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Increased specific resistivity of grain boundaries in nonequilibrium state in ultrafine-grained Al−Cu−Zr alloy

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In this work an Al−Cu−Zr alloy with ultrafine-grained (UFG) structure formed by high-pressure torsion is studied. Different structural states of grain boundaries in the UFG structure were achieved through subsequent annealing and additional deformation. The specific resistivity of the alloy in the temperature range 77−300 K has been experimentally determined for each state. Based on the microstructural parameters of the alloy, analysis of changes in average specific resistivity of grain boundaries was carried out. It is shown that additional deformation, which introduces excess grain boundary dislocation density (nonequilibrium state), leads to its increase by $\geqslant 20\,\%$.

Keywords: grain boundary resistivity, nonequilibrium grain boundaries, severe plastic deformation, microstructure.

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It is common knowledge that grain boundaries (GBs) raise the electrical resistance of metals due to by scattering conduction electrons [1]. Since bulk coarse-grained (CG) metals have a low density of GBs, their effect on the material resistivity is insignificant [1,2]. Bulk ultrafine-grained (UFG) and nanocrystalline (NC) metals and alloys structured by severe plastic deformation (SPD) are currently being studied extensively due to the engineering interest in their high strength [3]. Bulk UFG and NC materials have a high density of GBs; therefore, their influence on the material resistivity increases significantly [3]. In addition, when products made from such materials are miniaturized, the contribution of GBs to the resulting resistivity increases greatly. One of the main contributions to resistivity in nanoscale electrical connectors made of NC Cu in micro(nano)-electromechanical systems (MEMS/NEMS) is produced by carrier scattering by grain boundaries [4].

A large body of experimental data indicate that GBs in bulk NC and UFG metals and alloys structured by SPD may be in a non-equilibrium state (i.e., contain excess dislocations introduced during SPD processing), causing significant lattice distortion near the GBs [5,6]. In NC and UFG alloys, segregations of impurity elements and nanoprecipitates of secondary phases may also form at grain boundaries [7,8]. All this may affect significantly the resistivity of GBs. Therefore, the assessment of resistivity of GBs in their different states (with excess dislocations, segregations, nanoprecipitates) is of great importance for understanding the structure−properties relation and for the development of technological applications that implement the control of material properties through grain boundary engineering.

A fairly large number of papers focused on the contribution of GBs to the resistivity of a material have already been published. However, such studies have been largely limited to thin films of various metals [2,9–11]. It was found in studies of bicrystal thin Al films that the resistivity of high-energy GBs with a high value of parameter Σ (the degree of misorientation of neighboring grains) is ~ 2 times higher than the resistivity of special GBs $\Sigma 3$ [2]. The GB resistivity for thin films of nanocrystalline Ni and Co was determined in [11], and it was also demonstrated that the GB resistivity in thin NC films of the Ni−Fe alloy is equivalent to the GB resistivity in the Ni−Fe CG alloy [11]. Experiments with thin films of pure copper revealed that the curvature of GBs enhances their resistivity [10]. Theoretical and experimental studies show that segregation may both reduce and enhance the GB resistivity depending on the type of GBs and the doping (impurity) element [12]. One disadvantage of studies of the electrical conductivity of thin films is the influence of the surface layer, since the small thickness of such films is comparable to the mean free path of electrons.

Only a limited number of papers focused on the influence of the GB structure in bulk UFG and NC metals and alloys structured by SPD have been published. The authors of [13] have examined commercially pure Al with the UFG structure formed by repeated rolling. Having analyzed the experimental data, they concluded that the GB resistivity in the UFG structure does not differ from that in CG Al [13]. The effect of annealing on the resistivity of Al (99.2 %) processed by accumulative roll bonding was investigated in [14]. It was demonstrated that the electrical conductivity of UFG Al correlates to a greater extent with the GB misorientation than with the grain size. It was found in [15] that the GB resistivity in a non-equilibrium state is at least 1.5 times higher than in an equilibrium one. Having analyzed the change in resistivity of the Al−12Ca (wt.%) composite obtained by compacting a mixture of Al

