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Physic-Chemical Properties Forecasting for Manganese Ferroalloy Production Slag

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To forecast viscosity, electrical conduction, crystallization temperature and surface tension of manganese ferroalloy production slag, the models were developed taking into account the temperature factor and in view of physic-chemical model defining the slag melt of any composition as a chemically uniform system.

Keywords: SLAG, FERROALLOYS, CHEMICAL COMPOSITION, MODEL, INTEGRAL PARAMETERS, REGRESSION EQUATIONS, PHYSIC-CHEMICAL PROPERTIES OF SLAG

Introduction

Ferroalloys are produced primarily by carbothermal reduction of mineral raw materials in the electric furnace. Parameters of ore-smelting and product yield considerably depend on physic-chemical properties of oxide melts in both slag and nonslag processes. Ferroalloy is formed in a viscous semiliquid layer in case of nonslag technology when the furnace operates on a complete reduction of oxides. When smelting traditional alloys - silicomanganese and ferromanganese - the role of slag phase is obvious.

When smelting manganese ores and concentrates, slags represent a multicomponent system consisting of oxides of Mn, Si, Ca, Al, Mg and Fe. In this six-component system of oxides, its five- or four-component parts are of interest.

Results and Discussion

According to research data [1], reduction of iron oxides in ore electrometallurgy of manganese begins in the uppermost horizons of furnace at solid state of charge materials and is almost complete to zone of furnace with temperature 1300-1400 °C. Therefore, the final slag of manganese alloy production in the last stage of process in the electric furnace in most cases can be presented on the basis of four-component system MnO-CaO-Al_2O_3-SiO_2 as the total content of other components (MgO, FeO, P_2O_5, S) usually does not exceed 10 %.

Physic-chemical properties of latter system have a dominant effect on technology indexes as a whole. There are data on physic-chemical properties of melts referred to boundary triple diagrams of specified common system or local parts of its quaternary systems. The majority of natural slags cover only separate sections of above-stated system on their composition. In addition, these data are not systematized, there are no diagrams composition-property, which is primarily caused by the absence of effective techniques of multicomponent systems investigation.

There were numerous attempts to formulate the qualitative and quantitative dependences of properties of oxide materials on basicity defined by the ratio of basic oxides to acid ones. It was determined that values of properties could remain constant at change of basicity or, on the contrary, vary in a wide range at constant basicity. Therefore, in multicomponent slags at simultaneous change of concentration of several components even qualitative behavior forecasting by means of basicity concept is problematic, which is indirectly proved by formulas for this criterion evaluation. It is obvious that when estimating dependence of properties of oxide systems on the

composition it is necessary to consider the effect of all components. The known methods of calculation of oxide system properties (method of additivities, substitution, etc.) are restricted by rather narrow range of compositions, which is a logical consequence of not considering characteristics of interatomic interaction and role of melt structure in the formation of their properties.

Applied problems in the field of definition of basic physic-chemical properties of slag and estimation of their refining ability are usually solved by empirical method - direct experiment or on the basis of actual data processing by statistical methods. However, such regression equations as η, χ, σ = f (composition), without regard to approximation accuracy level have such disadvantage as partial contribution of each component is postulated as a constant value that does not dependent on the concentration of other components of the system. Attempts to eliminate this drawback at the expense of polynomial order increase lead to instability of models. Therefore, searching for nonconventional approaches and methods of this problem solution is essential. In the oxide system theory, this searching is related to, first of all, calculation of criteria connected with structure of corresponding melts.

The physic-chemical model of slag melts we used [2] allows considering all similar problems from uniform scientific positions. According to this model concepts based on the theory of silicate melts by A. A. Appen, the structure of molten slag can be presented in the form of anionic framework, a part of which octahedral and tetrahedral interstitial sites is filled by cations. This assumption considers the absence of cations of stationary anionic environment and assumes that effect of cationic composition on properties is accomplished via change of size and anionic polyhedrons joint pattern. The condition of "stability" of such structure is expressed in the form of equations 1 and 2. Equation 1 describes condition of equilibrium of forces acting on the atom in cation sublattice, the latter - in anionic sublattice in terms of effective charges (Z) and radius (R_u). To solve this set of equations by iteration method, the composition of multicomponent oxide melt is reduced to the form $Me_\rho O$, where ρ - stoichometry index. As a result, integral parameter of slag structure is defined by predetermined composition (irrespective of number of its components): Δe - chemical equivalent of composition characterizing interaction of given set of cations with anion-oxygen. Use of this parameter in combination with stoichometry index ρ allows generalizing empirical data in the form appropriate for solving the problem of forecasting irrespective of combination and relationship of concentrations of components of oxide systems.

