the wave number, \(\lambda = h/m^*u_f\) is the electron wavelength, \(m^*\) is the effective electron mass, \(u_f\) is the Fermi velocity, \(\hbar\) is Planck's constant, \(C_{sa}\) - atomic fraction of atoms \(a\) in solution, \(e\) 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 presence of dislocations increases the specific electrical resistance by the value of \(\rho_{dis}\) [4]:

$$\rho_{dis} = h k^2 \rho_s \left( 1 - \frac{\sin(2kl)}{2kl} \right) \left( 9e^2 n_e \right).$$

(2)

The contribution of large and small particles of secondary phases to resistivity was estimated according to the formula presented in [5]:

$$\rho_{sec} \approx \frac{N_{gb}}{V_{pa}} \varphi \frac{\pi}{V_p} (R + r)^2$$

(3)

where \(R\) is the radius of the interaction region of the electron with a particle \((R - \text{ particle radius})\), \(r\) is the screening length, \(r = 3 \times 0.554 \times 10^{-10} \text{ m}\), \(m_e\) is the electron mass. \(V_{pa}\) is the volume of spherical particles of a secondary phase. In the case of large misorientation angles, the average value of the contribution of GBs was estimated according to the formula \(\rho_{gb} = 5.6 \times 10^{-16} N_{gb}, N_{gb} = S/\Omega \approx 1/d, S\) is the area of boundaries in the volume \(\Omega\) [6, 4]. The contribution to the specific electrical resistance of thermal vibrations of Cu atoms in the lattice sites was taken equal to \(\rho_{TCu} = 1.724 \times 10^{-8} \Omega \cdot \text{m}\) similar to the case of pure coarse-grained copper [5].

3. Results and discussion

The solubility of Cr in Cu at 1000 °C is 0.4 wt.% (0.488 at.%), the solubility of Zr in Cu is 0.15 wt.% (0.104 at.%) [7]. Since the content of the alloying elements exceeds their solubility in Cu at the quenching temperature, spherical particles of undissolved phases appear in the alloy structure. After ECAP, fine particles with a size of 7–11 nm were detected [3]. During the deformation process, a partial dissolution of large particles occurred [3], and a supersaturated solid solution was formed. The solution contained Cr and Zr atoms, the atomic fractions of which were \(C_{Cr} = 0.3840\) at.% and \(C_{Zr} = 0.0821\) at.%, respectively. The atomic fraction \(C_{Cr}\) of Cr atoms dissolved in the matrix in the UFG alloy state was calculated taking into the assumed linear dependence of the variation in the lattice parameter on the concentration of Cr in solid solution. The lattice parameter in the IS was equal to \(a = 3.622 \pm 0.005\) Å. In pure Cu, the lattice parameter was assumed to be \(a_0 = 0.3615\) nm. The atomic fraction of Zr atoms \(C_{Zr}\) was determined similarly. For Cr atoms, the size of the electron scattering region was taken equal to \(l_{Cr} = 1.35b_0\) [4]. For Zr atoms, \(l_{Zr} = 1.73b_0\) according to the known experimental value of the electrical conductivity of the alloy in the initial state is \(\delta = 30.0\) ± 0.6% IACS. The increase in the size of the interaction region is due to the presence of a difference between the valences of Zr and Cu [8].

The contribution of dislocations to the resistivity (figure 1a) was calculated at \(l = 1.55b_0\) [4]. The dislocation density \(q\) (table 2) was calculated according to the formula \(q = 2\sqrt{3} \left( e^2 \right)^{1/2} / D_{sec} b_0\) [9] taking into account the value of the Burgers vector \(b_0\) and the known experimental data (table 1).

The volume fractions of large and small particles were calculated according to the formula \(f_{sec} = V_{pa} N_p / V_s\), where \(N_p\) - the number of particles in the sample, \(V_s\) - the sample volume, equal to
where

\[ f_{\text{secCr}} \approx 6.731 \times 10^{-3} \] and \[ f'_{\text{secCr}} \approx 1.156 \times 10^{-2} \] respectively. The volume fraction of large and small Cu-Zr particles after ECAP took the values \[ f_{\text{secZr}} \approx 1.219 \times 10^{-2} \] and \[ f'_{\text{secZr}} \approx 2.067 \times 10^{-2} \] respectively.

