ELECTRICAL RESISTIVITY OF LIQUID Fe–Mn ALLOYS

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The paper deals with the specific electrical resistivity of liquid Fe–Mn *alloys with the manganese content of 3.9, 6.0, 8.2, 10.3 and 13.2 at.%. A rotary-field electromagnetic method is used to measure this parameter. The experiments are conducted under heating conditions in the range from 1720 to 2070 K followed by the specimen cooling in pure helium. Most of alloys demonstrate a kink on the temperature curve of the specific electrical resistivity during heating up to 1900–2000 K. It is found that the specific electrical resistivity and the ratio between the conductivities of the liquid alloys and the inclusion grow with increasing manganese content in the alloy. Theoretical calculations are performed for the effective specific electrical resistivity of the liquid* Fe–10 at.% Mn *alloy in the temperature range 1720 to 2770 K. The certain temperature is determined, when the conductivity of the heterogeneous liquid alloy equals the conductivity of the iron solution in manganese with the uniform atom distribution. The obtained values of the certain temperature range between 2050–2100 K, i.e., are higher than 1900–2000 K, at which the kink appears on the temperature curve of the electrical resistivity. Theoretical studies are presented for the percolation transition in heterogeneous liquid* Fe–Mn *alloys. The limit value is identified for the ratio between the electrical resistivity of liquid alloys and the inclusion, when a percolation transition is possible. The percolation threshold is determined as a volume fraction of inclusions, at which the effective specific electrical resistivity significantly reduces. The latter is calculated for the heterogeneous liquid alloy in the Maxwell approximation (interpreted by A. A. Snarskii).*

Keywords: liquid Fe–Mn alloys, specific electrical resistivity, temperature coefficient, rotary-field electromagnetic method, structure modeling of heterogeneous liquid alloy, unit cell method, structural transition, percolation transition.

INTRODUCTION

Fe–Mn alloys are widely used as high-strength constructional materials [1]. Manganese is an alloying element for TWIP (twinning-induced plasticity) and TRIP (transformation-induced plasticity) steels that hardens the material [2]. A unique combination of strength and plasticity of manganese steels is explained by competition between different strain hardening mechanisms, i.e., the formation of martensite $\gamma(fcc) \rightarrow \varepsilon(hcp) \rightarrow \alpha'(bcc)$ and twinning [3]. The physical nature of the Fe–Mn alloy hardening is investigated *via* the conditions of their crystallization and kinetic properties in a liquid state. As is known, multi-component liquid alloys represent multi-phase systems in a definite temperature range and are chemically and structurally heterogeneous media.

Gel'd *et al*. [4] proposed to describe the conductivity of heterogeneous materials with the heterogeneity size substantially lower than the specimen using the generalized self-consistent field method.

The experimental data and theoretical calculations presented in [5] for the effective values of the kinetic properties (viscosity, electrical resistivity) of liquid alloys, identified the temperature at which the transition occurred from heterogeneous medium to the medium with a statistical atom distribution. Understanding of the nature of the

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temperature anomaly of the mentioned kinetic properties of the liquid alloys, was also based on the fact, that they were caused by the structural change or structural transitions, i.e., a fracture of microinhomogeneities [6–9].

The aim of this work is the experimental and theoretical research into the temperature dependences of the specific electrical resistivity of the liquid Fe–Mn alloy. These temperature dependences are studied to identify the temperature of the structural transition from the heterogeneous medium to the medium with the statistical atom distribution. The liquid Fe–Mn alloy is considered herein as a heterogeneous medium with atom clusters randomly distributed among manganese atoms.

MATERIALS AND METHODS

The Fe–Mn alloy specimens with the manganese content of 3.9, 6.0, 8.2, 10.3 and 13.2 at.% were fabricated in an inert gas under laboratory conditions. The initial materials (electrolytic manganese (~99.7% Mn) and carbonyl iron (~99.8% Fe)) fused at 1870 K, were prepared using an electrical resistance heating Tamman furnace. The chemical composition of the Fe–Mn alloy specimens was detected by a SPECTROMIDEX spectrometer (SPECTRO Analytical Instruments GmbH, Germany).

