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PHYSICAL CHEMISTRY

Electrical Resistivity of Cu–Zr Melts

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Abstract—For the first time, the electrical resistivity of liquid $Cu_{64.5}Zr_{35.5}$, $Cu_{50}Zr_{50}$, and $Cu_{33.3}Zr_{66.7}$ alloys at temperatures up to 1600 K has been measured by the contactless method in a rotating magnetic field. The measurements were taken during cooling in a helium atmosphere with a purity of 99.995%. The error of the electrical resistivity determination did not exceed 5%. It has been found that the electrical resistivity of liquid $Cu_{64.5}Zr_{35.5}$, $Cu_{50}Zr_{50}$, and $Cu_{33.3}Zr_{66.7}$ alloys decreases linearly with increasing temperature, while it increases with temperature for liquid copper and zirconium. The concentration dependences of the electrical resistivity and its temperature coefficient have a maximum at 55 at % and a minimum at about 60 at % Zr, respectively. These concentration dependences are similar to the dependences obtained for amorphous alloys and are explained in the framework of the Ziman theory.

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The Cu–Zr system is among a few binary metallic systems in which bulk amorphous samples have been obtained. It has been demonstrated that amorphous films in the Cu–Zr system can be produced in a wide range of compositions (30–70 at % Zr) [1], whereas bulk amorphous ingots up to 2 mm in diameter can be obtained in only narrow concentration ranges (near 36 and 50 at % Zr) [2].

For elucidating the nature of amorphization, it is necessary to study the physicochemical properties of alloys in this system not only in amorphous, but also in liquid and crystalline states. The thermophysical and electrical properties of the crystalline Cu–Zr alloys have been measured [3–5]. In the liquid state, the thermophysical properties of Cu–Zr alloys have been almost unexplored. This is primarily due to the complexity of the high-temperature experiment, especially with zirconium alloys with high chemical activity and aggressiveness. It should be noted that a few studies of the melts of this system [5] were carried out mainly by the levitation method in the pulsed mode. In this case, the dynamically obtained experimental data are far from equilibrium values, which is completely unacceptable for systems with large relaxation times, such as these glass-forming alloys.

In the present study, we measured, for the first time, the electrical resistivity of the $Cu_{64.5}Zr_{35.5}$, $Cu_{50}Zr_{50}$, and $Cu_{33.3}Zr_{66.7}$ alloys in the liquid state. The selection of compositions is first of all caused by that the first two have the highest amorphization ability, and the last two correspond to the compositions of intermetallic compounds.

Samples were synthesized by arc melting of a mixture of pure zirconium (99.95%) and copper (99.99%) in an argon atmosphere. They were remelted several times to reduce their composition heterogeneity.

The electrical resistivity was measured by the rotating magnetic field method on an original setup. The angle of rotation of the sample φ in a rotating magnetic field depends on its electrical resistance, size, the field strength and frequency, and the elasticity coefficient of a wire. In the relative variant of the method, the electrical resistivity ρ was calculated by the formula:

$$\rho = \rho_0 \frac{\varphi_0}{\varphi}\left(\frac{I}{I_0}\right)^2\left(\frac{V}{V_0}\right)^{5/3}, \tag{1}$$

where I is the current in the stator coil creating a rotating magnetic field, and V is the sample volume. The subscript "zero" refers to the reference sample (tungsten). The measurements were carried out in zirconia crucibles in an atmosphere of helium (purity of 99.995 vol %). The error of determination of electrical resistance of liquid alloys does not exceed 5%. The measurements were carried out during cooling from 1600 K to the alloy crystallization temperature at a rate of 5 K/min. To calculate V in Eq. (1), data on the density of Cu–Zr melts were used [6].

Figure 1 shows the temperature dependences of electrical resistivity $\rho(T)$ of $Cu_{64.5}Zr_{35.5}$, $Cu_{50}Zr_{50}$, and $Cu_{33.3}Zr_{66.7}$ melts. As is seen, the electrical resistance of these melts linearly decreases with increasing temperature. Conversely, in liquid copper [7] and zirco-

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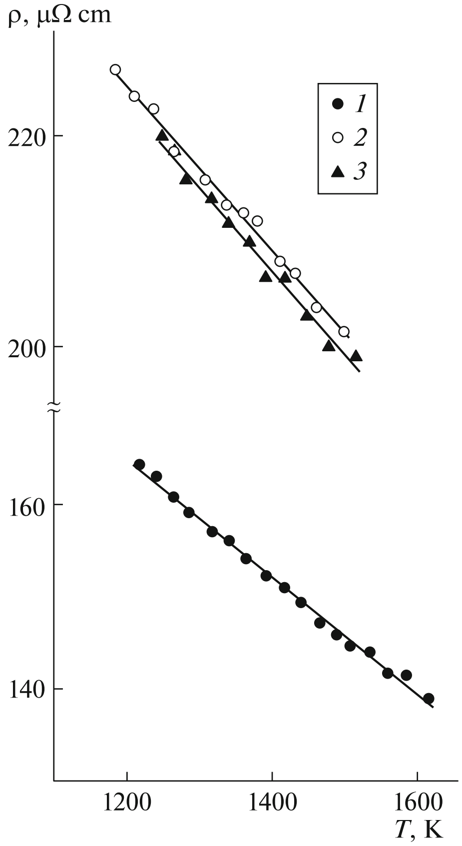

Fig. 1. Temperature dependences of the electrical resistivity of the (*1*) $Cu_{64.5}Zr_{35.5}$, (*2*) $Cu_{50}Zr_{50}$, and (*3*) $Cu_{33.3}Zr_{66.7}$ melts.

