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Electrical conductivity of alloys containing secondary phase particles

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The work is devoted to the study of electrically conductive properties of metallic materials from the point of view of quantum laws. Methods for describing the influence of various structural factors on their specific electrical resistance are considered. Using the example of the Cu-0.6 wt.% Cr-0.1 wt.% Zr alloy, it is shown that despite the release of alloying elements from the matrix into secondary phase particles as a result of annealing in order to increase electrical conductivity, at the same time the particles themselves can have an increased specific electrical resistance and significantly affect the electrical conductivity of the alloy. This circumstance, in turn, increases the requirements for the composition and volume fractions of the formed precipitates.

Keywords: specific electrical resistance, crystal lattice defects, phonons, secondary phase particles, electron-electron scattering, Cu-0.6 wt.% Cr-0.1 wt.% Zr alloy.

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1. Introduction

Copper is an ore-extracted metal that is anciently used by humans. It has high plasticity, malleability and can be easily drawn and rolled and it is resistant to corrosion. In terms of high conductance, this metal comes after silver. These properties make it and alloys based thereon a material demanded in music industry, minting, medicine, food industry, shipbuilding, in industry when manufacturing bearings, chemical industry parts, military parts, cartridge casings, springs, radiators, heat exchangers, elements of brake systems, in construction, thermal engineering, electrical engineering. The alloys are different in a composition and in properties, accordingly, thereby determining their application in various fields of human activity. But metal materials are especially interesting, since an electric current can flow through them. Pure copper has the highest conductance among industrial metals. However, many of its applications require strength that is higher than strength of pure copper. Then, it is necessary to use copper alloys. A shortcoming of the alloys hardened with a solid solution is that alloying elements increase resistivity. In order to restore conductance and improve strength, a procedure of annealing is applied at lower temperatures than a temperature, at which limit solubility of the elements is achieved. It results in producing alloys with a low content of alloying elements in a matrix due to releasing various precipitates. Released atoms form secondary phase particles that harden the material. Reducing a concentration of the alloying elements in the matrix results in an increase of conductance. At the same time, the alloys hardened with the secondary phase particles are resistant to relaxation under effect of increased temperatures. The particles do not dissolve at high temperatures and, accordingly, the increased strength properties are preserved. They are islands of a various size, composition, structure and morphology and also affect conductance of the alloys. When moving in the matrix, electrons can be scattered at boundaries of these islands. Electrons inside the particles can be scattered on point defects, phonons and electrons that stay within the very particles.

Physical properties of the metals and alloys are determined by quantum laws, whose systematic study as applied to such materials began in the 30s of the last century. A single-electron theory that did not take into account interaction of electrons with each other and a crystal lattice made it possible to describe such properties of the metals as heat capacity, thermal conductivity and conductance [1]. But it was not possible to develop the consistent single-electron theory of the physical properties with taking into account a lattice potential. The single-electron theory was further developed in studies of Lifshitz and his co-workers. They introduced a representation of a gas of weakly interacting quasiparticles, which allowed describing the system of interacting electrons.

In order to describe conductance of the metals in various conditions, it is important to develop a theory of the influence of defects on their conducting properties. An increment of electrical resistance due to point defects was calculated in the studies [2–5]. At the same time, it is necessary to know a type of a scattering potential associated with the defect. A vacancy is usually regarded as a negative charge that is localized in this area of the crystal and equal in magnitude to the charge of an absent ion. At the same time, the vacancy is matched with a positive repulsive potential shaped as a rectangular potential barrier or with a shielded Coulomb potential. An interstitial atom is matched with the negative potential. With more exact

calculation, redistribution of electrons is taken into account, which is induced by a scattering potential, thereby resulting in origination of a self-consistent potential generated by a shielding effect of the redistributed electrons. Full self-consistency when solving the problem by a method of partial waves is achieved as a result of applying a Friedel sum rule [6]. For this purpose, a value of the shielding multiplier or a potential barrier height is varied before fulfilling the Friedel condition. According to the performed calculations, for 1% of the vacancies or interstitial atoms in noble metals a value of resistivity is $1.5\,\mu\Omega\cdot$ cm, which coincides with experimental results [7]. At the same time, it was shown that resistivity did not significantly depend on a type of the scattering potential, if it satisfies the Friedel sum rule [6,8]. It was shown in the studies [9,10] that taking into account relaxation of the atoms around the vacancies insignificantly contributes to resistivity. The interstitial atoms result in higher deformation of the lattice. However, at the same time calculations of an increment of resistivity are not unambiguous. Different results were obtained by different authors [11]. Without taking into account lattice distortion, the calculations result in a value of resistivity induced by the interstitial atoms, which is close to resistivity due to the vacancies.

