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THERMODYNAMIC STABILITY OF MICROHETEROGENOUS STATES IN Fe – Mn – C MELTS

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Abstract. The probability of the existence of microheterogeneous states in Fe – Mn – C melts has been analyzed in accordance with the concepts of chemical thermodynamics. The microheterogeneous state of a chemically heterogeneous Fe – Mn – C melt was understood as the presence of dispersed Fe – C particles in it. These are suspended in the Mn – C medium and separated from it by an interface. The microheterogeneous state in Fe – Mn – C melts is destroyed as a result of heating to a temperature specific for each composition. The hypothesis of the microheterogeneous state of Fe – Mn – C melts is supported by a wide range of numerous experimental data on their thermodynamic and physical properties. The identification of anomalies in temperature dependences of physical properties of Fe – Mn – C melts has allowed for temperature values above which the melt superheating treatment (MST) causes destruction of microheterogeneity to be determined, i.e., liquid – liquid structure transition (LLT) in the melt. LLT is understood by the authors as a structural transition "microheterogeneous melt – homogeneous solution". This is expressed as the destruction of the microheterogeneous state when the Fe – Mn – C melt is heated to a temperature specific for each composition (MST). The authors have previously analyzed the effect of LLT in Fe – Mn – C melts on the microstructure, crystal structure and mechanical properties of solid metal in submicrovolumes. This paper describes a method of theoretical determination of the temperature range where the microheterogeneous state of the Fe – Mn – C melt is thermodynamically stable. The thermodynamic stability of dispersed Fe – C particles in the Mn – C medium has been estimated according to the equations proposed by G. Kaptay for a regular solution. It was assumed that the interface between the dispersed particle (Fe – C) and the dispersion medium (Mn – C) is enriched with carbon. The paper demonstrates the possibility of existence in the Fe – Mn – C melt of dispersed Fe – C particles with sizes from 2 to 34 nm, distributed in the Mn – C dispersion medium and separated from it by an interface with increased carbon content. The estimated result is consistent with the data on the size of structural units of a viscous flow, obtained earlier within the framework of the theory of absolute reaction rates.

Keywords: Fe – Mn – C, melts, liquid – liquid structure transition, melt superheating treatment, microheterogenity, thermodynamic stability

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Оригинальная статья

ТЕРМОДИНАМИЧЕСКАЯ УСТОЙЧИВОСТЬ МИКРОГЕТЕРОГЕННЫХ СОСТОЯНИЙ В РАСПЛАВАХ Fe – Mn – C

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Аннотация. Проведен анализ возможности существования микрогетерогенных состояний в расплавах Fe – Mn – C согласно представлениям химической термодинамики. Под микрогетерогенным состоянием химически неоднородного расплава Fe – Mn – C понималось наличие в нем дисперсных частиц Fe – C, которые взвешены в окружающей среде Mn – C и отделены от нее межфазной поверхностью. Микрогетерогенное состояние в расплавах Fe – Mn – C разрушается в результате нагрева до определенной для каждого состава температуры. В пользу гипотезы о микрогетерогенном состоянии расплавов Fe – Mn – C свидетельствуют многочисленные экспериментальные данные об их термодинамических и физических свойствах. Выявление аномалий температурных зависимостей физических свойств расплавов Fe – Mn – C позволило определить значения температур, перегрев расплава (*Melt Superheating Treatment*, MST) свыше которых приводит к разрушению микрогетерогенности, т. е. структурному переходу «жидкость – жидкость» (*Liquid – liquid structure transition*, LLT) в расплаве. Термин LLT понимается авторами как структурный переход «микрогетерогенный расплав – однородный раствор» и выражается в разрушении микрогетерогенного состояния при нагреве расплава Fe – Mn – C до определенной для каждого состава температуры (MST). Авторами ранее проведен анализ влияния LLT в расплавах Fe – Mn – C на микроструктуру, кристаллическое строение и механические свойства твердого металла в субмикрообъемах. В данной работе описан метод теоретического определения диапазона температур, где микрогетерогенное состояние расплава Fe – Mn – C термодинамически устойчиво. Проведена оценка термодинамической устойчивости дисперсных частиц Fe – C в среде Mn – C в формализме Гиббса по уравнениям, предложенным Г. Каптаем для регулярного раствора. Сделано предположение, что граница раздела дисперсная частица (Fe – C) и дисперсионная среда (Mn – C) обогащена углеродом. Показана возможность существования в расплаве Fe – Mn – C дисперсных частиц Fe – C, имеющих размеры от 2 до 34 нм, распределенных в дисперсионной среде Mn – C и отделенных от нее межфазной границей с повышенным содержанием углерода. Результат оценки согласуется с данными о размере структурных единиц вязкого течения, полученными ранее в рамках представлений теории абсолютных скоростей реакций.