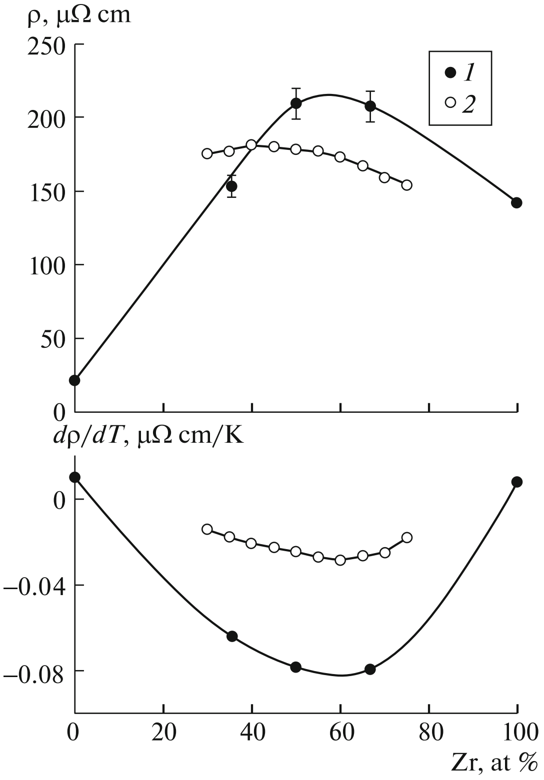

Fig. 2. Electrical resistivity and its temperature coefficient vs. zirconium content in the Cu–Zr alloys (*1*) in the liquid state at 1400 K and (*2*) in the amorphous state at 290 K [9]. For liquid copper and zirconium, data were taken from [7] and [8], respectively.

nium [8], like in other normal liquid metals, electrical resistance increases with temperature.

The concentration dependences of electrical resistance ρ(*x*) of the melts and temperature resistance coefficient (TRC) have a maximum at 55 at % and a minimum at about 60 at % Zr, respectively (Fig. 2). For comparison, Fig. 2 shows the concentration dependences of electrical resistance and TRC of amorphous Cu–Zr alloys at 290 K [9]. It follows from Fig. 2 that the concentration dependences of electrical resistance and TRC in the liquid state are analogous to the dependences obtained for amorphous alloys. The ρ(*x*) maximum in the liquid state as compared with the amorphous alloy is 16% higher and is displaced by 15 at % to a zirconium-rich region. The positions of the minima on the concentration dependence of TRC in both states coincide, but in the liquid state, the TRC magnitude is approximately three times higher than in the amorphous state.

The concentration dependences of electrical resistance and TRC of liquid (or amorphous) alloys can be explained in the framework of the Ziman theory [10]. For liquid and amorphous metal alloys based on transition metals, the *d*-phase shifts near the Fermi level of a transition metal account for the largest contribution to the electrical resistance. Therefore, three partial structure factors can be replaced by one partial structure factor for a transition metal, and the resistivity can be described by the equation [11]

$$\rho \propto \frac{\Gamma^2}{\Gamma^2 + 4(E_d - E_F)^2} S(2k_F), \tag{2}$$

where Γ and E_d are the *d*-state scattering resonance width and energy, E_F is the Fermi energy, and k_F is the Fermi wave vector calculated by the equation

$$k_F^3 = \frac{3\pi^2 \bar{Z} N_A d}{\bar{A}}, \tag{3}$$

where N_A is the Avogadro number, *d* is the density of an alloy, $\bar{A} = x_1A_1 + x_2A_2$, $\bar{Z} = x_1Z_1 + x_2Z_2$, x_i, A_i, and Z_i are the concentration, atomic mass, and effective valence of the *i*th component in the alloy. It follows from Eq. (2) that the electrical resistance of liquid (or amorphous) alloys based on transition metals is dominated by two contributions depending on the resonance scattering and the partial structure factor on the Fermi surface $S(2k_F)$. As compared with the structure factor, the resonance contribution slightly changes