Investigation of interrelation composition-property at such approach is divided in two parts. The first one comes to calculation of parameters reflecting the features of structure, and the second - to determination of correlations of properties with application of present mathematical processing methods. Experimental data about physic-chemical properties of manganese-containing slags were analyzed in view of suggested model: viscosity (η), electrical conductivity (χ), surface tension (σ), end crystallization temperature (T).

Base "Slag" [3] was applied as information support for forecasting physic-chemical properties of manganese slag. Melts of system MnO-CaO-Al_2O_3-SiO_2 were the basis of investigated experimental data array.

Viscosity of slag

Viscosity of slag is known to have a great effect on conditions of separation and deposition of molten metal drops as well as heat- and mass exchange between ferromanganese layer and oxide melt. Viscosity of slag should promote fast outdropping of metal in alloy, rapid interdiffusion of oxides and reductant as well as optimum distribution of temperature gradient in the melt. Unfortunately, loss of manganese with slag only in the form of metal beads is considerable when producing manganese alloys. In particular, when smelting silicon manganese loss reaches 7.0 % due to high viscosity of final slag as oxidation rate of metal beads through a slag layer is inversely related to viscosity all other things being equal.

$$Z_{Me(Me-E)} - Z_{Me(Me-Me)} = \frac{R_{uE}/R_{uMe} - 0.53}{15.45(tg\alpha_{Me})^{1.507}} + 0.51 \quad \text{(Eq. 1)}$$

$$Z_{E(E-Me)} - Z_{E(E-E)} = \frac{R_{uMe}/R_{uE} - 0.485}{6.067 tg\alpha_{E} - 0.1927} + 0.275 \quad \text{(Eq. 2)}$$

As shown in [4], experimental data of many contributors about viscosity and other properties of slag of system $MnO-CaO-Al_2O_3-SiO_2$ differ essentially, which makes it difficult to generalize them in order to forecast properties by chemical composition.

In publication [5], when researching the interrelation between makeup of 100 slags of system $SiO_2-Al_2O_3-CaO-MgO-MnO$ with their viscosity and melting temperature, regression equations were obtained in the form of incomplete cube polynomial. Such equations are lengthy and applicable for a limited range of given system compositions with low content of MnO, and analysis of their physical sense is complicated.

From E. V. Prikhodko`s theory [2], the model for forecasting viscosity of system $MnO-CaO-Al_2O_3-SiO_2$ was obtained taking into account the temperature factor. For this purpose we used experimental data about viscosity from [8]. The content range of components (mass. %) is following: MnO 5-20; CaO 20-50; SiO_2 35-50; Al_2O_3 10. Results of conducted investigation showed that to forecast viscosity of system $MnO-CaO-Al_2O_3-SiO_2$ it was possible to recommend an option with minimum number of used parameters. So, equation 3 is characterized by correlation coefficient between computation and experimental data r = 0.97 in the temperature range 1250-1700 °C.

$$\lg\eta = 0.0757\Delta e - 1.15\rho + 7388\cdot T^{-1} - 4.42 \quad \text{(Eq. 3)}$$

Compositions of system $MnO-CaO-Al_2O_3-SiO_2$ [6] are presented in **Table 1**. **Figure 1** illustrates the results of integrating data.

Table 1. Chemical composition and model parameters of quaternary oxide system $MnO-CaO-Al_2O_3-SiO_2$

No.	Chemical composition, mass. %				Model parameters			
	MnO	CaO	SiO_2	Al_2O_3	d	Δe	ρ	tgα
1	20.0	25.0	45.0	10.0	3.188	-3.743	0.664	0.1131
2	20.0	35.0	35.0	10.0	3.165	-3.349	0.712	0.1193
3	15.0	30.0	45.0	10.0	3.094	-3.429	0.666	0.1164
4	15.0	35.0	40.0	10.0	3.079	-3.228	0.690	0.1195
5	10.0	30.0	50.0	10.0	3.005	-3.294	0.647	0.1166
6	10.0	35.0	45.0	10.0	2.986	-3.085	0.669	0.1196
7	5.0	45.0	40.0	10.0	2.830	-2.469	0.694	0.1258
8	5.0	50.0	35.0	10.0	2.862	-2.614	0.684	0.1247