Ключевые слова: Fe – Mn – C, расплавы, структурный переход «жидкость – жидкость», обработка расплава перегревом, микрогетерогенность, термодинамическая устойчивость

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INTRODUCTION

The Fe – Mn – C melts are used widely in the industry as structural materials with high strength. However, almost all studies aimed at improving the strength properties of Fe – Mn – C melts are reduced to the temperature effect on the crystallized metal. The actual objective is to study the structural state of Fe – Mn – C melts for their preparation for casting and crystallization, in order to ensure a consistently high level of strength properties of finished products. The key factor for the implementation of this method of melt preparation is the information relating to structure transitions in the superliquid part (the "liquid" zone) of the Fe – Mn – C system state diagram [1].

The concepts of physical chemistry relating to the liquid-liquid structure transition (LLT) in multicomponent melts are consistent with the concept of the microheterogeneous state, formulated and developed by P.S. Popel. The microheterogeneous state of a chemically heterogeneous Fe – Mn – C melt is understood as the presence of dispersed particles rich in one of the components in it, suspended in a medium of another composition and separated from it by an interface [2]. The microheterogeneous state is destroyed as a result of energetic impact on the melt, such as heating to a temperature specific for each composition. After the irreversible destruction of the microheterogeneous state, the melt transforms into a molecular solution state and its crystallization conditions change. This is reflected in the microstructure, crystal structure and mechanical properties of the crystallized metal. The concept of the microheterogeneous state of liquid multicomponent melts has been substantiated experimentally. P.S. Popel, U. Dahlborg and M. Calvo-Dahlborg, using the method of small-angle neutron scattering in Pb – Sn and Al – Si eutectic melts, detected regions enriched in one of the elements and separated from the rest of the liquid melt by a transition layer. Two families of particles have been identified: small particles sized 10 – 40 Å; and large particles sized up to 90 Å. As the temperature increases, the particles dissolve and recombine into smaller ones [3]. The use of LLT as a strategy for creating materials with predetermined properties has proven to be practical and effective. LLT appeared not only to control the nucleation rate of crystals, but also to control the structure of crystallites, determining the mechanical and thermal properties of the material [4, 5].

The concept of microheterogeneity of liquid multicomponent melts also agrees with the concepts of Melt Superheating Treatment (MST) as a method of improving the mechanical properties of castings. The effect of MST of the Fe – 12 % wt. Mn – 1 % wt. C melt on the ingot microstructure has been studied in detail. It was established that the MST of this melt causes an increase in austenite grains (solid solution of carbon in iron) and decrease in the number of precipitating carbides during subsequent cooling and crystallization. This can be explained by a decrease in the number of crystallization centers with increasing temperature [6].

Previously, the authors have found anomalies of temperature dependences of kinematic viscosity and specific electrical resistivity of Fe – (5.0 – 25.0) % wt. Mn – (0.4 – 2.2) % wt. C melts, interpreted as an evidence of irreversible destruction of microheterogeneity. The values of temperatures T^* at which the microheterogeneous state of the Fe – Mn – C melt of specific chemical composition is destroyed have also been determined [7, 8].

This article discusses the theoretical justification of the possibility of existence of thermodynamically stable microheterogeneous states in Fe – Mn – C melts at temperatures close to liquidus in the framework of the chemical thermodynamics concepts. The identification of anomalies in temperature dependences of melts physical properties allowed for temperature values above which MST causes destruction of microheterogeneity to be determined, i.e., LLT in the melt. The effect of LLT in the Fe – Mn – C melt on the microstructure, crystal structure and mechanical properties of a solid metal in submicrovolumes has been analyzed. Theoretical determination of the temperature range where the microheterogeneous state of the Fe – Mn – C melt is thermodynamically stable is the purpose of this work.

EXPERIMENTAL EVIDENCE OF MICROHETEROGENEITY OF Fe – Mn – C MELTS

The hypothesis of the possibility of microheterogeneous states in Fe – Mn – C melts is supported by the data of the diagram of states and the results of measurements of thermodynamic properties. The diagram of states of the system, including isothermal and polythermal sections, has been studied in detail [9 – 11]. According to experimental data of thermodynamic properties of Fe – Mn, Fe – C, Mn – C melts on the distribution of Mn and between liquid ferrite and austenite, isothermal sections of the diagram of the Fe – Mn – C state at temperatures of 1760 and 1750 K have been built by calculation [9]. The polythermal sections of the diagram of the Fe – Mn – C system states appeared to have zones with the ε-phase: four-phase eutectic-peritectic $\gamma + L + C + \varepsilon$ at 1430 K; and eutectoid-peritectoid $\alpha + \gamma + C + \varepsilon$ at 840 [10]. The possibility of the existence of manganese carbide Mn_7C_3 in the system has been demonstrated by means of calculation. The weak dependence of the chemical composition of carbide phases (cementite and ε-phase) on temperature has been established. Taking this into account, the cementite contains ~30 % Mn and 25 % C, and the ε-phase contains ~37.5 % Mn and 30 % C. It has been demonstrated that the manganese distribution coefficient between the melt and austenite $\left(K_{\mathrm{Mn}}^{L-\gamma} = 1.32\right)$ and between the melt and ferrite $\left(K_{\mathrm{Mn}}^{L-\alpha} = 1.36\right)$ in the temperature range of 1470 – 1500 °C depends on temperature weakly [9].