Resistivity induced by presence of dislocations was estimated for the first time by authors of the study [12]. Elastic expansion of the lattice near a dislocation, inside its core, results in redistribution of electrons, which provides constancy of a Fermi level. As a result, the scattering deformation potential appears. According to the calculations, resistivity due to scattering of electrons on the deformation potential is $\rho_d/N = 0.4\cdot 10^{-26}\,\Omega\cdot\mathrm{m}^3$ (N is a density of dislocations). This result turned to be by two orders less than experimentally obtained values [13,14–17]. When considering additional scattering on anharmonic displacements, the study [5] obtained a value $\rho_d/N = 0.6\cdot 10^{-26}\,\Omega\cdot\mathrm{m}^3$ that slightly differed from the previous result. Divergence with the experimental data was due to the fact that scattering by the dislocation core was not taken into account. Scattering on the dislocation core was calculated by Harrison [18]. He showed that when electrons were scattered on the dislocations resistivity is mainly contributed by the dislocation core, which was presented a hollow negatively-charged prism of a square section. With a value of a square side that is assumed to be equal to an interatomic distance, he obtained the value $\rho_d/N = 5.0\cdot 10^{-26}\,\Omega\cdot\mathrm{m}^3$ in a Thomas-Fermi approximation. The obtained result was about a half of the experimental value obtained in the study [13]. The calculations provided in the studies [19] and [20] result in the values $\rho_d/N = 0.78\cdot 10^{-25}\,\Omega\cdot\mathrm{m}^3$ and $1.9\cdot 10^{-25}\,\Omega\cdot\mathrm{m}^3$, respectively. The results of the experimental studies, which are provided in the publications [14] and [15], showed that $\rho_d/N = (1.6\pm 0.2)\cdot 10^{-25}\,\Omega\cdot\mathrm{m}^3$ and $\rho_d/N = 1.7\cdot 10^{-25}\,\Omega\cdot\mathrm{m}^3$, respectively, while the authors of the studies [16] and [17] obtained the value $\rho_d/N = (1.8-2.3)\cdot 10^{-25}\,\Omega\cdot\mathrm{m}^3$. The experimentally-consistent results are obtained via the formulas of Basinski, Dugdale and Howie [21]:

$$\frac{\rho_d}{N} = \begin{cases} \alpha b^2 V^{2/3} M \Theta_{\mathrm{D}}^2 \rho_i(T)/T, \\ \beta b^2 \rho_L(T_m), \end{cases}$$

where $\rho_i(T)$ is resistivity of a defectless solid metal, $\rho_L(T_m)$ is resistivity of a liquid metal in a melting point, Θ_{D} is the Debye temperature, M is an atomic weight, α and β are constants that are different for various metals, b is a value of the Burgers vector. Usually, the constants α and β are experimentally found for a certain metal, whose value of ρ_d is known. Further, it is assumed that they will be the same for all the metals. When obtaining the formulas, it was believed that resistance due to the dislocation was like phonon resistance of the ideal crystal lattice when thermal oscillations are quite high. When obtaining the second formula, it was assumed that the dislocation was a liquid metal cylinder.

In recent years, there is an increased interest to metals and alloys with high strength and a balanced combination of thermal stability and high conductance due to a growing demand for such materials by electrical engineering and electronics industry. A special emphasis is made on alloys based on Cu and Al. A large volume of studies, primarily experimental ones, is accumulated, which consider various methods of processing metals that contain alloying elements in various concentrations, and provide results of mechanical tests, measurements of conductivity and research of their microstructure. High strength is achieved by deformation of the alloys under conditions of applied high pressures, which includes introduction of defects into their crystal structure, which usually reduce conductance. Varying the material processing temperature makes it possible to achieve an acceptable combination of its physical and mechanical properties [22–28]. Conductance is restored by applying not only thermal, but electric impact on the alloy. For example, the microstructure and conductance of the DC-aged Cu−Cr−Zr alloy were studied to show that the electric current accelerated an alloy aging process. At the same time, its conductance is increased. Variously-shaped chromium-rich phases were detected. It was believed that acceleration of particle release was caused by enhancement of diffusion of dissolved atoms and mobility of the vacancies under DC (direct current) impact [29].

Currently, a disbalance between the experimental and theoretical studies has emerged. Understanding, generalizing, patterning and identifying causes of the experimentally-observed phenomena requires theoretical surveys that are currently absent except for very rare exclusions, but fundamentals for them were laid in the last century yet [30–32].

The present study describes the quantum laws of conductance of the metal materials and presents results of consideration of the conducting properties of the Cu-0.6 wt.% Cr-0.1 wt.% Zr alloy.

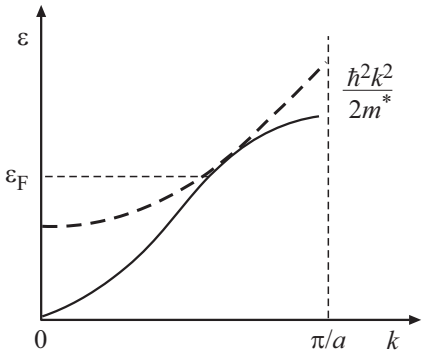

Figure 1. Replacement of the real spectrum $\varepsilon(k)$ with a quadratic spectrum $\hbar^2k^2/2m^*$ [33].

2. Formalism of describing conductance in the metals

The metals are characterized by presence of partially filled Brillouin zones. Only electrons near the Fermi surface can change their states at small temperatures or applied voltages. They determine properties of a metal and are responsible for magnetic susceptibility, heat capacity, thermal conductivity and conductance. Only the density of electron states at the Fermin surface $D(\varepsilon_F)$ (a number of electrons in a unit interval of energies), where ε_F is the Fermi energy, will play an important role. At the same time, it is unimportant how depth states are arranged. Then, it is possible to replace an available complex spectrum (Figure 1) with a simpler one, which will well describe a real initial system at the same time.

In order to equalize $D(\varepsilon_F)$ of the model system with that of the real system, a dynamic effective mass m^* is used, which is defined as a coefficient that relates a group velocity υ with the Fermi momentum p_F.