Table 1. Main parameters of the alloy microstructure in different states determined in [17] (a — lattice parameter, L_{dis} — integral dislocation density, d_{av} — average grain size, and d_{AlCu} — average size of Al_2Cu particles)

State	a, Å	$L_{dis} \cdot 10^{13}$, m^{-2}	d_{av}, nm	d_{AlCu}, nm
HPT	4.0504 ± 0.0001	2.6	285 ± 23	25 ± 7
HPT+AN	4.0500 ± 0.00003	1.7	360 ± 25	55 ± 10
HPT+AN+0.25HPT	4.0502 ± 0.00006	3.0	315 ± 24	55 ± 20

and Ca powders with subsequent extrusion, the authors of [16] concluded that GB segregations of Ca lead to a twofold increase in the fraction of electrons reflected from grain boundaries (compared to the case of reflection from boundaries in pure Al). Thus, the available literature data indicate that the GB resistivity (averaged over a set of GBs) in UFG and NC materials depends strongly on the fine structure of GBs, which is specified by the method and the mode of formation of the UFG or NC structure.

Special attention is currently being paid to the study of low-alloy high-strength UFG Al alloys with a small Zr and Cu content developed for modern electrical engineering applications [17]. Alloying with Cu has a significant positive effect on the strength characteristics of the alloy, and when Zr interacts with aluminum, intermetallic Al_3Zr compounds are formed, ensuring thermal stability. The aim of the present study is to determine the influence of the structural state of grain boundaries (equilibrium–non-equilibrium state) on their resistivity in a conductive UFG alloy of the Al–Cu–Zr system.

An alloy of the Al–Cu–Zr system (Cu — 1.47 wt.%, Zr — 0.34 wt.%, Si — 0.04 wt.%, Zn — 0.014 wt.%, and V — 0.01 wt.%) was examined. To form a homogeneous structure, the alloy was annealed for 140 h at a temperature of 375 °C. The samples were then subjected to deformation by high-pressure torsion (HPT) at a Walter Klement GmbH HPT-07 press under a pressure of 6 GPa (10 turns at room temperature). Disks with a diameter of 20 mm and a thickness of ~ 1.0 mm were obtained as a result. This alloy state is hereinafter referred to as HPT. After HPT processing, degree of true deformation e at a distance of 5 mm from the center of the disk was ~ 6.6. The samples were then annealed at a temperature of 125 °C for 4 h (HPT+AN state). After annealing, some of the samples were subjected to additional deformation (AD) by HPT to 0.25 turns. This state was denoted as HPT+AN+0.25HPT. Samples for resistivity measurements were cut from the obtained disks in accordance with the diagram shown in Fig. 1. The resistivity of these samples was measured by the standard four-point method within the temperature range of 77–300 K with an accuracy of ±2%. A more detailed description of the measurement procedure was provided in [15].

The structure of the alloy in all three states was studied in detail in [17]. All the studied states are characterized by an equiaxial UFG structure with an average grain size close to 300 nm (Table 1). In all three states, the particles

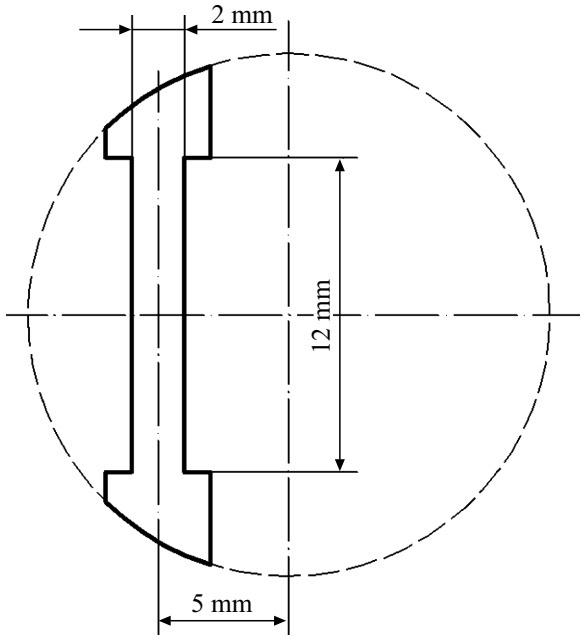

Figure 1. Cut-up sketch for HPT samples for resistivity measurements.