The grain boundaries in the alloy after ECAP were assumed to have high-angle misorientations.

| Table 1. Microstructure parameters of Cu-1.8 wt.%Cr-0.8 wt.%Zr alloy in 4ECAP and 4ECAP+A states. |
| State | \( D_{\text{GDRD}} \) (nm) | \( \langle a \rangle \) (\( \overline{\text{A}} \)) | \( a \) (\( \overline{\text{A}} \)) | \( d_{\text{av}} \) (nm) | \( d \) (nm) | \( L_{\text{av}} \) (nm) |
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 4ECAP | 34±2            | 0.20±0.02       | 3.620±0.002     | (1.9±0.1) \( \times 10^3 \) | 155±10         | 21.0±10         |
| 4ECAP+A | 35±2           | 0.18±0.01       | 3.615±0.002     | (1.8±0.1) \( \times 10^3 \) | 175±10         | 18.2±10         |

It was assumed that the contribution of the specific resistance \( \rho_t \) of the thermal vibrations of atoms in the lattice sites in the 4ECAP state is equal to \( \rho_t = (1 - f_{\text{secCr}} - f'_{\text{secCr}}) \rho_{\text{Cu}} + (f_{\text{secCr}} + f'_{\text{secCr}}) \rho_{\text{Cr}} \), where \( \rho_{\text{Cr}} = 2.7 \times 10^4 \Omega \cdot \text{m} \) - the specific electrical resistance of Cr at room temperature. It was assumed that the specific resistance of the Cu-Zr compound is of the order of the specific electrical resistance of the matrix. The contributions of all factors that increase the specific electrical resistance \( \rho \) of the alloy in the 4ECAP state are presented in figure 1 and the resulting value of \( \rho \) and electrical conductivity \( \delta \) are summarized in table 2.

The solubility of Cr in Cu at 450 °C is 0.03 wt. % (3.661 \( \times 10^{-3} \) at. %), Zr - 0.005 wt. % (3.477 \( \times 10^{-3} \) at.%) [7]. It is known that as a result of primary aging of the CG Cu-0.78% Cr-0.13% Zr alloy at a temperature of 460 °C for 3 h, fine particles precipitated, containing Cr and Zr atoms, the average size of which is \( \approx 3 \) nm. Additional aging contributes to the enlargement of small particles precipitated during primary aging [10]. As a result, the concentration of such particles in the sample decreases \( g \) times. Let us take the following model of the alloy aged after ECAP. Particles precipitated as a result of dynamic aging (primary aging) are enlarged after aging at a temperature of 450 °C for 1 h. Moreover, their volume fraction remains almost unchanged. The number of particles \( N_{\text{sec}} \) is proportional to their volume fraction \( f_{\text{sec}} \): \( N_{\text{sec}} = 3V_{\text{sec}} f_{\text{sec}} / 4\pi R_{\text{sec}}^3 \), where \( f_{\text{sec}} \) and \( R_{\text{sec}} \) are the volume fraction and radius of particles precipitated as a result of dynamic aging in the ECAP process correspondingly. It follows that the radius of the particles \( R_{\text{secA}} \) after aging will be equal \( R_{\text{secA}} = R_{\text{sec}} \sqrt{f_{\text{secA}} / f_{\text{sec}}} \), where \( f_{\text{secA}} \) is the volume fraction of particles after aging, \( f_{\text{secA}} \approx f_{\text{sec}} \).