A conductance electron inside the crystal is a quasi-particle with the effective mass m^*. It has an energy spectrum $\varepsilon(p)$ inside the crystal. The electron quasi-momentum increases linearly in time, unless there are scattering processes. If there were no scattering process, electric current would not appear in the crystals and Bloch oscillations would be observed.

Let us consider conductance of an electron gas with scattering. It is known that conductivity of the metal, which is calculated as a result of solving the kinetic Boltzmann equation and determining a function of distribution of electron and hole excitations [34], is

$$\sigma = \frac{e^2\tau\upsilon_F^2 D(\varepsilon_F)}{3V}, \qquad (1)$$

where τ, υ_F is relaxation time (mean free time) and the group velocity of electrons (holes) on the Fermi surface, respectively [34,35]. If using a notion of the effective mass, then by taking into account a formula for the density of states

$$D(\varepsilon_F) = p_F m^* V/\hbar^3\pi^2$$

the conductivity expression will be written as

$$\sigma = \frac{e^2 n_e \tau}{m^*}, \qquad (2)$$

where e is the charge of the electron, n_e is a concentration of electrons. Unlike the formula (1), here is included the experimentally-determined effective mass of electron m^* and there is no dependence of the magnitude σ on the spectrum.

3. Processes that limit the mean free time of electrons

3.1. Scattering of electrons on point defects

Let us consider a system of N_e electrons — non-interacting fermions with a spin $s = 1/2$, which are contained in a volume V, at the temperature $T = 0$. In order to calculate a relaxation time (an average time, in which an electron impacts vacancies or impurity atoms) $\tau_{e,imp}$, it is necessary to know probability P that in a unit time the electron impacts the vacancy/atom. At the same time, $\tau_{e,imp} = 1/P$.

Let us calculate probability of a transition of the electron from a state with the wave number k into a state k' in the wavenumber space. According to the non-stationary perturbation theory [36], probability of the transition into all the states in a solid angle $d\omega$ in the k-space for a unit time is

$$P_\omega = \frac{2\pi}{\hbar}\left\langle |H'_{k'k}|^2 \right\rangle g_\omega = \frac{2\pi}{\hbar}\left\langle |H'_{k'k}|^2 \right\rangle D(\varepsilon)\,\frac{d\omega}{4\pi}, \qquad (3)$$

where $H'_{k'k}$ is a scattering matrix element, $g_\omega = D(\varepsilon)(d\omega/4\pi)$ is a number of the states in the solid angle $d\omega$. The density of states can be presented as

$$D(\varepsilon) = 2\,\frac{4\pi(\hbar k)^2 d(\hbar k)V}{(2\pi\hbar)^3\upsilon_{gr}dp} = 2\,\frac{4\pi p^2 V}{(2\pi\hbar)^3\upsilon_{gr}}, \qquad (4)$$

where υ_{gr} is the group velocity of electrons.

The vacant area in the crystal is represented as a cube. The vacant area potential U is determined as a ratio of the number of electrons in the sample to the density of states $g(\varepsilon) = D(\varepsilon)$ on the Fermi surface (the Thomas-Fermi approximation): $U = N_e/D(\varepsilon_F) = (2/3)\varepsilon_F$ [18].

Let us calculated the scattering matrix element. Perturbation of the Hamilton operator $\widehat{H}'$ is assumed to be equal to the vacant area potential U. In elastic scattering, the energy of the particle is preserved: $|\pi P| = |\mathbf{p}'|$, but its quasi-momentum is changed. A stationary solution of the Schrödinger equation in the initial state is an incident wave $\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})\exp(i\mathbf{kr})/\sqrt{V}$. In the final state, it is a scattered wave $\psi_{\mathbf{k}'}(\mathbf{r}) = u_{\mathbf{k}'}(\mathbf{r})\exp(i\mathbf{k}'\mathbf{r})/\sqrt{V}$.The wave functions of the stationary state are normalized to the sample volume V. Then

$$H'_{k'k} = \int_\Omega \psi^*_{k'}\widehat{H}'\psi_k d\Omega = \frac{2}{3}\,\frac{\varepsilon_F}{V}\,\frac{\sin|\mathbf{k}'-\mathbf{k}|(l/2)}{|\mathbf{k}'-\mathbf{k}|(l/2)}\,l^3. \qquad (5)$$

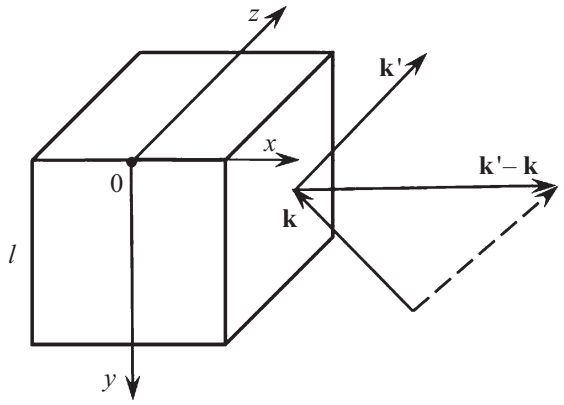

Figure 2. Vacant area in the structure of the crystal material.

The vector $\mathbf{k}' - \mathbf{k}$ is parallel to one of a facet of the cube. Its module is $q = 2k\sin(\Theta/2)$, where Θ is an angle between the vectors $\mathbf{k}'$and $\mathbf{k}$. An interaction area volume Ω is l^3 (Figure 2).