The specific electrical resistivity ρ of the liquid Fe–Mn alloy specimens was measured by the torsion angle of a box with the specimen, that was suspended by an elastic thread in the rotating magnetic field (Regel' method). A. R. Regel' [10] demonstrated that the torsion angle of a suspended system was proportional to the specific electrical resistivity of metal, if the radius of a cylindrical sample was comparable with its height [11, 12]. Our measurements of the specific electrical resistivity were conducted in the temperature range of 1720–2070 K, during heating followed by the specimen cooling. The furnace chamber was preliminary vacuumized to 0.001 Pa, and then filled with helium up to a pressure of ~105 Pa. The specimens were exposed to the inert gas for 5–8 min at 1640 K, and then were gradually heated up to 2070 K with a step size of 30 or 40 K. The specific electrical resistivity was measured on a setup proposed by Tyagunov *et al.* [13]. The systematic inaccuracy of ρ parameter measurements was 3%, whereas the random error determining the spread of points during one test, did not exceed 1.5% at 0.95 confidence probability.

Figures 1 and 2 demonstrate the temperature dependences of the specific electrical resistivity of the liquid Fe–Mn alloy specimen in the temperature range 1720 to 2070 K followed by its cooling. The obtained values of this parameter ρ match the experimental data from [14]. As can be seen in Fig. 1, a kink on the temperature curve is observed for all alloy specimens during heating within 1900–2000 K. According to our experiments, during heating, the specific electrical resistivity ρ is significantly lower than during cooling, that is accompanied by the decrease in the temperature coefficient $\frac{d\rho}{dT}$. The concentration dependences presented in Fig. 2*a, b* show that during cooling, ρ parameter and its temperature coefficient increase with growing content of manganese in the Fe–Mn alloy.

In [16, 17], it was reported that the kink on the temperature curve of the specific electrical resistivity denoted a structural transition during heating the alloy up to a certain temperature T^*, which caused the fracture of its heterogenous medium. It should be noted that the kink observed after heating to T^* temperature was accompanied by a drastic fall in the temperature coefficient $\frac{d\rho}{dT}$ (see Fig. 1, Table 1). The temperature T^* during the transition from the heterogeneous medium to the medium with a statistical atom distribution and the liquid alloy overheat $\Delta T = T^* - T_L$ required for the structural transition reduced with increasing manganese content in the alloy. According to Nagel and Tauc [18], the temperature coefficient $\frac{d\rho}{dT}$ tending to zero indicated to the excess free volume of the liquid alloy, which, in turn, was a prerequisite for the metal amorphization during the successive cooling and crystallization. When $\frac{d\rho}{dT}$ tended to zero, the number z of conductivity electrons grew as well as the Fermi wavenumber k_F, *viz.*