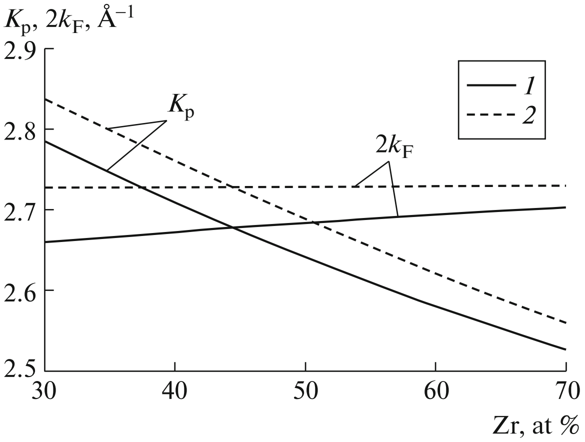

Fig. 3. Fermi wave vector k_F and the position of the first peak of structure factor K_p vs. Zr concentration in (*1*) liquid and (*2*) amorphous Cu–Zr alloys.

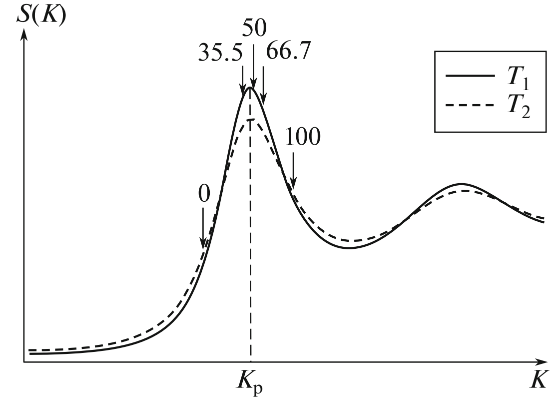

Fig. 4. Schematic presentation of structure factor $S(K)$ of Cu–Zr alloys for two temperatures T_1 and T_2 ($T_2 > T_1$). The arrows show the $2k_F$ position for the alloy, the numbers near the arrows denote the zirconium concentration in the alloy, and K_p corresponds to the position of the first $S(K)$ peak.

with temperature and composition, and it can be neglected in analysis of the temperature and concentration dependences of electrical resistivity.

According to the Ziman theory [10], the electrical resistance and its temperature coefficient for liquid and amorphous alloys depend on the $2k_F$ position with respect to the position of the first peak of the structure factor K_p. For calculation of k_F, we used the data on the density of liquid [6] and amorphous [12] Cu–Zr alloys. The effective valence of copper and zirconium was taken to be, respectively, 1 and 2, as in [13]. The K_p values for liquid and amorphous Cu–Zr alloys were taken from [14]. The concentration dependences of k_F and K_p for liquid and amorphous Cu–Zr alloys are shown in Fig. 3. It is seen that the intersection point of $2k_F$ and K_p in both the liquid and amorphous states corresponds to the composition with 45 at % Zr. This point is consistent well with the position of the maximum on the concentration dependence of electrical resistance of liquid and amorphous Cu–Zr alloys. Specific behavior of the electrical resistivity and TRC is clearly shown in Fig. 4. According to this figure, at constant temperature, the increase in the electron concentration caused by the addition of zirconium with the higher valence leads to the rapid increase in k_F and in the electrical resistance to the maximal value at $2k_F \approx K_p$; when $2k_F > K_p$, ρ decreases.

With increasing temperature, the height of the first peak decreases, and its width increases (Fig. 4). Therefore, in the alloys for which $2k_F \approx K_p$, the $S(2k_F)$ value decreases with increasing temperature, and the TRC becomes negative. In alloys rich in copper or zirconium, $S(2k_F)$ increases with temperature, and TRC is positive.

At $2k_F \approx K_p$, the TRC can be expressed through the temperature dependence of the first peak of the structure factor:

$$\frac{d\rho}{dT} \propto \frac{dS(K_p)}{dT}. \tag{4}$$

Equation (4) allows us to explain the threefold excess of the TRC of the liquid Cu–Zr alloys over the TRC of the amorphous alloys. According to X-ray diffraction studies [15], the $dS(K_p)/dT$ value for the $Cu_{50}Zr_{50}$ alloy is -6.8×10^{-4} K^{-1} in the liquid and -2.3×10^{-4} K^{-1} in the amorphous states; i.e., $dS(K_p)/dT$ in the liquid state is three times higher than in the amourphous state.

Thus, it has been shown that the electrical resistance of liquid $Cu_{64.5}Zr_{35.5}$, $Cu_{50}Zr_{50}$, and $Cu_{33.3}Zr_{66.7}$ alloys linearly decreases with increasing temperature, whereas in the liquid copper and zirconium, it increases with temperature. The concentration dependences of the electrical resistivity and its temperature coefficient have a maximum at 55 at % and a minimum at about 60 at % Zr, respectively. The resulting concentration dependences of electrical resistivity and its temperature coefficient for Cu–Zr melts are analogous to the dependence obtained for the amorphous alloys. The position of these extreme points and negative TRC values for the liquid (or amorphous) Cu–Zr alloys are determined by the condition $2k_F = K_p$.

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