By calculating probability of scattering P_ω per unit time into the solid angle $d\omega = 4\pi\sin^2(\Theta/2) = 4\pi(q/2k)^2$ in the momentum space, one can also determine probability of scattering P in any direction per unit time:

$$P_\omega = \frac{2\pi}{\hbar}\left\langle |H'_{k'k}|^2\right\rangle g_\omega = \frac{2k^4\hbar^2}{9Vm^{*2}}\frac{l^4}{\pi\upsilon_{\rm gr}}\sin^2\left(\frac{ql}{2}\right), \quad (6)$$

$$P = \frac{2k^4\hbar^2}{9Vm^{*2}}\frac{l^4}{\pi\upsilon_{\rm gr}}\left(\frac{1}{kl}\int\limits_0^{kl}\sin^2\left(\frac{ql}{2}\right)d\left(\frac{ql}{2}\right)\right)$$
$$= \frac{k^3\hbar l^4}{9Vm^*\pi}\left[1 - \frac{\sin 2kl}{2kl}\right]. \quad (7)$$

Probability of scattering per unit time P_N in the sample with $N_\upsilon = C_{\upsilon V}V = C_{\upsilon a}n_a V$ vacancies/atoms, where n_a is a volume density of the atoms in the sample, $C_{\upsilon V}$ and $C_{\upsilon a}$ are volume and atom concentrations of the vacancies/inclusion atoms, respectively, is

$$P_N = \frac{k^3\hbar l^4 C_{\upsilon V}}{9m^*\pi}\left[1 - \frac{\sin 2kl}{2kl}\right]$$
$$= \frac{k^3\hbar l^4 C_{\upsilon a}n_a}{9m^*\pi}\left[1 - \frac{\sin 2kl}{2kl}\right]. \quad (8)$$

Then, a contribution by the vacancies/atoms to resistivity will be determined by the expression:

$$\rho_\upsilon = \frac{m^*}{n_e e^2}\frac{1}{\tau_{\rm e,imp}} = \frac{k^3\hbar l^4 n_a C_{\upsilon a}}{9e^2\pi n_{\rm e}}\left[1 - \frac{\sin 2kl}{2kl}\right]. \quad (9)$$

According to the formula (9), the contribution by the vacancies to copper resistivity is $\approx 1.4C_{\upsilon a}\,\mu\Omega\cdot$m or $1.4\,\mu\Omega\cdot$cm/at.%, when assuming that the interaction area volume $l^3 = a^3/4$, where a is a lattice parameter, for Cu $a = 3.615$ Å. The obtained estimate agrees in an order of the magnitude with known theoretical and experimental estimates. The studies [37] and [38] have obtained the values $1.7\,\mu\Omega\cdot$cm/at.% and $1.64\,\mu\Omega\cdot$cm/at.%, respectively. Let us note that the obtained result coincides in an order of the magnitude with calculated values of resistivity induced by impurity interstitial or substitutional atoms [39]. The value of ρ_υ, which is obtained using the potential U [18], depends on a size of the interaction area l. Therefore, the formula (9) can be also used for evaluating this parameter.

3.2. Scattering of electrons on secondary phase particles

The distance transmitted by an electron at the velocity $\upsilon_{\rm gr} = \upsilon_{\rm F}$ from one particle to another for the time $\tau_{{\rm pl}(s)}$ is $\lambda = \upsilon_{\rm F}\tau_{{\rm pl}(s)}$. At the same time, the increase of resistivity by scattering on the particles can be written as

$$\rho_{{\rm e,pl}(s)} = \frac{m^*}{n_{\rm e}e^2}\frac{1}{\tau_{{\rm pl}(s)}} = \frac{m^*}{n_{\rm e}e^2}\frac{\upsilon_{\rm F}}{\lambda}, \quad (10)$$

$$\lambda = \frac{1}{n_{{\rm pl}(s)}\pi r_a^2}, \quad (11)$$

where $n_{{\rm pl}(s)}$ is a density of large (small) secondary phase particles, $n_{\rm e}$ is a density of electrons in the matrix, πr_a^2 is a section of scattering of the inclusion atom. The electron is scattered on an atom located on the particle surface. The density of the particles is $n_{{\rm pl}(s)} = N_{{\rm pl}(s)}/V$, where $N_{{\rm pl}(s)}$ is a number of the particles in the sample, V is a volume of the sample. If the volume of one particle is $V_{{\rm pl}(s)}$, then the volume fraction of the particles in the sample will be $f_{{\rm pl}(s)} = N_{{\rm pl}(s)}V_{{\rm pl}(s)}/V$. Accordingly, taking into account the formula (11), the expression (10) will be rewritten as:

$$\rho_{{\rm e,pl}(s)} = \frac{m^*}{n_{\rm e}e^2}\frac{1}{\tau_{{\rm pl}(s)}} = \frac{m^*}{n_{\rm e}e^2}\frac{\upsilon_{\rm F}f_{{\rm pl}(s)}\pi r_a^2}{V_{{\rm pl}(s)}}. \quad (12)$$

The electron can be scattered on any atom on the particle surface. If the number of the atoms on the scattering surface is $N_{\rm at}$, then the increase of resistivity due to scattering on the secondary phase particle will be

$$\rho_{{\rm e,pl}(s)} = \frac{m^*}{n_{\rm e}e^2}\frac{\upsilon_{\rm F}f_{{\rm pl}(s)}\pi r_a^2}{V_{{\rm pl}(s)}}N_{\rm at} \approx \frac{m^*}{n_{\rm e}e^2}\frac{\upsilon_{\rm F}f_{{\rm pl}(s)}}{V_{{\rm pl}(s)}}S_{{\rm pl}(s)}, \quad (13)$$

$\upsilon_{\rm F} = \hbar k_{\rm F}/m^*$, $\pi r_a^2 N_{\rm at} \approx S_{{\rm pl}(s)}$ — is an area of the scattering surface.