The results of analysis of the calculated isothermal [9] and polythermal [10] sections of the Fe – Mn – C states diagram allow the structure formation in manganese- and high-manganese steels to be judged. In the process of cooling, a specific component from a mixture of austenite and carbides with laminar morphology is formed in the structure of high-manganese steels. It has been demonstrated that during very slow cooling dense clusters of carbide plates are formed in some isolated areas, resembling a pearlitic structure. A transition to thin-plate pearlite occurs at the edges of these areas bordering the unconverted austenite [11]. A study of regularities in the formation of the Fe – Mn – C melts microstructure and the morphology of austenitic dendrites showed that the introduction of carbon into the Fe – Mn melt causes an increase in the lateral dimension of primary branches of dendrites. It also changes the size of secondary branches by increasing the interphase energy at the crystallization front [12]. It can be assumed that destruction of the microheterogeneous state during subsequent cooling and crystallization will cause a decrease in the interphase energy at the crystallization front. This is due to destruction of tthe dispersed particles in turn being destroyed and transition of the melt to the molecular solution state. This will eventually change the microstructure and the crystal structure of the ingot significantly.

The hypothesis about the possibility of a microheterogeneous state of Fe – Mn – C melts is supported by a significant deviation of the system from the ideal: enthalpy of the Fe – Mn – C liquid melt is negative and decreases with the increasing Mn and C content [13]. Evaluation of the thermodynamic properties of Fe – C and Fe – Mn melts showed the presence of strong interparticle interaction, causing short-range ordering [14, 15]. Fe – Mn melts have a negative enthalpy of mixing, confirming strong interparticle interaction [16]. The Mn – C melts are also characterized by a negative enthalpy of mixing [15]. In the process of crystallization, the Mn_3C compound precipitates together with cementite Fe_3C at the austenite grains boundaries [17]. Carbon dissolves well (up to ~17 % (at.)) in liquid iron [18]. In Fe – Mn – C melts, the solubility of carbon increases with increasing manganese content [19]. On the basis of this it can be assumed that in Fe – Mn – C melts all carbon will be either dissolved in iron or bound by manganese compounds.

The hypothesis of the possibility of microheterogeneous states in Fe – Mn – C melts is supported by experimental data on their physical properties. Anomalies of temperature dependences of kinematic viscosity and specific electrical resistance of Fe – (5.0 – 25.0) % Mn – (0.4 – 2.2) % C melts observed at temperatures T^* specific for each composition have also been interpreted by the authors as indirect evidence of destruction of the Fe – Mn – C melts microheterogeneity during heating to T^* [7, 8].