Electric conduction

Electric conduction is the major physical property of molten slag. Electric conduction depends on size of cations and anions and interaction between them, i.e. is defined, first of all, by slag composition. Melt temperature has an essential effect on ion mobility, electric conduction of slag melt grows contrary to electric conduction of metal with a rise in temperature. In industrial practice of manganese ferroalloy production by three-phasic silicothermal method, chemical compositions of oxide (slag melts) differ significantly. If high-manganese low-phosphorus charge slag is adequately presented by system $MnO-SiO_2$ on the content of basic components, the final slag of metal manganese smelting has rather high basicity and its properties should be considered within the limits of three-component system $CaO-SiO_2-MnO$. Using experimental data [7], it was determined by correlative-regression analysis that electric conduction of $CaO-SiO_2-MnO$ melts at 1500 °C can be presented as follows:

$$\lg\chi = 6.63\ \rho - 0.175\ \Delta e - 5.55 \quad \text{(Eq. 4)}$$

Figure 2 illustrates comparison of experimental and calculation values χ of oxide melts of three-component system $CaO-SiO_2-MnO$ presented in [7].

We analyzed data about electric conduction of $MnO-CaO-Al_2O_3-SiO_2$ melts taking into account temperature in the interval 1250-1700 °C. As a result of processing data presented in [6] we obtained the following equation:

$$\lg\chi = 4.65\ \rho - 0.397\ \Delta e - 7380 \cdot T^{-1} - 0.005 \quad \text{(Eq. 5)}$$

It follows from represented results that combination of model parameters ρ and Δe ensures high accuracy ($r = 0.99$) of describing empirical data in the content range (% mass.): MnO 5-20; CaO 20-50; SiO_2 35-50; Al_2O_3 10.

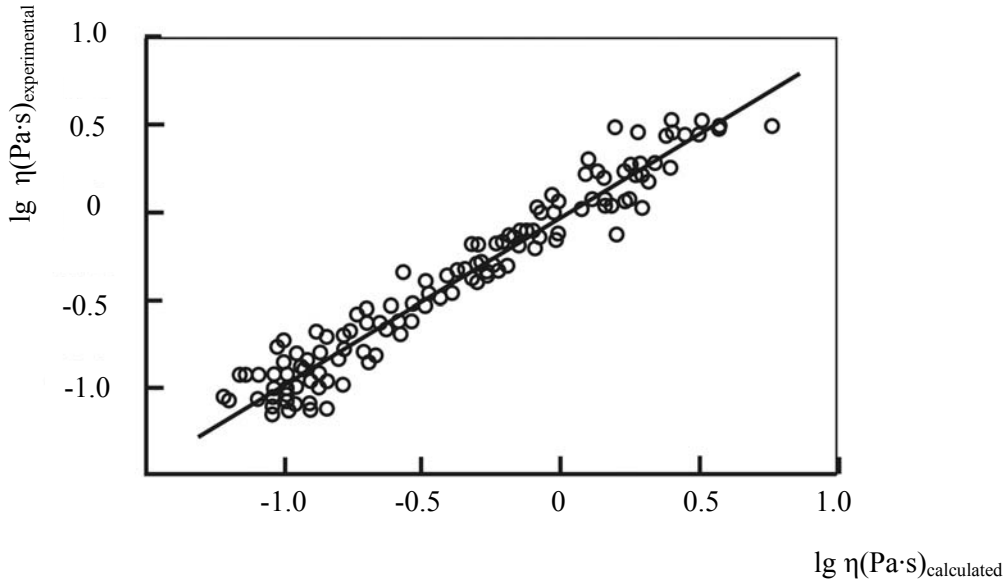

Figure 1. Comparison of experimental and calculated viscosity values of melts of oxide system $MnO-CaO-Al_2O_3-SiO_2$ by equation (3)