$k_F = \left(\frac{3\pi^2 z}{\Omega}\right)^{1/3}$. In that case, Faber and Ziman [19] considered the growth in the structural factor $a(2k_F)$ as a determinant. When the doubled Fermi wavenumber $2k_F$ equaled the wavenumber corresponded to the first peak
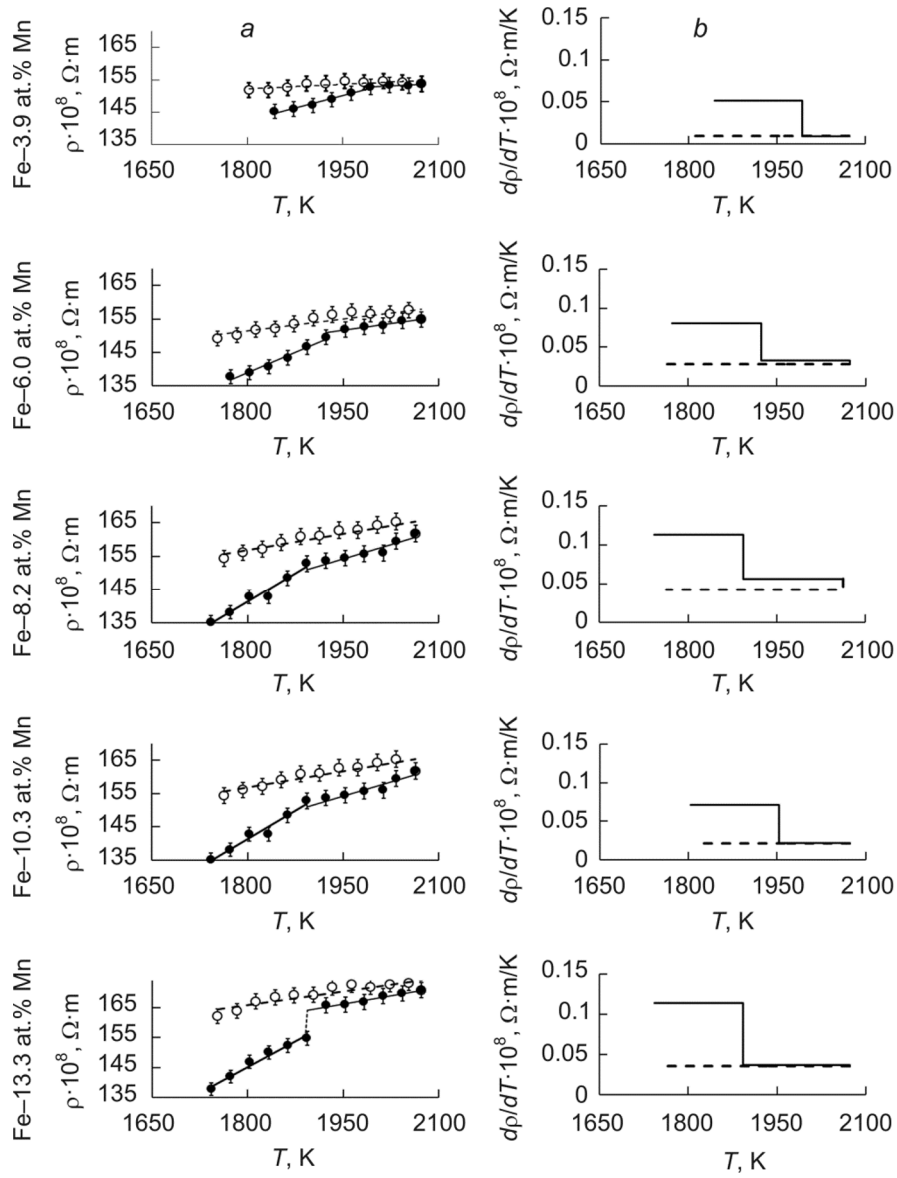
Fig. 1. Temperature curves of specific electrical resistivity (*a*) and its temperature coefficient (*b*) of Fe–Mn alloy specimens. Signs: ● heating, ○ cooling, ——— heating, - - - - cooling.

position of the structural factor ($2k_F = K_p$), the electrical resistivity reached its maximum. At $2k_F \approx K_p$, the temperature coefficient was either close to zero or negative, because the height of the first peak of the structural factor lowered with the temperature growth. The $2k_F = K_p$ condition provided the ideas by Nagel and Tauc about the amorphization process of metal alloys, i.e., the nucleation of crystal grains was prevented by the appeared potential barrier, the melting temperature lowered, and the vitrification temperature grew, thereby promoting the amorphization process.

Based on the approach proposed by Jia *et al*. [9], we calculate the specific electrical resistivity of the liquid Fe–Mn alloy as a heterogenous medium consisting of the atom clusters in the matrix of a different elemental composition. Using the data from the stable state-transition diagram for the Fe–Mn system [20], we propose the following elemental composition for the clusters and the matrix: Fe–3 at.% Mn and Fe–56 at.% Mn, respectively. The specific electrical resistivity is the sum of contributions from the clusters and the matrix:

TABLE 1. Liquidus Temperature T_L, Transition Temperature T^* from Heterogeneous Medium to Medium with Statistical Atom Distribution, Liquid Alloy Overheat $\Delta T = T^* - T_L$ Required for Structural Transition