A.A. Wertman and A.M. Samarin were the first to develop a hypothesis of colloidal microheterogeneity of Fe – C melts on the basis of sedimentation experiment data. Experiments by A.A. Wertman, A.M. Samarin and A.M. Jacobson on the centrifugation of liquid cast iron show that the radius of carbon atoms groupings is close to 10 nm [20]. In their papers, A.A. Wertman and A.M. Samarin linked colloidal microheterogeneity of the melt with the presence of a nonequilibrium dispersed phase which gradually dissolves in the dispersion medium [21]. Such dynamic (fluctuational) microheterogeneity has an inherited short-range order of solid eutectic phase structure. Its lifetime is commensurate with the relaxation time in the atomic arrangement. According to the ideas of A.A. Wertman and A.M. Samarin, colloidal microheterogeneity is attained only in the limit case of solutions with strong covalent interaction of atoms of one of the components. In other eutectic systems, microheterogeneity is of a fluctuational nature. The study of the microheterogeneous (colloidal) state of liquid cast irons leads A.A. Wertman and A.M. Samarin to consider the nonequilibrium nature of such a state. This would explain the branching of temperature dependences of their physical properties obtained in the modes of heating and subsequent cooling of the melt [22]. The iron-carbon melt was also considered as a nonequilibrium system with a particular temporal colloidal heterogeneity, in which all the carbon is in the form of disperse graphite particles [23]. Subsequently, the concepts of the microheterogeneous state of iron–carbon melts were developed. They were considered a temporary, nonequilibrium state gradually passing into the equilibrium state of a molecular solution. V.M. Zalkin understood eutectic Fe – C melts in a liquid state as a thermodynamically stable two-phase state (microemulsion) preconditioned by the delayed dissolution of one of the components and gradually passing to a molecular (homogeneous) solution state. In other words the Fe – C melts were understood as lyophilic two-phase systems [24]. Transition from the microemulsion state in this case is reversible. When a homogeneous solution cools, the initial microheterogeneity is restored. The existence of a stable two-phase region leads to objections by A.A. Wertman due to the violation of the phase rule in the eutectic point [21]. However, the invalidity of this assertion was pointed out even by J.I. Fraenkel [25]. If dispersion of one of the phases to the colloidal scale occurs, an additional degree of freedom, such as pressure inside disperse particles or their radius appears [26]. With regard to the structure of the iron–carbon system melt, V.M. Zalkin assumes a limited solubility of carbon in liquid iron, not exceeding 6.5 – 8.5 % (at.) [24]. At higher concentrations of carbon in the melt, the spontaneous formation of carbon-enriched ordered groupings of dissimilar atoms, similar in structure to cementite and separate phases, occurs. The formation of disperse cementite particles in liquid alloys at this temperature range occurs during melting of alloys with both cementite and graphite in the initial structure, as well as during dissolution of graphite in liquid iron. An increase in the carbon content in the melt to more than 12.4 – 14.2 % (at.) results in the appearance of submicrogroups of carbon atoms ordered by the graphite type [23]. P.S. Popel formulated the hypothesis of metastability of the melts microheterogeneous state in systems with eutectics and monotectics. The issue of metastability of the microheterogeneous state caused a heated dispute between V.M. Zalkin, who rejected the idea of metastability of microheterogeneous states, and P.S. Popel on the pages of scientific journals [27 – 30]. In order to substantiate this hypothesis, P.S. Popel analyzed the stability of a disperse particle in the surrounding melt in the framework of the gradient approximation of the thermodynamics of heterogeneous systems thermodynamics [31]. This paper presents the result of evaluation of the thermodynamic stability for microheterogeneous states in Fe – Mn – C melts, i.e., the fundamental probability of such states in these melts was evaluated and the corresponding temperature and composition range was determined. The authors performed calculations for the different models of the Fe – Mn – C microheterogeneous melt: Mn – C particles in the Fe – C medium and Fe – C particles in the Mn – C medium. In both cases it was assumed that the "particle – medium" interface is represented by a saturated solution of carbon in iron. As a result of the calculation, the possibility of thermodynamically stable microheterogeneous states in Fe – Mn – C melts was demonstrated only for the case when disperse particles (Fe – C) were in the dispersion medium (Mn – C) and the "particle – medium" interface was represented by a saturated solution of carbon in iron.

RESULT OF EVALUATION OF THERMODYNAMIC STABILITY FOR MICROHETEROGENEOUS STATES IN FE – MN – C MELTS

Considering Fe – Mn – C melt as a microheterogeneous system, let us then denote the amounts (mol) of iron, manganese, and carbon as n_{Fe}, n_{Mn}, n_{C} and assume that $n_{\text{Fe}} > n_{\text{Mn}} > n_{\text{C}}$. Then considering liquid Fe and Mn as mutually insoluble phases at fixed temperature T and fixed standard pressure $p_o = 1$ bar, let carbon have limited solubility in both liquid iron and liquid manganese. The mutual exchange energy (Ω, J/mol) between dissimilar iron, carbon, and manganese atoms is positive which is essential in the regular solution model. Thus supposing suppose there are disperse Fe – C particles in the Mn – C melt medium, we can express the volume equilibrium condition for carbon in such a heterogeneous system as

$$G_{\text{C}}^{\circ} + RT\ln\left(X_{\text{C(Fe, }b)}\right) + \Omega_{\text{Fe – C}}\left(1 - X_{\text{C(Fe, }b)}\right)^2 =$$
$$= G_{\text{C}}^{\circ} + T\ln\left(X_{\text{C(Mn, }b)}\right) + \Omega_{\text{Mn – C}}\left(1 - X_{\text{C(Mn, }b)}\right)^2, \quad (1)$$

where G_{C} (J/mol) is the standard Gibbs energy of pure carbon; $X_{\text{C(Fe, }b)}$ (dimensionless) is the volume mole fraction of carbon in the Fe – C solution; and $X_{\text{C(Mn, }b)}$ (dimensionless) is the volume mole fraction of carbon in the Mn – C solution.