4. Processes that limit the mean free time of electrons in the Cu-0.6 wt.% Cr-0.1 wt.% Zr alloy

4.1. Scattering of electrons in internal areas of the secondary phase particles

Let us consider scattering on the point defects as exemplified by the Cu-0.6 wt.% Cr-0.1 wt.% Zr alloy, which includes large and small secondary phase particles with

Table 1. Atom concentration of the alloying atoms C_{ai}, the concentration of electrons in the particles n_{ei}, the concentration of atoms in the particles n_{ai}, volume fractions of large $f_{\mathrm{secl}i}$ and small $f_{\mathrm{secs}i}$ particles of phases in the coarse-crystalline state of the Cu-0.6 wt.% Cr-0.1 wt.% Zr alloy [40], the phase number is i

Phases	C_{ai}	n_{ei}, m^{-3}	n_{ai}, m^{-3}	$f_{\mathrm{secs}i}$	$f_{\mathrm{secl}i}$	i
Cr	–	$8.33 \cdot 10^{28}$	$8.33 \cdot 10^{28}$	$1.0 \cdot 10^{-4}$	$5.8 \cdot 10^{-3}$	1
$CuCr_4$	0.800	$8.36 \cdot 10^{28}$	$8.36 \cdot 10^{28}$	$1.3 \cdot 10^{-4}$	$5.2 \cdot 10^{-4}$	2
CuCr	0.500	$8.40 \cdot 10^{28}$	$8.40 \cdot 10^{28}$	$3.1 \cdot 10^{-4}$	$1.3 \cdot 10^{-3}$	3
$Cu_{51}Zr_{14}$	0.215	$7.00 \cdot 10^{28}$	$7.00 \cdot 10^{28}$	$4.6 \cdot 10^{-4}$	$1.9 \cdot 10^{-3}$	4
Cu_5Zr	0.167	$7.28 \cdot 10^{28}$	$7.28 \cdot 10^{28}$	$3.6 \cdot 10^{-4}$	$1.5 \cdot 10^{-3}$	5

respective volume fractions $f_{\mathrm{sec}1i}$ and $f_{\mathrm{sec}si}$ (Table 1) [40]. In the phases $i = 1, 2, 3, 4, 5$, if assuming that the Cu, Cr and Zr atoms donate one electron each, the concentration of electrons in the $Cu_XCr(Zr)_Y$ particles will be

$$n_{ei} = \frac{X+Y}{X\Omega_{\mathrm{Cu}} + Y\Omega_{\mathrm{Cr}}(\Omega_{\mathrm{Zr}})}, \ i = 1, 2, 3, 4, 5, \qquad (14)$$

where $\Omega_{\mathrm{Cu}}, \Omega_{\mathrm{Zr}}, \Omega_{\mathrm{Cr}}$ — are volumes of the Cu, Zr and Cr atoms, respectively. $\Omega_{\mathrm{Cu}} = \mu_{\mathrm{Cu}} m_0/\rho_{\mathrm{densCu}} \approx 11.82 \cdot 10^{-30}\,\mathrm{m}^3$, $\Omega_{\mathrm{Zr}} = \mu_{\mathrm{Zr}} m_0/\rho_{\mathrm{densZr}} \approx 23.28 \cdot 10^{-30}\,\mathrm{m}^3$, $\Omega_{\mathrm{Cr}} = \mu_{\mathrm{Cr}} m_0/\rho_{\mathrm{densCr}} \approx 12.00 \cdot 10^{-30}\,\mathrm{m}^3$; ρ_{densCr}, ρ_{densCu}, ρ_{densZr} — are densities of Cr, Cu and Zr, respectively; m_0 is an atomic mass unit. Then, according to the formula (9) we obtain

$$\rho_{\mathrm{e,at}i} = \frac{k_{\mathrm{F}i}^3 \hbar l^4 n_{ai} C_{ai}}{9e^2\pi n_{ei}} \left[1 - \frac{\sin 2k_{\mathrm{F}i} l}{2k_{\mathrm{F}i} l}\right]. \qquad (15)$$

C_{ai} — is a concentration of the alloying atoms Cr ($i = 2, 3$) or Zr ($i = 4, 5$): $C_{ai} = Y/(X+Y)$, $l^3 = a^3/4$. The concentration of the atoms in the particle is $n_{ai} = (X+Y)/(X\Omega_{\mathrm{Cu}} + Y\Omega_{\mathrm{Cr}}(\Omega_{\mathrm{Zr}}))$ (Table 1). The wave number on the Fermi surface is calculated for each particle according to the formula $k_{\mathrm{F}i} = (3\pi^2 n_{ei})^{1/3}$. The calculated values of $\rho_{\mathrm{e,at}i}$ are presented in Table 2. They are determined by a concentration of inclusions C_{ai} in the particles (Table 1): $\rho_{\mathrm{e,at}i} \propto C_{ai}$.