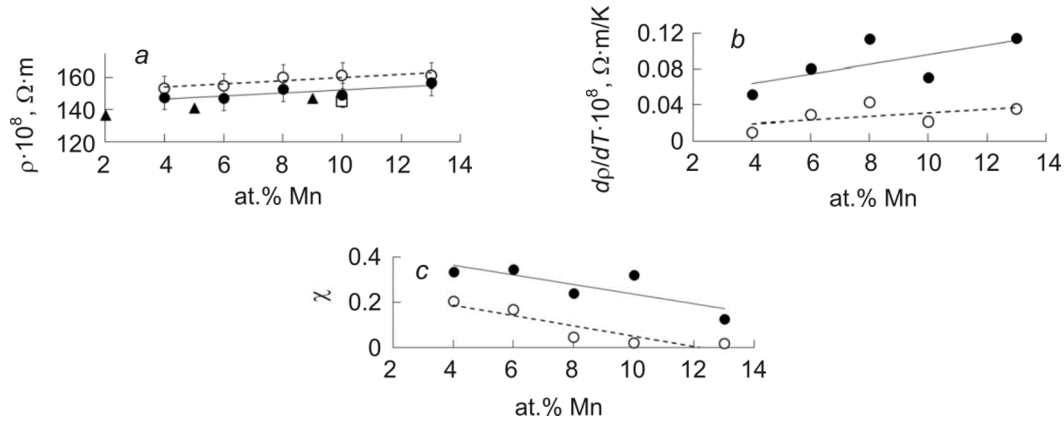| Alloys	T_L, K	$\Delta T = T^* - T_L$, K	T^*, K
Fe–3.9 at.% Mn	1790	200	1990
Fe–6.0 at.% Mn	1770	150	1920
Fe–8.2 at.% Mn	1760	130	1890
Fe–10.3 at.% Mn	1750	200	1950
Fe–13.3 at.% Mn	1730	160	1890

Fig. 2. Concentration dependences of specific electrical resistivity (*a*), its temperature coefficient (*b*) and volume fraction of atom clusters (*c*) in liquid Fe–Mn alloy specimens at $T = 1900$ K. Signs: ● heating, ○ cooling, ▲ data from [15], □ data from [14].

$$\rho = \chi \rho_c + (1 - \chi)\rho_m, \tag{1}$$

where χ is the volume fraction of clusters; ρ_c and ρ_m are specific electrical resistivities of the clusters and the matrix, respectively. The specific electrical resistivity ρ_m of the matrix can be obtained from

$$\rho_m = c\rho_{Mn} + (1 - c)\rho_{Fe} + c(1 - c)\rho_R, \tag{2}$$

where c is the manganese concentration, ρ_{Fe} and ρ_{Mn} are specific electrical resistivities of iron and manganese, respectively; ρ_R is Nordheim's constant [21]. Let us assume that the volume fraction χ of the clusters tends to unit when the clusters completely fracture. In this case, we can calculate the specific electrical resistivity ρ_c and the volume fraction χ of the clusters [9]. Based on the experimental data from [14], we calculate the volume fractions of the clusters and the matrix, *viz.* Fe–3 at.% Mn and Fe–56 at.% Mn, respectively. We also find that the volume fraction χ reduces with increasing manganese content in the alloy (see Fig. 2*c*).

THEORETICAL CALCULATIONS

Theoretical calculations are performed for the specific electrical resistivity of the liquid Fe–10 at.% Mn alloy in the temperature range of 1700–2300 K. These calculations concern the temperature T^*, at which the conductivity of this alloy equals the conductivity of the iron solution in manganese with the homogeneous atom distribution. The model is

proposed for the structural transition from the heterogeneous medium to the homogeneous medium with a statistical atom distribution in manganese during the alloy heating up to T^* temperature. The liquid Fe–10 at.% Mn alloy as a heterogeneous medium is considered as a matrix made of liquid manganese and clusters of the iron atoms. The specific electrical resistivity of the liquid Fe–10 at.% Mn alloy as a heterogeneous medium, is calculated in terms of the percolation theory and conductivity of strongly inhomogeneous media and using the model of the effective electric resistivity of mixtures. The effective value of the specific electrical resistivity is obtained by using four methods; the temperature dependences are determined for ρ_{eff}, ρ_{iso}, ρ_L, and ρ_{Zh} parameters. The parameter ρ_{iso} is calculated by the relation proposed by Dul'nev and Novikov [21] for heterogeneous media, which is based on the unit cell method, which divides the cell with isothermal and adiabatic planes:

$$\rho_{iso} = \rho_1 \left(1 - \frac{m_2}{(1-\nu)^{-1} + (1+m_2)(1-m_2^{2/3})(1+m_2^{1/3})} \right)^{-1},$$ (3)

where ρ_{iso} is the specific electric resistivity of heterogeneous liquid Fe–Mn alloy, ρ_1 is the specific electric resistivity of the matrix (medium), $\nu = \dfrac{\rho_1}{\rho_2}$ is the ratio between the specific electric resistivities of the medium and the cluster (inclusion), m_2 is the volume fraction of clusters (inclusions). The ρ_{eff} parameter is obtained from the Odelevskii [22] equation:

$$\rho_{eff} = \rho_1 \left(1 - m_2 \left(\frac{1}{1-\nu} - \frac{1-m_2}{3} \right)^{-1} \right)^{-1}.$$ (4)