In general, equation (1) is solved numerically relative to $x_{\text{C (Fe, }b)}$ as a function of $x_{\text{C (Mn, }b)}$ at a fixed value of T and taking into account the parameters of the model – interchange energy of $\Omega_{\text{Fe – C}}$ and $\Omega_{\text{Mn – C}}$. If carbon forms dilute solutions in both iron and manganese, the solution of equation (1) can be written approximately as

$$X_{\text{C(Fe, }b)} \cong KX_{\text{C(Mn, }b)}, \quad (2)$$

where K – is the coefficient of carbon distribution between the Mn – C medium and disperse Fe – C particles:

$$K \equiv \exp\left(\frac{\Omega_{\text{Mn – C}} - \Omega_{\text{Fe – C}}}{RT}\right). \quad (3)$$

Let us assume that liquid iron and manganese are mutually insoluble. The free surface energy at the melt interface ($\sigma_{\text{Fe/Mn}}$) will be much greater than the free surface energy at the interface of carbon and manganese ($\sigma_{\text{C/Mn}}$) and pure carbon and iron ($\sigma_{\text{C/Fe}}$). Therefore, the following ratio is met: $\sigma_{\text{Fe/Mn}} \gg \sigma_{\text{C/Mn}}, \sigma_{\text{C/Fe}}$. Consequently, carbon will be a surface-active component at the interface of a disperse particle (Fe – C) and dispersion medium (Mn – C). Let us assume that the interface between a disperse particle (Fe – C) and dispersion medium (Mn – C) is enriched in carbon, then we find the mole fraction of carbon in the dispersion medium $X_{\mathrm{C(Mn},\,b)}$ using formula [32]

$$X_{\mathrm{C(Mn},\,b)} \cong \frac{n_{\mathrm{C}} - \dfrac{3,24}{r} n_{\mathrm{Fe}} \dfrac{V^{\circ}_{m,\,\mathrm{Fe}}}{\overset{\circ}{\omega}_{\mathrm{Fe-C}}}}{n_{\mathrm{Mn}} + K n_{\mathrm{Fe}}}, \tag{4}$$

where n_i is the number of moles of the i-th component; $V^{\circ}_{m,\,\mathrm{Fe}}$ is the molar volume of iron; and $\overset{\circ}{\omega}_{\mathrm{Fe-C}}$ is the area of the molar surface of the "particle – medium" transition layer.

During the dispersion of particles their radius r decreases, thus according to equation (4) $X_{\mathrm{C(Mn},\,b)}$ decreases as well. However, the mole fraction of $X_{\mathrm{C(Mn},\,b)}$ cannot be a negative value. Consequently, the minimum particle size at which $X_{\mathrm{C(Mn},\,b)} = 0$ can be obtained from equation (4) is

$$r_{\min} = 3,24 \frac{n_{\mathrm{Fe}} V^{\circ}_{m,\,\mathrm{Fe}}}{n_{\mathrm{C}} \overset{\circ}{\omega}_{\mathrm{Fe-C}}}. \tag{5}$$

The Gibbs energy of a dispersed system is calculated using the following formulas [32]:

$$G_{em} = n_{\mathrm{Fe}} \left(1 + \frac{X_{\mathrm{C(Fe},\,b)}}{1 - X_{\mathrm{C(Fe},\,b)}}\right) G_{m,\,b,\,\mathrm{Fe-C}} + $$
$$+ n_{\mathrm{Mn}} \left(1 + \frac{X_{\mathrm{C(Mn},\,b)}}{1 - X_{\mathrm{C(Mn},\,b)}}\right) G_{m,\,b,\,\mathrm{Mn-C}} + 4\pi r^2 N \sigma; \tag{6a}$$

$$G_{m,\,b,\,\mathrm{Fe-C}} = RT\Big[X_{\mathrm{C(Fe},\,b)} \ln\left(X_{\mathrm{C(Fe},\,b)}\right) + $$
$$+ \left(1 - X_{\mathrm{C(Fe},\,b)}\right) \ln\left(1 - X_{\mathrm{C(Fe},\,b)}\right)\Big] + $$
$$+ \Omega_{\mathrm{Fe-C}} X_{\mathrm{C(Fe},\,b)} \left(1 - X_{\mathrm{C(Fe},\,b)}\right); \tag{6b}$$

$$G_{m,\,b,\,\mathrm{Mn-C}} = RT\Big[X_{\mathrm{C(Mn},\,b)} \ln\left(X_{\mathrm{C(Mn},\,b)}\right) + $$
$$+ \left(1 - X_{\mathrm{C(Mn},\,b)}\right) \ln\left(1 - X_{\mathrm{C(Mn},\,b)}\right)\Big] + $$
$$+ \Omega_{\mathrm{Mn-C}} X_{\mathrm{C(Mn},\,b)} \left(1 - X_{\mathrm{C(Mn},\,b)}\right); \tag{6c}$$