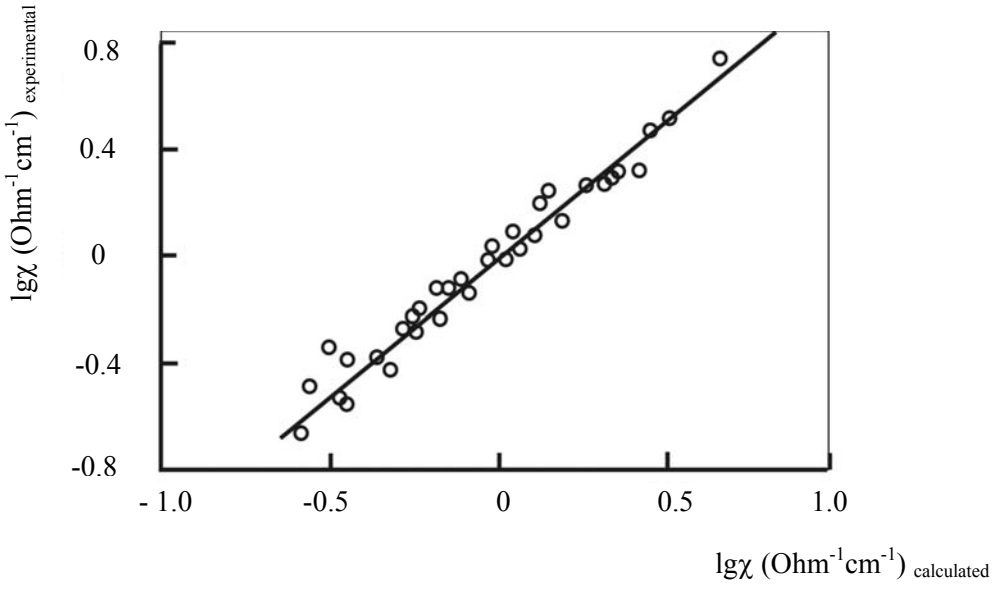

Figure 2. Comparison of experimental and calculated values χ of oxide melts of three-component system $CaO-SiO_2-MnO$ at 1500 ºC

Surface tension

Surface tension investigation gives the information about forces of particle interaction in oxide melts. Value and change of surface tension are caused by many surface phenomena induced by excess of free energy in the boundary layer - surface energy, hyperactivity and orientation of molecules of diffusion layer, features of itsstructure and composition. Analysis of surface tension of manganese oxide - silica - aluminum oxide melts [8] at 1500 °C showed that value σ is most closely related to Δe and ρ and presented by the following regression equation (r = 0.98):

$$\sigma = 2004.0\ \rho - 62.4\ \Delta e - 1206.9 \qquad \text{(Eq. 6)}$$

Comparison of calculated **(**equation 5**)** and experimental values [8] is presented in **Figure 3.**

When estimating accuracy of given interrelation it is necessary to consider that although results of σ measurements by various authors are qualitatively similar, however they differ in a quantitative sense.

It is obvious that specification of experimental data about surface tension of industrial slags of low-phosphorus carbonaceous ferromanganese production [9] at 1500 °C which composition was changed by addition of corresponding oxides for obtaining set ratios CaO/SiO_2 (**Table 2**) by equation with correlation coefficient (r = 0.95) should be considered satisfactory.

$$\sigma = 12147\ \rho - 822.7\ \Delta e - 11076 \qquad \text{(Eq. 7)}$$

Such accuracy allows assuming that effect of chemical composition change on σ in the whole range of its empirical values is reflected correctly and, using equation σ = f (Δe, ρ), it is possible to evaluate theoretically efficiency of effect of any additives in the oxide melt on its surface tension.

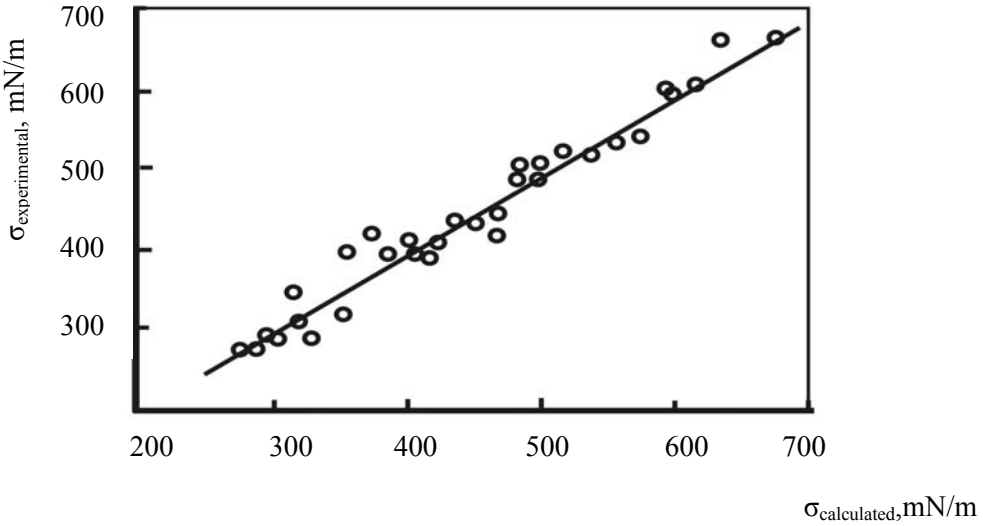

Figure 3. Correlation of experimental and calculated values σ for system $MnO\text{-}SiO_2\text{-}Al_2O_3$ at 1500 ºC