The parameter ρ_L is determined by Landauer's equation [23] for the effective electric resistivity of a binary-metal mixture with a random distribution of components:

$$\rho_L = \left(\frac{1}{4} \left(\frac{3x_2-1}{\rho_2} + \frac{3x_1-1}{\rho_1} + \left[\left\{ \frac{3x_2-1}{\rho_2} + \frac{3x_1-1}{\rho_1} \right\}^2 + \frac{8}{\rho_1\rho_2} \right]^{\frac{1}{2}} \right) \right)^{-1}.$$ (5)

Using the model approximation by Zhao [24] for viscosity of the binary-metal system, we determine the electric resistivity ρ_{Zh} of the mixture with a regular distribution of components:

$$\rho_{Zh} = \rho_1 \left[1 - \left(\frac{b}{a} \right)^2 \right] + \rho_2 \left(\frac{b}{a} \right)^2, \quad \left(\frac{b}{a} \right)^3 = \frac{w_b/d_b}{w_a/d_a + w_b/d_b},$$ (6)

where w and d are the weight and density of each volume fraction, respectively; ρ_1 and ρ_2 are the specific electric resistivities of the medium and inclusion, respectively; a, b are linear dimensions of the unit cell and inclusion.

Let us assume that in heating the liquid Fe–Mn alloy up to the certain temperature T^*, the transition occurs from the heterogeneous medium to the homogeneous manganese solution in iron with a statistical atom distribution. The specific electric resistivity ρ_{add} of this homogeneous solution is calculated by the additional dependence using the experimental data from [25, 26] concerning $\rho_{Mn}(T)$ and $\rho_{Fe}(T)$ functions. The temperature T^* is found to be 2020–2100 K, at which the electric resistivity of the heterogeneous medium equals that of the manganese solution in iron with the statistical atom distribution. The temperature T^* is determined by zero values of $\rho_{iso} - \rho_{add}$, $\rho_{eff} - \rho_{add}$, $\rho_L - \rho_{add}$, and $\rho_{Zh} - \rho_{add}$ parameters (see Fig. 3). The obtained result we interpret as a transition model from the heterogeneous medium to the homogeneous iron solution in manganese with the statistical atom distribution during heating up to T^*
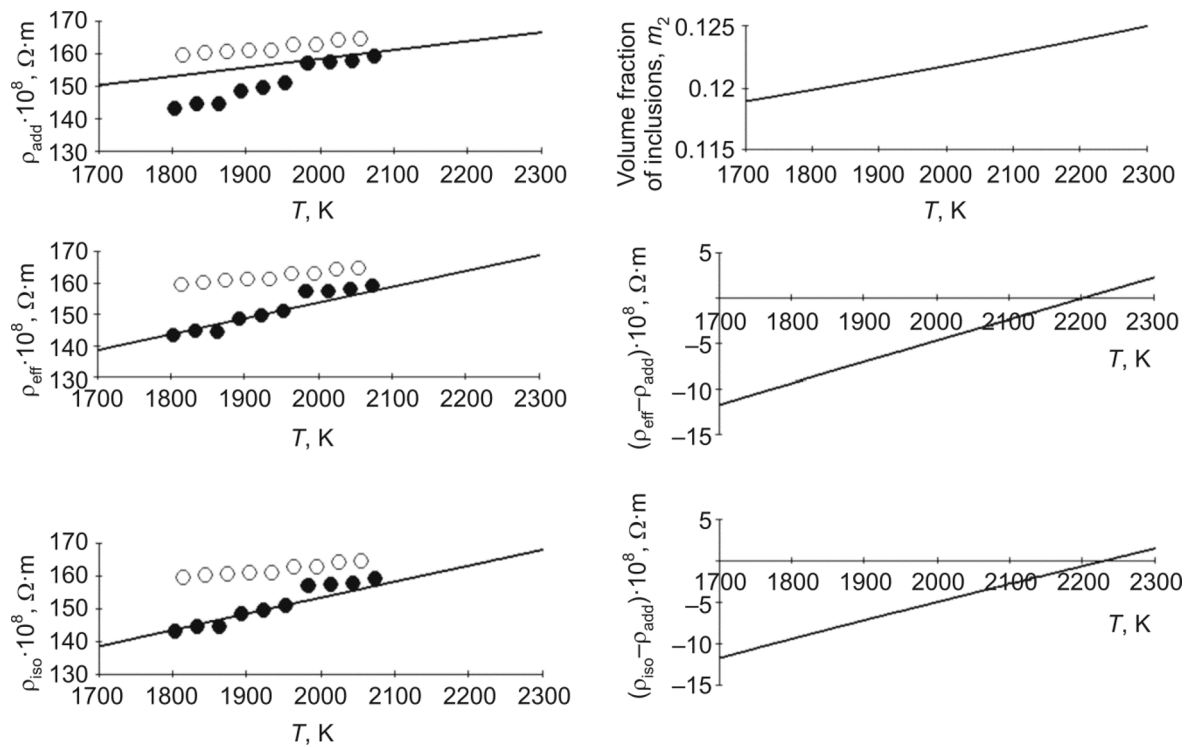
Fig. 3. Temperature dependences of specific electric resistivity of liquid Fe–10 at.% Mn alloy derived from Eqs. (3) and (4), volume fraction m_2 of clusters, $\rho_{iso} - \rho_{add}$ and $\rho_{eff} - \rho_{add}$ parameters: ● experimental data on heating, ○ cooling.