$$\sigma = \overset{\circ}{\sigma}_{\mathrm{Fe-C}} - \frac{RT}{\overset{\circ}{\omega}_{\mathrm{Fe-C}}} \ln\left(X_{\mathrm{C(Fe},\,b)}\right) - \frac{\Omega_{\mathrm{Fe-C}}}{\overset{\circ}{\omega}_{\mathrm{Fe-C}}} = $$
$$= \overset{\circ}{\sigma}_{\mathrm{Fe-C}} - \frac{RT}{\overset{\circ}{\omega}_{\mathrm{Fe-C}}} \ln\left(X_{\mathrm{C(Mn},\,b)}\right) - \frac{\Omega_{\mathrm{Mn-C}}}{\overset{\circ}{\omega}_{\mathrm{Fe-C}}}, \tag{6d}$$

where G_{em} is the Gibbs energy of a dispersed system; $G_{m,\,b,\,\mathrm{Fe-C}}$ is the contribution to the Gibbs energy of a dispersed system of G_{em} disperse particles; $G_{m,\,b,\,\mathrm{Mn-C}}$ is the contribution to the Gibbs energy of a dispersed system of G_{em} dispersion medium; σ is excess free energy of the transition layer at the disperse particle and medium interface.

The total number of disperse particles per unit volume N is calculated by the formula

$$N \cong \frac{3 n_{\mathrm{Fe}} V^{\circ}_{m,\,\mathrm{Fe}}}{4\pi r^3} \left(1 + \frac{X_{\mathrm{C(Fe},\,b)}}{1 - X_{\mathrm{C(Fe},\,b)}}\right). \tag{7}$$

Let us determine the Gibbs energy of a dispersed system with a particle size of $r \gg r_{\min}$ (calculation by formula (5)), consisting of three macroscopic phases (a phase with high manganese content, a phase with high iron content, and a phase with high carbon content with a negligibly small interface area between them):

$$G_{no\ em} = n_{\mathrm{Fe}} \left[1 + \frac{X_{\mathrm{C(Fe},\,b,\,eq)}}{1 - X_{\mathrm{C(Fe},\,b,\,eq)}} \left(1 - \frac{n_{\mathrm{C(C-Mn-Fe)}}}{n_{\mathrm{Fe}}}\right)\right] \times$$
$$\times G_{m,\,b,\,\mathrm{Fe-C},\,eq} + n_{\mathrm{Mn}} \left[1 + \frac{X_{\mathrm{C(Mn},\,b,\,eq)}}{1 - X_{\mathrm{C(Mn},\,b,\,eq)}} \times \right.$$
$$\left. \times \left(1 - \frac{n_{\mathrm{C(C-Mn-Fe)}}}{n_{\mathrm{Mn}}}\right)\right] G_{m,\,b,\,\mathrm{Mn-C},\,eq} + n_{\mathrm{C-Mn-Fe}} G_{m,\,b}, \tag{8}$$

where $X_{i(j,\,b,\,eq)}$ is the mole fraction of substance i in the saturated solution in substance j; $G_{m,\,b,\,\mathrm{Fe-C},\,eq}$ (J/mol) is the molar Gibbs energy of the saturated Fe – C solution calculated by substituting $X_{\mathrm{C(Fe},\,b,\,eq)}$ into equation (6*b*) for $G_{m,\,b,\,\mathrm{Fe-C}}$ instead of $X_{\mathrm{C(Fe},\,b)}$; $G_{m,\,b,\,\mathrm{Mn-C}}$ (J/mol) is the molar Gibbs energy of the Mn – C saturated solution, calculated by substituting $X_{\mathrm{C(Mn},\,b,\,eq)}$ into equation (6*c*) for $G_{m,\,b,\,\mathrm{Mn-C}}$ instead of $X_{\mathrm{C(Mn},\,b)}$; $G_{m,\,b}$ is the molar Gibbs energy for the carbon-enriched region; and n_{Fe} and n_{Mn} are the number of iron and manganese moles, respectively.