Table 2. Chemical composition, model parameters and surface tension of low-phosphorus ferromanganese slag at 1500 °C

No.	Chemical composition, % mass.					Model parameters		
	MnO	CaO	MgO	SiO_2	S	Δe	ρ	σ, mJ/m^2
1	11.8	38.8	5.8	33.2	0.8	-3.096	0.739	448
2	10.8	40.1	6.0	32.9	4.36	-2.919	0.748	406
3	10.5	41.8	5.8	32.0	4.20	-2.858	0.757	445
4	10.2	43.4	5.7	31.1	4.10	-2.798	0.760	456
5	9.9	44.9	5.5	30.3	4.0	-2.739	0.765	468

Melting temperature

Definition of melting range for real multicomponent metallurgical slag is associated with some difficulties, and available data about start and end temperatures of crystallization are rather conditional and often inconsistent. Generalization of experimental information is complicated by variety of methods to define temperature range of melting or crystallization of oxide systems. As a result, published data frequently do not specify what temperature was defined: start or end of crystallization, start or end of melting, etc. According to [10], end crystallization temperature (T_{ec}) corresponds to sharp increase in viscosity of slag melt to - 5 Pa·s when cooling.

As value Δe is integral characteristic of interaction of cations with anions, comparison of T_{ec} with Δe allows evaluating indirectly the contribution of bonds cation-anion in forming structure and complex of basic thermodynamic properties of oxide melts. This contribution is defining though does not eliminate essential effect of other factors. One of such factors is parameter ρ characterizing probability of filling anionic interstitial sites with cations. The complex account of parameters ρ and Δe allowed obtaining equation 8 with correlation coefficient (r = 0.92)

$$T_{ec} = 240.3\ \rho + 92.8\ \Delta e + 1355.3 \qquad \text{(Eq. 8)}$$

Such accuracy at minimum number of variables allows recommending equation 8 for forecasting the temperature of end crystallization (commencement of liquefaction) of manganese slag of any composition. The composition of several manganese slags and their model parameters are presented in **Table 3**.

Table 3. Composition, parameters of structure and end crystallization temperature of manganese slags

No.	Chemical composition, % mass.							Parameters		T_{ec},
	SiO_2	FeO	Al_2O_3	MnO	CaO	MgO	P_2O_5	ρ	Δe	°C
1	18.0	2.37	5.72	54.7	16.3	0.67	-	0.811	-4.790	1060
2	14.4	0.68	4.60	47.9	12.2	0.46	-	0.814	-4.867	1075
3	20.6	4.16	4.38	59.3	9.62	0.57	-	0.796	-5.072	1130
4	16.68	7.97	5.68	43.76	26.5	0.81	-	0.828	-4.378	1170
5	28.8	0.24	8.20	21.0	39.1	1.18	-	0.749	-3.422	1240
6	29.6	0.38	9.17	15.9	42.13	0.70	-	0.742	-3.104	1245
8	18.2	32.0	2.30	14.0	25.1	6.0	1.45	0.816	-4.028	1170

Thus, model parameters Δe and ρ have accurate and substantial interpretation, characterize chemical activity of multicomponent oxide systems at any combination and ratio of components. It allows recommending the models for calculation of physic-chemical properties of manganese slag melts in order to control the processes of manganese ferroalloy smelting.

Conclusions

1. Correlation relationships between physic-chemical properties of oxide (slag) melts with integral parameters of interatomic interaction Δe and ρ were determined.

2. To forecast properties (viscosity, electrical conduction, surface tension and end crystallization temperature) of manganese ferroalloy production slag at change of their chemical composition, the models were developed taking into account the temperature factor and in view of physic-chemical model defining the slag melt of any composition as a chemically uniform system.

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Прогнозирование физико-химических свойств шлаков производства марганцевых ферросплавов

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С позиций физико-химической модели, трактующей шлаковый расплав любого состава как химически единую систему, с учетом температурного фактора, разработаны модели для прогнозирования вязкости, электропроводности, температуры кристаллизации и поверхностного натяжения шлаков производства марганцевых ферросплавов.