temperature. Note that T^* temperature range of 2020–2100 K is higher than 1900–2000 K range corresponding to the kink on the temperature curve of the electric resistivity of the liquid Fe–Mn alloy (see Fig. 1). The specific electric resistivity of the liquid Fe–10 at.% Mn alloy determined by the additional dependence is in agreement with our experimental data obtained for the liquid Fe–Mn alloys during cooling, as shown in Fig. 3. The specific electric resistivity of the liquid Fe–10 at.% Mn alloy as a heterogenous medium, determined by Eqs. (3)–(6), is in agreement with our experimental data obtained for the liquid Fe–Mn alloys during heating.

The specific electric resistivity of the liquid Fe–10 at.% Mn alloy as a heterogeneous medium, is also obtained from Eqs. (3) and (4). In this system, the clusters are distributed in the matrix, which is the liquid Fe–56 at.% Mn alloy. The T^* temperature is identified to be 2200 K, when the specific electric resistivity of the heterogeneous medium equals that of the manganese solution in iron with the statistical atom distribution. This is presented in Fig. 4.

According to theoretical calculations of the percolation transition in heterogeneous liquid Fe–Mn alloys, the limit value is identified for the ratio between the electric resistivity ρ_1 of the medium and the electric resistivity ρ_2 of the inclusion, when the percolation transition is possible [27–30]. The percolation threshold is determined as the volume fraction m_2 of inclusions, at which the conductivity of the heterogeneous medium significantly grows, viz. $\sigma_e = \dfrac{1}{\rho_e}$. The effective electric resistivity of the heterogeneous medium is calculated in the Maxwell approximation using the relation proposed by Snarskii [26]:

$$\rho_e = \rho_1 \left[1 - 3m_2 \frac{\rho_1 - \rho_2}{2\rho_2 - \rho_1} \right], \tag{7}$$
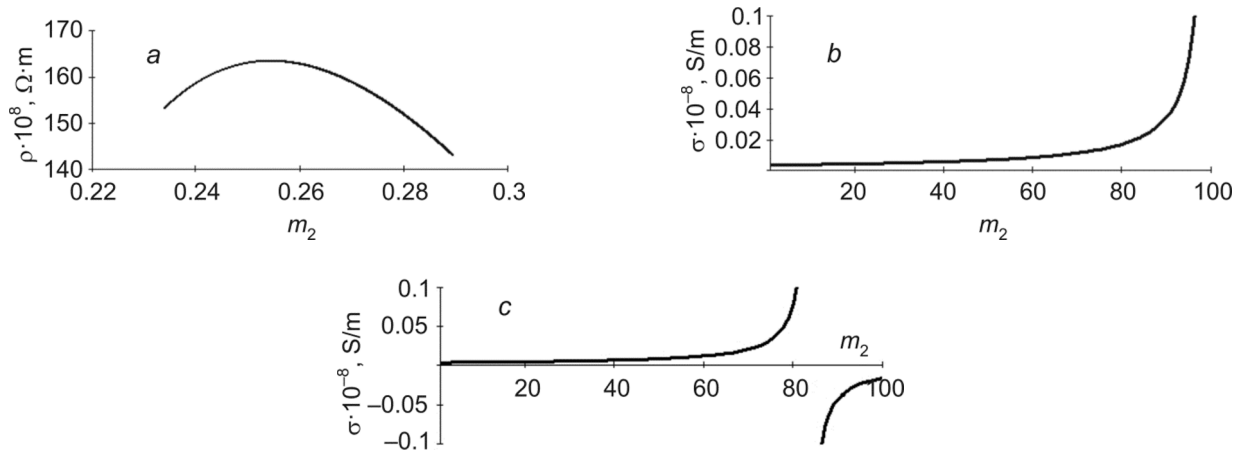
Fig. 4. Functions $\rho_e(m_2)$ and $\sigma_e(m_2)$ of liquid Fe–20 at.% Mn alloy at $T = 2400$ K (*a*, *b*) and $\sigma_e(m_2)$ function of liquid Fe–20 at.% Mn alloy at $T = 3000$ K (*c*).