The concentration of particles having an average size after ECAP, equal to 9 nm, decreases approximately by \( g = 5 \) times [10]. Consequently, the average particle size becomes \( 2R_{\text{secA}} = 16 \) nm. The sizes and density of large particles after aging practically did not change and remained the same as after ECAP (table 1). Accordingly, their volume fractions did not change. During aging, decomposition of the supersaturated solid solution occurred. The volume fractions of the precipitated small particles of the secondary phases Cr and Cu-Zr were, respectively, \( f_{\text{AsecCr}} \approx 5.444 \times 10^{-3} \), \( f_{\text{AsecZr}} \approx 5.444 \times 10^{-3} \). In NS materials, diffusion processes are accelerated. Therefore, it can be expected that the average diameter of particles containing Cr and Zr will be higher than 3 nm. Let us take the value of their radius \( r \) close to the maximum radius \( r_{\text{max}} \), which is cut by dislocations. \( r_{\text{max}} = ab \sqrt{2}r_{\text{a}} \), where \( r_{\text{a}} \) is the factor of size mismatch, \( a = (r_{\text{c}} - r_{\text{m}}) / r_{\text{m}} \), \( r_{\text{c}} \) is the radius of the atoms of the solute, \( r_{\text{m}} \) is the radius of the atoms of the matrix. The parameter \( \alpha \) was taken equal to 0.39, based on the known value of the true yield strength \( \sigma_{\text{vexp}} \) in the initial quenched state, \( \sigma_{\text{vexp}} = 77.9 \text{ MPa} \). It was assumed that the yield stress of an alloy taken in the IS is determined by the contribution of four factors: \( \sigma_{\text{vexp}} = \sigma_t + \sigma_s + \sigma_{\text{dial}} + \sigma_{\text{sec}} \), \( \sigma_s \) is the solid-solution hardening ( \( \sigma_s \approx MG \xi^{1/2}C_{\text{cr}} / 760 \) ) [5], which was calculated with the parameter \( \xi \) taken to be 2.3 for Zr and 0.6 for Cr. \( \sigma_{\text{sec}} \) - hardening by incoherent particles of the secondary phases, calculated in the framework of the Orowan model \( \sigma_{\text{sec}} = QMG \Phi (\ln (L_{\text{av}} / d_{\text{av}}) / 4ab) / (2\pi L_{\text{av}} d_{\text{av}}) \) taking into account the values of the parameters presented in table 1, as well as the given values of the parameters \( Q = 0.83 \), \( \Phi = 1 \). \( \sigma_t \) is the Peierls stress, which was calculated according to the simplified formula \( \sigma_t = MG \exp (2\pi (1-\nu)/(1-\nu)) \) [5], where the Poisson's ratio is \( \nu = 0.343 \). \( \sigma_{\text{dial}} \) - dislocation hardening, \( \sigma_{\text{dial}} = Ma \Phi \beta (q) / 2 \) [5]. For Cr atoms in the Cu
matrix, the size mismatch factor is \( \xi = 0.0156 \). Accordingly, \( r_{\text{max}} \approx 3.2 \text{ nm} \). Cu\textsubscript{5}Zr particles are not cut by dislocations. The average value of the contribution of GBs into the specific electrical resistance was estimated as \( \rho_{\text{gb}} = \rho_{\text{gb}}^{0.705} \times 10^{-8} \) \[6, 4\]. In assessing the contribution of thermal lattice vibrations \( \rho_{\text{T}} \) to the specific electrical resistance of the alloy, the areas occupied by small Cr particles precipitated during aging were taken into account. The contributions of all factors that increase the specific electrical resistance of the alloy in ECAP+A state are summarized in table 2 and shown in figure 1.

Figure 1. Contribution to the specific electrical resistance of alloying atoms (\( \rho_{\text{Cr}}, \rho_{\text{Zr}} \)), thermal vibrations of the crystal lattice (\( \rho_{\text{T}} \)), dislocations (\( \rho_{\text{disl}} \)), GBs (\( \rho_{\text{gb}} \)), large particles (\( \rho_{\text{secCr}}, \rho_{\text{secZr}} \)) precipitated during quenching and small particles (\( \rho_{\text{secCr}}, \rho_{\text{secZr}} \)) of secondary phases precipitated during the ECAP process, as well as small particles precipitated as a result of aging (\( \rho_{\text{secCr}}, \rho_{\text{secZr}} \)) in 4ECAP (a) and 4ECAP+A (b) states.

Table 2. The model values of dislocation density \( q \) and specific electrical resistance \( \rho \), the model \( \delta \) and the experimental \( \delta_{\text{exp}} \) value of the electrical conductivity.

| State       | \( q \) (m\textsuperscript{-2}) | \( \rho \) (\( \Omega \cdot \text{m} \)) | \( \delta \) (IACS, %) | \( \delta_{\text{exp}} \) (IACS, %) |
|-------------|-------------------------------|-------------------------|-----------------------|-------------------|
| 4ECAP       | \( 7.96 \times 10^{14} \)       | \( 5.662 \times 10^{-8} \) | \( 30.5 \)           | \( 29.0 \pm 0.6 \) |
| 4ECAP+A     | \( 6.96 \times 10^{14} \)       | \( 2.398 \times 10^{-8} \) | \( 71.9 \)           | \( 70.0 \pm 0.6 \) |

4. Conclusions

According to the results of the modeling, a significant contribution to the resistivity of the alloy in the 4ECAP state is made by the dissolved alloying atoms and the thermal oscillations of the crystal lattice. An order of magnitude smaller contribution is made by the GBs, as well as particles of secondary phases of Cr and Cu\textsubscript{5}Zr precipitated during the ECAP process. The contribution of the large Cr and Cu\textsubscript{5}Zr particles precipitated during the quenching process is negligible. Aging after 4 ECAP passes contributes to the formation of a specific structure, which allows increasing the electrical conductivity as a result of separating alloying atoms from the matrix into small particles of secondary phases, coarsening the fine particles precipitated after ECAP and reducing the misorientation angle between the grains.

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