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ACTIVITIES OF CONSTITUENTS IN METALLURGICAL SLAGS ON THE BASIS OF MARGULES EQUATIONS

AKTYWNOŚCI SKŁADNIKÓW W ŻUŻLACH METALURGICZNYCH NA PODSTAWIE ZASTOSOWANYCH RÓWNAŃ MARGULESA

Complex thermodynamic calculations are contemporarily performed using specialist computer software. An integral part of such systems are databases with thermochemical data. The computer system TERMO, developed at the Chair of Extraction and Recycling of Metals of the Technical University of Częstochowa, comprises an extensive database containing thermochemical data for substances useful in metallurgy, including those for slag solutions. The database contains among other things, data and parameters for such models of the thermodynamic description of slags, as G a y e' s model and the regular solutions model. These models are used for the calculations of equilibrium states in heterogeneous systems. It has been found based on the experience gained that these models are characterized in certain cases by a little accurate description of the activities of constituents, which is particularly true for systems with highly diverse interactions in acid slags. Therefore, a proposal is put forward in this study to represent deviations from ideality (in binary and ternary slag solutions) using M a r g u l e s polynomials, as against results obtained using the regular solutions model. The M a r g u l e s model relies on using the expansion of the polynomial of constituent concentrations (up to a specific degree) for the description of the excess free enthalpy of solution, on the assumption that the expression for G^E reaches the value of zero when the mole fractions of the constituents of that solution are equal to unity. The form of the M a r g u l e s polynomial should constitute an optimum of the precision of description and the level of its complexity. For the description of the excess free enthalpy of the binary solution, a fourth-degree polynomial of the following form was employed:

$$G^E_{1-2} = X_1 X_2 (W_{1112} X_1 + W_{1222} X_2 + W_{1122} X_1 X_2),$$

where: X_1, X_2 — mole fractions of solution constituents,
W_{ijkl} — M a r g u l e s parameters fitting the model to experimental data.

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For the performed calculations fitting the parameters W_{ijkl}, a uniform reference state was adopted for the activities of particular solution constituents — in the form of a pure liquid constituent. The calculations concerned the following binary systems: $CaO-SiO_2$, SiO_2-MnO, $CaO-FeO$ and $FeO-SiO_2$, a result of which the parameters W_{ijkl} and their temperature relationships were obtained. Moreover, relationships describing the excess free enthalpies of constituents in the ternary slag $FeO-SiO_2-CaO$ were determined. It has been found on the basis of the analysis carried out that IV-order polynomials can be used for the description of binary and multi-constituent slag solutions more successfully than regular solution models either in their classical formulation or as corrected by S. Ban-ya. The method of proceeding for obtaining the parameters of the model based on Margules polynomials, as presented in this article: will be a basis for the development of a new and alternative variant of thermochemical database for the computer system aiding the caculations of equilibrium states in heterogeneous systems.

Współcześnie złożone obliczenia termodynamiczne przeprowadza się przy użyciu specjalistycznego oprogramowania komputerowego. Integralną częścią takich systemów są bazy danych termochemicznych. Opracowany w Katedrze Ekstrakcji i Recyrkulacji Metali Politechniki Częstochowskiej komputerowy system TERMO zawiera obszerną bazę danych termochemicznych substancji przydatnych w metalurgii, w tym dla roztworów żużlowych. Między innymi zawarte są w bazie dane i parametry dla takich modeli opisu termodynamicznego żużli, jak model Gaye'a i model roztworów regularnych. Modele te są używane do obliczeń stanów równowagi w układach heterofazowych. W wyniku zebranych doświadczeń stwierdzono, że te modele w niektórych przypadkach charakteryzują się mało dokładnym opisem aktywności składników, szczególnie dla układów o silnie zróżnicowanych oddziaływaniach w żużlach kwaśnych. Dlatego w niniejszym opracowaniu poddano propozycję odwzorowania (w roztworach żużlowych dwu i trójskładnikowych) odstępstw od idealności za pomocą wielomianów Margulesa, w porównaniu z wynikami uzyskiwanymi za pomocą modelu roztworów regularnych. Model Margulesa polega na wykorzystaniu do opisu nadmiarowej entalpii swobodnej roztworu rozwinięcia (do określonego stopnia) wielomianu stężeń składników przy założeniu, że wyrażenie dla G^E osiąga wartość zero, gdy ułamki molowe składników tego roztworu równają się jedności. Postać wielomianu Margulesa powinna stanowić optimum precyzji opisu i stopnia jego złożoności. Dla opisu nadmiarowej entalpii swobodnej roztworu dwuskładnikowego zastosowano wielomian czwartego stopnia (*four degree - four suffix*) o następującej postaci

$$G^E_{1-2} = X_1 X_2 (W_{1112} X_1 + W_{1222} X_2 + W_{1122} X_1 X_2),$$

gdzie X_1, X_2 — ułamki molowe składników roztworu,

W_{ijkl} — parametry Margulesa dopasowujące model do danych eksperymentalnych.