In the carbon-enriched regions of the dispersed system (the transition layer between a disperse particle and dispersion medium), we calculated the following quantities:

– the number of carbon moles

$$n_{\mathrm{C(C-Mn-Fe)}} = n_{\mathrm{C}} - n_{\mathrm{Fe}} \frac{X_{\mathrm{C(Fe},\,b,\,eq)}}{1 - X_{\mathrm{C(Fe},\,b,\,eq)}} - $$
$$- n_{\mathrm{Mn}} \frac{X_{\mathrm{C(Mn},\,b,\,eq)}}{1 - X_{\mathrm{C(Mn},\,b,\,eq)}}; \tag{9}$$

– the total number of moles

$$n_{\mathrm{C-Mn-Fe}} = n_{\mathrm{C(C-Mn-Fe)}} \times $$
$$\times \left(1 + \frac{X_{\mathrm{C(Fe},\,b,\,eq)}}{1 - X_{\mathrm{C(Fe},\,b,\,eq)}} + \frac{X_{\mathrm{C(Mn},\,b,\,eq)}}{1 - X_{\mathrm{C(Mn},\,b,\,eq)}}\right); \tag{10}$$

– the mole fractions of carbon, manganese and iron

$$X_{\mathrm{C(C)}} = \frac{1}{1 + \dfrac{X_{\mathrm{C}(\mathrm{Fe},\,b,\,eq)}}{1 - X_{\mathrm{C}(\mathrm{Fe},\,b,\,eq)}} + \dfrac{X_{\mathrm{C}(\mathrm{Mn},\,b,\,eq)}}{1 - X_{\mathrm{C}(\mathrm{Mn},\,b,\,eq)}}},$$

$$X_{\mathrm{Mn(C)}} = \frac{\dfrac{X_{\mathrm{C}(\mathrm{Mn},\,b,\,eq)}}{1 - X_{\mathrm{C}(\mathrm{Mn},\,b,\,eq)}}}{1 + \dfrac{X_{\mathrm{C}(\mathrm{Fe},\,b,\,eq)}}{1 - X_{\mathrm{C}(\mathrm{Fe},\,b,\,eq)}} + \dfrac{X_{\mathrm{C}(\mathrm{Mn},\,b,\,eq)}}{1 - X_{\mathrm{C}(\mathrm{Mn},\,b,\,eq)}}}, \tag{11}$$

$$X_{\mathrm{Fe(C)}} = \frac{\dfrac{X_{\mathrm{C}(\mathrm{Fe},\,b,\,eq)}}{1 - X_{\mathrm{C}(\mathrm{Fe},\,b,\,eq)}}}{1 + \dfrac{X_{\mathrm{C}(\mathrm{Fe},\,b,\,eq)}}{1 - X_{\mathrm{C}(\mathrm{Fe},\,b,\,eq)}} + \dfrac{X_{\mathrm{C}(\mathrm{Mn},\,b,\,eq)}}{1 - X_{\mathrm{C}(\mathrm{Mn},\,b,\,eq)}}};$$

– the molar Gibbs energy

$$G_{m,\,b} = RT\Big[X_{\mathrm{C(C)}}\ln\big(X_{\mathrm{C(C)}}\big) + X_{\mathrm{Mn(C)}}\ln\big(X_{\mathrm{Mn(C)}}\big) + \\ + X_{\mathrm{Fe(C)}}\ln\big(X_{\mathrm{Fe(C)}}\big)\Big] + X_{\mathrm{C(C)}}X_{\mathrm{Fe(C)}}\Omega_{\mathrm{Fe-C}} + \\ + X_{\mathrm{C(C)}}X_{\mathrm{Mn(C)}}\Omega_{\mathrm{Mn-C}}.$$

The values of parameters $n_{\mathrm{Fe}} = 9$, $n_{\mathrm{Mn}} = 0.95$, $n_{\mathrm{C}} = 0.04$, $V^{\circ}_{m,\,\mathrm{Fe}} = 7.92\cdot10^{-6}$, $V^{\circ}_{m,\,\mathrm{C}} = 5.2\cdot10^{-6}$, $T = 1900$ K, $\Omega_{\mathrm{Fe-C}} = = 90{,}000$ J/mol, $\Omega_{\mathrm{Mn-C}} = 65{,}000$ J/mol were determined according to the authors [33]. The dependence of excess free energy of the transition layer at the interface of a disperse particle and medium on the disperse particle radius σ(*r*) for the Fe – 10 % Mn – 0.9 % C melt, calculated by formula (6*d*) at $T = 1900$ K, is presented in Figure 1. It is worth noting that at $r > 7\cdot10^{-9}$ m the excess free energy of the transition layer at the interface of a disperse particle and medium is $\sigma < 0$, According to [32] this is a condition of spontaneous dispersion of the system, i.e. disperse particles with radius $r > 7\cdot10^{-9}$ m are thermodynamically unstable.

Figure 2 shows the dependence of the Gibbs free energy of a dispersed system on the disperse particle radius *G*(*r*) for the Fe – 10 % Mn – 0.9 % C melt, calculated at $T = 1900$ K with formula (8), with due regard to the transition layer at the disperse particle and medium interface, and with no regard to it.

The Gibbs free energy of a dispersed system *G*(*r*), calculated with due regard to the transition layer at the disperse particle and medium interface (saturated solution of carbon in iron) appeared to be less than the Gibbs energy of a dispersed system *G*(*r*), calculated with no regard to the transition layer, if the disperse particle radius is $(7.1 – 13.6)\cdot10^{-9}$ m (Figure 2).