A contribution by electron-electron scattering to resistivity is induced by overshooting processes. In case of interaction of electron excitations, a characteristic relaxation time for the spherical Fermi surface is inversely proportional to a square of the temperature T [34,35], or $\tau_{\mathrm{e,e}}^{-1} \approx T^2/\hbar E_{\mathrm{at}}$, where E_{at} is an atomic scale energy. Within the intermediate temperatures, $T \ll \Theta_{\mathrm{D}}$, in the metals with the open Fermi surface, the electron-electron contribution to resistivity is less than the phonon contribution until reaching the temperature $T^* \approx \Theta_{\mathrm{D}}\sqrt{\Theta_{\mathrm{D}}/E_{\mathrm{at}}}$. This scattering mechanism is manifested only at low temperatures in very pure metals. The electron-phonon contribution turns out to be more significant. The formula (2) includes the effective mass of electron, which is only true for the quadratic law of dispersion. In the metals, all the states up to the Fermi level ε_{F} are filled. The first, or next Brillouin zone is partially filled. In order to describe all the properties of a gas of electrons in the metal, it can be neglected that electrons can have a certain complex spectrum that is different from a quadratic parabola for the ideal Fermi gas. It can be replaced with a parabolic spectrum: $\hbar^2 k^2/2m^*$, therefore, conductance will be described in the same way as in the case of the Fermi gas.

Scattering is possible only for electrons that are near the Fermi surface smeared by thermal motion. As noted above, it is generally possible to introduce the dynamic effective mass as $m^* v|_{\varepsilon} = p_{\mathrm{F}}$, which includes properties of the spectrum.

The quasi-momentum conservation law in the process of electron-electron scattering is written as $\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}_1' + \mathbf{k}_2' + \mathbf{G}$, where $\mathbf{G}$ — is a reciprocal lattice vector. In order to realize this process, the condition $4k_{\mathrm{F}} > G$ shall be fulfilled, where $k_{\mathrm{F}} = (3\pi^2 n_{\mathrm{e}})^{1/3}$. For example, in case of the simple cubic lattice the minimum value of the vector $\mathbf{G}$ is $G = 2\pi/a$, a is a lattice parameter. If the Fermi surface is close to a boundary of the Brillouin zone, then it will favor the overshooting process. The performed estimates of a condition of a capability of the overshooting processes in the present phases with taking into account the calculated values of the electron concentration (Table 1) show that they can be realized.

Electron-electron scattering exceeds resistivity in the phases i by the value

$$\rho_{\mathrm{e},ei} = \frac{m^*}{n_{ei}e^2}\frac{1}{\tau_{\mathrm{e},ei}} = \frac{m^*}{n_{ei}e^2}\frac{T^2}{\hbar\varepsilon_{\mathrm{F}i}}, \qquad (16)$$

where $\varepsilon_{\mathrm{F}i} = \hbar^2 k_{\mathrm{F}i}^2/2m^*$. The calculated values of $\rho_{\mathrm{e},ei}$ are summarized in Table 2. This contribution to resistivity increases with a decrease of the electron concentration n_{ei} in the particles: $\rho_{\mathrm{e},ei} \propto n_{ei}^{-5/3}$.

Taking into account that the phonon contribution to resistivity of the metals with the open Fermi surface within the intermediate temperatures (the low-temperature conductance is determined by scattering on the impurities), when $T \ll \Theta_{\mathrm{D}}$, behaves as $\rho \propto T^5$ [34,35]: $(\tau_{\mathrm{e,ph}}^U)^{-1} \approx T^5/\hbar\Theta_{\mathrm{D}}^4$, we will evaluate the increment of resistivity in the particles of the secondary phases $i = 2, 3, 4, 5$ based on the formula

$$\rho_{\mathrm{e,ph}i} = \frac{m^*}{n_{ei}e^2}(\tau_{\mathrm{e,ph}}^U)^{-1} \approx \frac{m^*}{n_{ei}e^2}\frac{T^5}{\hbar\Theta_{\mathrm{D}}^4}. \qquad (17)$$

The known value of $\rho_{\mathrm{e,ph}1}$ has been used for the Cr particles [41]. In the said phases, the Debye temperature was assumed to be equal to the Debye temperature in

Table 2. Phase number i, the increase of resistivity in the phases i as a result of scattering of electrons on the atoms of the alloying elements $\rho_{e,ati}$, the phonons $\rho_{e,phi}$, the small secondary phase particles$\rho_{e,psi}$, the large secondary phase particles $\rho_{e,pli}$ and on the electrons $\rho_{e,ei}$