where m_2 is the volume fraction of inclusions, ρ_1 is the specific electrical resistivity of the medium, ρ_2 is the specific electrical resistivity of inclusions.

These calculations show that the percolation transition is available only for alloys with the manganese content over 15 at.%. Let us consider the obtained results for the liquid Fe–20 at.% Mn alloy, regarded as a heterogeneous medium, in which the clusters of the iron atoms are distributed in the matrix, i.e., liquid manganese. Functions $\rho_e(m_2)$ and $\sigma_e(m_2)$ are analyzed by Eq. (7). As can be seen from Fig. 4*b*, the conductivity increases with growing content of inclusions at 2400 K, but the percolation transition is not observed. According to Fig. 4*c*, the latter occurs at 3000 K. Since the elemental composition of manganese steels includes carbon, fluorine, aluminum, and sulfur in addition to iron and manganese and affects the $\dfrac{\sigma_1}{\sigma_2}$ ratio, we find the conditions for the percolation transition. The percolation transition is observed at $\dfrac{\sigma_1}{\sigma_2} = 2.7$ and the volume fraction of inclusions $m_2 = 0.92$. When $\dfrac{\sigma_1}{\sigma_2} > 2.7$, percolation occurs at lower values of the volume fraction m_2 of inclusions in the liquid alloy.

CONCLUSIONS

The temperature dependences were suggested for the specific electrical resistivity of liquid Fe–Mn alloys with the manganese content of 3.9, 6.0, 8.2, 10.3 and 13.2 at.%. Most of alloys demonstrated a kink on the temperature curve of the specific electrical resistivity during heating up to T^* temperature, that indicated to the structural transition from the heterogeneous medium to the iron solution in manganese with the statistical atom distribution. The kink on the temperature curve observed in manganese during the Fe–Mn alloy heating up to T^* temperature was accompanied by a drastic fall in the temperature coefficient $\dfrac{d\rho}{dT}$ of the specific electrical resistivity. The temperature T^* and the liquid alloy overheat $\Delta T = T^* - T_L$ required for the structural transition, decreased with increasing manganese content in the alloy. The analysis of the concentration dependences suggested for the liquid Fe–Mn alloy showed that during cooling, its specific electrical resistivity and temperature coefficient increase with growing manganese content.

Theoretical calculations were performed for the effective specific electrical resistivity of the liquid Fe–10 at.% Mn alloy to determine the temperature of the structural transition, at which the conductivity of the heterogeneous liquid alloy equaled the conductivity of the iron solution in manganese with the uniform atom distribution. The specific electrical resistivity of the heterogeneous medium was calculated in terms of the percolation theory and conductivity of strongly inhomogeneous media. The obtained values of T^* temperature ranged between

2050–2100 K, which was in agreement with the experimental value of 1950 K for the Fe–10 at.% Mn alloy. The effective specific electrical resistivity of heterogeneous liquid Fe–Mn alloys was calculated in the Maxwell approximation (interpreted by A. A. Snarskii). It was found that the percolation transition occurred in alloys with the manganese content not over 15 at.%. The percolation threshold was determined as a volume fraction of inclusions, at which the conductivity of the heterogeneous medium significantly reduced. The percolation threshold in liquid Fe–20 at.% Mn alloys was observed at 3000 K. It was detected that the percolation transition occurred when the ratio between the conductivities of the liquid alloys and the inclusion was 2.7 and the volume fraction of inclusions was 0.92.

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