Thus, the Fe – 10 % Mn – 0.9 % C melt at $T = 1900$ K can be represented as a dispersed system consisting of disperse particles (Fe – C) $(7.1 – 13.6)\cdot10^{-9}$ m in size and dispersion medium (Mn – C), where the "particle – medium" interface is represented by the saturated solution of carbon in iron. The critical radius of a disperse particle is $6.7\cdot10^{-9}$ m.

Previously, when studying the temperature dependences of kinematic viscosity and specific electrical resistance of Fe – (5.0 – 25.0) % Mn – (0.4 –2.2) % C melts, indirect evidence of their microheterogeneity at temperatures close to liquidus was found [7, 8]. Analysis of temperature dependences of kinematic viscosity in the framework of the theory of absolute reaction rates gave an

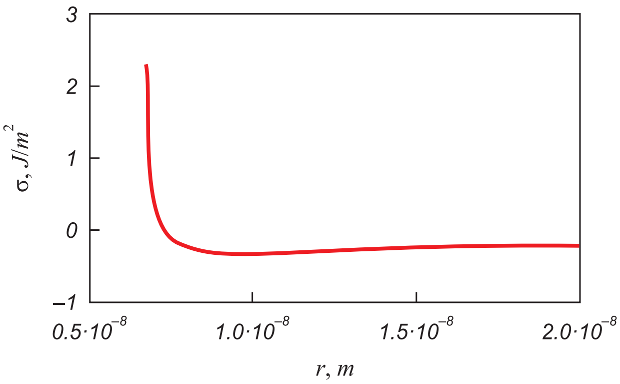

Figure 1. Dependence of excess free energy of the transition layer at the interface of a disperse particle and medium on the disperse particle radius σ(*r*) for the Fe – 10 % Mn – 0.9 % C melt at $T = 1900$ K

Рис. 1. Зависимость избыточной свободной энергии переходного слоя на границе дисперсной частицы и среды от радиуса дисперсной частицы σ(*r*) для расплава Fe – 10 % Mn – 0,9 % C при $T = 1900$ К

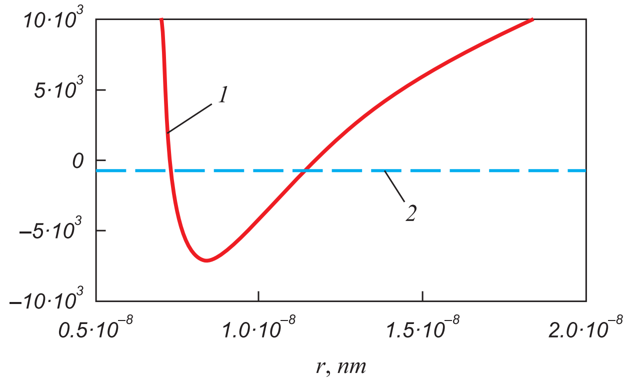

Figure 2. Dependence of Gibbs free energy in a dispersed system on the disperse particle radius *G*(*r*) for the Fe – 10 % Mn – 0.9 % C melt, calculated at $T = 1900$ K with due regard to the transition layer at the disperse particle and medium interface (*1*) and with no regard to the transition layer (*2*)

Рис. 2. Зависимость свободной энергии Гиббса дисперсной системы от радиуса дисперсной частицы *G*(*r*) для расплава Fe – 10 % Mn – 0,9 % C, рассчитанная при $T = 1900$ К с учетом переходного слоя на границе дисперсной частицы и среды (*1*) и без учета наличия переходного слоя (*2*) estimate of the size of structural units of the Fe – Mn – C microheterogeneous melts viscous flow as 34 – 5 nm [7]. This agrees with the estimate of the size of thermodynamically stable disperse particles in this paper.

Conclusion

The study evaluated thermodynamic stability of microheterogeneous states in Fe – Mn – C melts at temperatures close to the liquidus. The Fe – Mn – C melt was considered as a microheterogeneous system. This assumed the existence of disperse particles (Fe – C) in dispersion medium (Mn – C), where the "particle – medium" interface is represented by a saturated solution of carbon in iron. The thermodynamic possibility of disperse particles (Fe – C) existence in dispersion medium (Mn – C), where the "particle – medium" interface is represented by a saturated solution of carbon in iron at $T = 1900$ K is demonstrated. Values of the size of a thermodynamically stable disperse particle concur with the data of the estimate of size of the viscous flow structural unit from the analysis of temperature dependences of the Fe – Mn – C melts kinematic viscosity within the framework of concepts of the absolute reaction rates theory.

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