Phases	$\rho_{e,ati}$, $\Omega \cdot m$	$\rho_{e,phi}$, $\Omega \cdot m$	$\rho_{e,psi}$, $\Omega \cdot m$	$\rho_{e,pli}$, $\Omega \cdot m$	$\rho_{e,ei}$, $\Omega \cdot m$	i
Cr	0.0	$2.70 \cdot 10^{-8}$	$7.75 \cdot 10^{-10}$	$5.70 \cdot 10^{-12}$	$1.11 \cdot 10^{-10}$	1
$CuCr_4$	$7.91 \cdot 10^{-7}$	$1.67 \cdot 10^{-8}$	$9.95 \cdot 10^{-11}$	$1.39 \cdot 10^{-12}$	$1.11 \cdot 10^{-10}$	2
CuCr	$4.96 \cdot 10^{-7}$	$1.67 \cdot 10^{-8}$	$2.58 \cdot 10^{-10}$	$3.71 \cdot 10^{-12}$	$1.10 \cdot 10^{-10}$	3
$Cu_{51}Zr_{14}$	$2.38 \cdot 10^{-7}$	$2.00 \cdot 10^{-8}$	$3.45 \cdot 10^{-10}$	$4.61 \cdot 10^{-12}$	$1.49 \cdot 10^{-10}$	4
Cu_5Zr	$1.89 \cdot 10^{-7}$	$1.92 \cdot 10^{-8}$	$1.36 \cdot 10^{-10}$	$4.11 \cdot 10^{-12}$	$1.40 \cdot 10^{-10}$	5

Table 3. Areas of the scattering surfaces of the small Spsi and large Spli particles and their volumes V_{psi}, V_{pli}, respectively, the phase number i

Phases	S_{psi}, m^2	S_{pli}, m^2	V_{psi}, m^3	V_{pli}, m^3	i
Cr	$28.3 \cdot 10^{-18}$	$6.3 \cdot 10^{-12}$	$25.1 \cdot 10^{-27}$	$4.2 \cdot 10^{-18}$	1
$CuCr_4$	$20.2 \cdot 10^{-18}$	$1.5 \cdot 10^{-12}$	$16.8 \cdot 10^{-27}$	$3.8 \cdot 10^{-19}$	2
CuCr	$62.8 \cdot 10^{-18}$	$4.08 \cdot 10^{-12}$	$50.3 \cdot 10^{-27}$	$9.4 \cdot 10-^{19}$	3
$Cu_{51}Zr_{14}$	$72.0 \cdot 10^{-18}$	$4.64 \cdot 10^{-12}$	$64.0 \cdot 10^{-27}$	$1.3 \cdot 10^{-18}$	4
Cu_5Zr	$62.8 \cdot 10^{-18}$	$4.2 \cdot 10^{-12}$	$50.3 \cdot 10^{-27}$	$1.0 \cdot 10^{-18}$	5

copper: $\Theta_D \approx 315\,K$. The calculated values of $\rho_{e,phi}$ are provided in Table 2. For Cu, the formula (17) results in the value $\rho_{e,phCu} = 1.65 \cdot 10^{-8}\,\Omega \cdot m$. The phonon contribution to resistivity decreases with an increase of the electron concentration n_{ei} (Table 1): $\rho_{e,phi} \propto n_{ei}^{-1}$.

Resistivity of the particles is significantly affected by scattering of electrons on the inclusion atoms. A contribution by scattering on phonons turns out to be smaller by one order. At the same time, the contribution by electron-electron scattering is $\sim (0.01-0.07)\,\%$ of the contribution by the inclusion atoms.

4.2. Resistivity of the alloy Cu-0.6 wt.% Cr-0.1 wt.% Zr

The increase of resistivity related to presence of precipitates is induced by scattering of electrons that are in the copper matrix of the Cu-0.6 wt.% Cr-0.1 wt.% Zr alloy, on the particle surfaces, as well as by scattering of electrons that are inside the particles, on the point defects, phonons and electrons that are inside the very particles.

The phonon contribution to resistivity is induced by scattering of electrons on phonons in the copper matrix as well as scattering of electrons inside the particles:

$$\rho_{e,ph} = \left(1 - \sum_{i=1}^{5}(f_{secsi} + f_{secli})\right)\rho_{e,phCu} + \sum_{i=1}^{5}(f_{secsi} + f_{secli})\rho_{e,phi}. \quad (18)$$

During the calculations, the temperature was expressed in Kelvins:

$$\rho_{e,phi} \approx m^* k_B T^5/(n_{ei} e^2 \hbar \Theta_D^4),$$

where k_B is the Boltzmann constant. It was estimated when $T = 20\,^\circ C$.

The contribution by point defects that are in the matrix and in the secondary phase particles, to resistivity of the alloy is

$$\rho_{e,at} = \left(1 - \sum_{i=1}^{5}(f_{secsi} + f_{secli})\right)\rho_{e,atCr} + \sum_{i=1}^{5}(f_{secsi} + f_{secli})\rho_{e,ati}, \quad (19)$$

where, according to the formula (15), the increment of resistivity due to scattering of electrons on the Cr atoms dissolved in the matrix is $\rho_{e,atCr} = 2.44 \cdot 10^{-10}\,\Omega \cdot m$ when $C_{aCr} \approx 2.442 \cdot 10^{-4}$ [40].

The increment of resistivity as a result of scattering on the particle of the secondary phase i, which is calculated according to the formula (13):

$$\rho_{e,pl(s)i} = \frac{m^*}{n_e e^2}\frac{\upsilon_F f_{pl(s)i}}{V_{pl(s)i}} S_{pl(s)i}, \quad (20)$$

at the known values of the surface of the scattering area in the small and large particles S_{psi}, S_{pli}, respectively, as well as at the known values of the volumes of the small and large particles V_{psi}, V_{pli}, respectively, (Table 3) results in values shown in Table 2. At the same time, the increment of resistivity by scattering of electrons on the secondary phase particles will be determined as

$$\rho_{e,p} = \sum_{i=1}^{5}\rho_{e,pli} + \sum_{i=1}^{5}\rho_{e,psi}.$$

Table 4. Model value of resistivity ρ of the Cu-0.6 wt.% Cr-0.1 wt.% Zr alloy and its components induced by scattering of electrons on the structural defects, the model δ and the experimental value of conductance of the δ_{exp} alloy as expressed in % IACS