of secondary phase Al_3Zr are located mostly in the body of grains, and their average size is ~ 18 nm. In the HPT state, GBs also contain elliptical Al_2Cu particles with an average size of $d_{pt} \sim 25$ nm. Annealing leads to an increase in the size of Al_2Cu ($d_{pt} \sim 55$ nm) particles and a change in their shape (they become faceted and polyhedral), while additional deformation after annealing does not alter the average size and distribution of particles. According to the X-ray diffraction analysis data, the dislocation density in the HPT state is as high as $2.6 \cdot 10^{13}\ m^{-2}$. A fraction of dislocations annihilate after annealing (state HPT+AN), and the dislocation density decreases to $1.7 \cdot 10^{13}\ m^{-2}$. Following additional deformation (state HPT+AN+0.25HPT), the dislocation density increases to the level characteristic of HPT state [17]. Scanning transmission electron microscopy studies revealed a virtually complete lack of intragranular dislocations in all three states; therefore, the change in dislocation density was attributed to grain boundaries and boundary regions [17]. The lattice parameter remained virtually unchanged after annealing and AD, indicating that the Cu concentration in the solid solution is preserved in all states. The microstructure parameters are listed in Table 1.

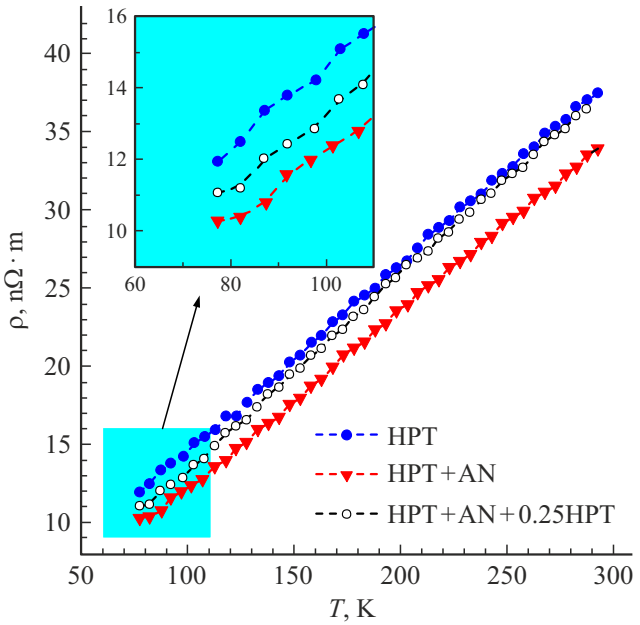

Figure 2. Temperature dependence of resistivity of the UFG alloy in different structural states.

The electrical properties of the alloy were measured in three states: HPT, HPT+AN, and HPT+AN+0.25HPT. The temperature dependences of resistivity of the samples are shown in Fig. 2. These dependences are linear for all the studied states, which is typical of metals and alloys. At 77 K, the resistivity of the samples in the HPT state is $\sim 11.94\,\mathrm{n\Omega \cdot m}$. Annealing leads to a reduction of resistivity throughout the entire temperature range, while subsequent AD enhances it (Fig. 2). At 77 K, the resistivity increase as a result of AD is $\Delta\rho = 0.8\,\mathrm{n\Omega \cdot m}$ relative to the state after annealing (Table 2). Earlier microstructural studies have revealed that additional deformation after low-temperature annealing alters only the dislocation density at grain boundaries (in the boundary regions); average grain size d_{av} changes insignificantly, and the size and shape of Al_2Cu precipitates at GBs are preserved. The experimentally observed variation of resistivity of the alloy is then associated with a small change in GB density (the area of grain boundaries per unit volume, which may be estimated as $3/d_{av}$ [15]) and with a possible change in GB resistivity. Accordingly, variation $\Delta\rho$ of resistivity of the alloy in transition from the HPT+AN state to the HPT+AN+0.25HPT state may be written in the following form in accordance with Matthiessen's rule [1]:

$$\Delta\rho = \delta\rho^*_{\mathrm{GB}}(3/d^*_{av}) - \delta\rho_{\mathrm{GB}}(3/d_{av}), \qquad (1)$$

where $\delta\rho_{\mathrm{GB}}$ and $\delta\rho^*_{\mathrm{GB}}$ are the values of GB resistivity (resistance of a unit GB area) in HPT+AN and HPT+AN+0.25HPT states, respectively, and d_{av} and d^*_{av} are the values of average grain size in HPT+AN and HPT+AN+0.25HPT states, respectively. $\delta\rho^*_{\mathrm{GB}}$ may be written as $\delta\rho_{\mathrm{GB}} + \Delta(\delta\rho_{\mathrm{GB}})$, where $\Delta(\delta\rho_{\mathrm{GB}})$ is the magnitude

Table 2. Resistivity of the UFG alloy in different states (ρ_{77} — resistivity at 77 K and ρ_{RT} — resistivity at room temperature)

State	ρ_{77}, nΩ · m	ρ_{RT}, nΩ · m
HPT	11.94	37.48
HPT+AN	10.27	34.98
HPT+AN+0.25HPT	11.07	38.50

of resistivity variation of GBs due to the introduction of additional dislocation density into them (increase in the degree of their non-equilibrium). Using the experimentally obtained value of $\Delta\rho = 0.8\,\mathrm{n\Omega \cdot m}$ (Table 2) and the average grain sizes in the HPT+AN and HPT+AN+0.25HPT states (Table 1) and assuming that the GB resistivity in the annealed state is close to the average value in coarse-grained aluminum, which is $\delta\rho_{\mathrm{GB}} = 2.6 \cdot 10^{-16}\,\Omega \cdot \mathrm{m}^2$ [18], we found $\Delta(\delta\rho_{\mathrm{GB}}) \approx 0.5 \cdot 10^{-16}\,\Omega \cdot \mathrm{m}^2$. It is known that the introduction of external (lattice) dislocations into the structure of GBs transfers the boundaries into non-equilibrium state, while proper annealing leads to GB relaxation due to annihilation and restructuring of their dislocation structure [6,15,19]. Thus, in the studied Al–Cu–Zr UFG alloy, the transition of GBs from the equilibrium state (HPT+AN) to the non-equilibrium one (HPT+AN+0.25HPT) induces at least a $\sim 20\,\%$ enhancement of the GB resistivity. It should be noted that the obtained estimate of $\sim 20\,\%$ is the lower limit, since the performed annealing at 125 °C for 4 h may not have led to complete relaxation of the entire GB network in the HPT+AN state. The obtained results support the conclusion made in [17] that a small additional deformation by HPT processing (0.25 turns) after low-temperature annealing introduces an additional dislocation density precisely into the GB structure. Simple estimates show that the introduction of an additional dislocation density of $1.3 \cdot 10^{13}\,\mathrm{m}^{-2}$ (Table 2) into the bulk of grains should raise the alloy resistivity by just $\Delta\rho_{dis} \approx 0.004\,\mathrm{n\Omega \cdot m}$, which is two orders of magnitude smaller than the experimentally obtained resistivity variation $\Delta\rho \approx 0.5\,\mathrm{n\Omega \cdot m}$ (with account for additional contribution $\Delta\rho_{\mathrm{GB}} \approx 0.3\,\mathrm{n\Omega \cdot m}$ due to a slight grain size reduction). Since the contribution of GBs to the overall resistance of metals is small, the influence of the state of grain boundaries on their resistivity was examined at a low temperature (77 K), when the large background contribution of phonons is suppressed [9].

Thus, the variation of resistivity of grain boundaries in the Al–Cu–Zr UFG alloy in their transition from an equilibrium state to a non-equilibrium one, which was induced by a slight additional HPT after low-temperature annealing, has been investigated for the first time. It was demonstrated that additional deformation, which disrupts the equilibrium GB structure by introducing an additional dislocation density, raises the GB resistivity by $\geqslant 20\,\%$.

Conflict of interest

The authors declare that they have no conflict of interest.

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