Factors increasing resistivity	Increment of resistivity
ρ_{ep}, $\Omega \cdot \text{m}$	$9.4 \cdot 10^{-10}$
$\rho_{\text{e,ph}}$, $\Omega \cdot \text{m}$	$1.7 \cdot 10^{-8}$
$\rho_{\text{e,at}}$, $\Omega \cdot \text{m}$	$2.5 \cdot 10^{-9}$
$\rho_{\text{e,e}}$, $\Omega \cdot \text{m}$	$1.1 \cdot 10^{-10}$
$\rho_{\text{e,disl}}$, $\Omega \cdot \text{m}$	$1.1 \cdot 10^{-12}$
$\rho_{\text{e,gb}}$, $\Omega \cdot \text{m}$	$2.2 \cdot 10^{-12}$
ρ, $10^{-8}\,\Omega \cdot \text{m}$	$2.06 \cdot 10^{-8}$
δ, % IACS	83.7
δ_{exp}, % IACS	84.0 ± 0.6

The calculated values of $\rho_{\text{e,at}}$, $\rho_{\text{e,ph}}$, $\rho_{\text{e,p}}$ are provided in Table 4.

The contribution to resistivity of the alloy by electron-electron scattering, which is calculated according to the formula,

$$\rho_{\text{e,e}} = \left(1 - \sum_{i=1}^{5}(f_{\text{secs}i} + f_{\text{secl}i})\right)\rho_{\text{e,eCu}} + \sum_{i=1}^{5}(f_{\text{secs}i} + f_{\text{secl}i})\rho_{\text{e,e}i}, \qquad (21)$$

is shown in Table 4. At the same time, the increment of resistivity $\rho_{\text{e,eCu}}$ in the copper matrix, which is calculated according to the formula (16), where the density of electrons is $8.46 \cdot 10^{28}\,\text{m}^{-3}$ according to the formula (14): $n_{ei} = 1/\Omega_{\text{Cu}}$, results in the value $1.09 \cdot 10^{-10}\,\Omega \cdot \text{m}$.

Table 4 shows values of the increment of resistivity, which are induced by scattering of electrons on the dislocations ρ_{disl} and the grain boundaries ρ_{gb}, which were estimated in the study [40]. The estimate calculations based on the presented conductance model make it possible to obtain values of resistivity of the alloy in question, which are experimentally consistent by an order of the magnitude.

Resistivity of the alloy is primarily determined by scattering of electrons on phonons $\rho_{\text{e,ph}}$. Scattering on the inclusion atoms also makes a significant contribution, which is $\rho_{\text{e,at}}$. The increment of resistivity induced by scattering on the small particles exceeds that for the large particles by two orders (Table 2). They exactly determine a contribution by the secondary phase particles ρ_{ep} to resistivity of the alloy. Some influence is also made by electron-electron scattering, but its contribution is by two orders less than the phonon contribution. The contribution by the dislocations and the grain boundaries is negligible.

5. Conclusion

The metal materials are objects that are difficult for description. Their properties are determined by the quantum laws. Based on the theoretically-revealed laws, we have analyzed the influence of the secondary phase particles on resistivity of the Cu-0.6 wt.% Cr-0.1 wt.% Zr alloy in its initial coarse-crystalline state. The sample structure included the dissolved Cr atoms, the secondary phase particles of the different composition, of the different morphology and size, and dislocations and grain boundaries. The resistivity of the alloy is determined by scattering of electrons on electrons and phonons, on the said structure elements as well as by scattering of electrons on the alloying atoms, on electrons and phonons inside the particles themselves. Resistivity of the alloy and the increments of resistivity due to the structural factors present in the alloy were estimated to show agreement with the known experimental data. According to the obtained data, the contribution by electron-electron scattering in the particles that are present in the alloy is by two orders less than in the copper matrix and has a value of $\sim 1.5 \cdot 10^{-12}\,\Omega \cdot \text{m}$. Scattering on phonons increases resistivity in them by $\sim 2.8 \cdot 10^{-10}\,\Omega \cdot \text{m}$, which is by two orders less than that in the matrix. However, the contribution by scattering on the alloying atoms inside the particles turned out to be by one order more and was $\sim 2.2 \cdot 10^{-9}\,\Omega \cdot \text{m}$. At the same time, scattering of electrons on the released particles increased resistivity by $\sim 9.4 \cdot 10^{-10}\,\Omega \cdot \text{m}$. As a result, the secondary phase particles increased resistivity of the alloy by $\sim 17\%$. The Cr atoms dissolved in the matrix increase resistivity by $\sim 2.4 \cdot 10^{-10}\,\Omega \cdot \text{m}$, so do the secondary phase particles totally by $\sim 3.4 \cdot 10^{-9}\,\Omega \cdot \text{m}$. Therefore, cleaning the matrix from the impurity atoms as a result of annealing at the temperatures below a temperature of limit solubility of the alloying elements in order to reduce resistance of the alloy is accompanied by formation of precipitates, which can noticeably contribute to its resistivity. It is important to control a composition and volume fractions of the secondary phase particles in order to achieve the required best result.

Conflict of interest

The authors declare that they have no conflict of interest.

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