Dla przeprowadzonych obliczeń dopasowujących parametry W_{ijkl} przyjęto jednolity stan odniesienia dla aktywności poszczególnych składników roztworu — w postaci czystego ciekłego składnika. Obliczenia dotyczyły następujacych układów podwójnych: $CaO-SiO_2$, SiO_2-MnO, $CaO-FeO$ i $FeO-SiO_2$, w wyniku których otrzymano parametry W_{ijkl} oraz ich zależności temperaturowe. Ponadto określono zależności opisu nadmiarowych entalpii swobodnych składników w żużlu trójskładnikowym $FeO-SiO_2-CaO$.

Na podstawie przeprowadzonej analizy okazało się, że wielomiany IV-rzędu mogą być z lepszym skutkiem stosowane do opisu roztworów dwu- i wieloskładnikowych żużli, niż modele roztworów regularnych w ujęciu klasycznym lub poprawionym przez S. Ban-ya.

Przedstawiony w artykule sposób postępowania dla otrzymywania parametrów modelu opartego na wielomianach Margulesa będzie podstawą opracowania nowego alternatywnego wariantu bazy danych termochemicznych dla komputerowego systemu wspomagania obliczeń stanów równowagi w układach heterofazowych.

1. Introduction

The thermodynamic properties of slags have been absorbing the attention of researches for many decades. During this time, a considerable number of laboratory studies have been carried out on the behaviour of individual constituents in binary and multi-constituent oxide solutions. A substantial part of the results of investigations concerning the properties of slags, including the activities of constituents, have been collected in works [1 – 3]. Independently, theoretical studies were conducted aiming at the formulation of mathematical models that would describe the effect of the chemical composition on the change in the physicochemical and thermodynamic properties of slags. Frequently, a ionic character of the structural constitution of liquid slags was assumed [4 – 5]. For binary and ternary solutions, interesting results have been obtained within new interpretations, as well as a good agreement with the proposed model formalisms. Quasi-chemical models by Yokokawa and Niwa [6] and by Pelton and co-workers [7 – 8] should be mentioned here. The proposals by Masson *et al.* [9 – 10] for the use of the polymerization theory for the explanation of bongs and interactions in silicate solutions look interesting. However, the generalization of all description proposals to cover multi-constituent solutions has not proved to be successful. There are many reasons for this situation, but the most important ones include: a difficult and complex mathematical description and problems in defining the missing parameters of the model based on available experimental data. Therefore, two models with slightly lesser complexity are adopted to the description of multi-constituent slags and are wide used in iron metallurgy, namely: Gaye's model [11], and the regular solutions model. Gaye's model, being an extension of the Frohberg-Kapoor model [12], proves correct for the evaluation of constituent activities in steelmaking slags. The regular solutions model has a longer history. Kozheurov [13], and a little later J. Lumdsen [14], proved sufficiently well the usefulness of this model for the description of equilibrium states in the metal-slag system, and particularly for strongly oxidizing slags. Today, it is widely applied and presented in the publications of Japanese researchers, above all for the analysis of steel refining processes with the participation of a wide range of slags and additional refining agents. The greatest contribution to the propagation of this model was made by S. Ban-ya with his co-workers [15 – 16]. By subjecting to analysis a large collection of experimental data, they determined the parameters of the model for a quite large scale of metallurgical slags.

Complex thermodynamic calculations are contemporarily performed using specialist computer software. An integral part of such systems are databases of thermochemical data. The computer system TERMO, developed at the Department of Metals Extraction and Recirculation of the Technical University of Częstochowa, comprises an extensive database containing thermochemical data for substances useful in metallurgy. The database includes, among other things, data and parameters for such slag thermodynamic description models as G a y e' s model and the regular solutions model. These models are used for the calculations of equilibrium states in heterophasic systems. It has been found based on the experience gained that these model are characterized in some cases by a little accurate description of the activities of constituents, which is particularly true for systems with highly diverse interactions in acid slags. Therefore, a proposal is put forward in this study to represent deviations from ideality (in binary and ternary slag solutions) using M a r g u l e s polynomials, as against results obtained using the regular solutions model.

2. Regular solutions model

According to the regular model, expressions for the description of multi-constituent slag solutions are the following:

$$\overline{G}_i^E = \Delta\overline{H}_i = RT\ln\gamma_i \quad (\overline{S}_i^E = 0), \tag{1}$$

$$RT\ln\gamma_i = \sum_j a_{ij}X_j^2 + \sum_j\sum_k (a_{ij} + a_{ik} - a_{jk})X_jX_k, \tag{2}$$

where: X_j, X_k — mole fractions of the slag constituent cations (j,k),
a_{ij}, a_{ik}, a_{jk} — energies of interaction between corresponding slag cation pairs,
R — gas constant,
T — temperature (K).

The verification of real slag systems shows that some of them, and particularly those which exhibit strong and asymmetric interactions of constituents, should not be described by this type of model formalism, because a very little agreement with experimental data occurs. To improve the model's agreement with the experiment, S. B a n - y a introduced into expression (2) an additional parameter representing an energy change caused by the transformation between the hypothetic regular solution and the real solution, and then expression (2) taken on the form of:

$$RT\ln\gamma_y = \sum_j a_{ij}X_j^2 + \sum_j\sum_k (a_{ij} + a_{ik} - a_{jk})X_jX_k + \Delta G_{\text{trans}}\,. \tag{3}$$

S. B a n - y a defined functional dependencies for ΔG_{trans} for some slag constituents. In spite of the fact that the fitting of the regular model to the experimental results improved to a certain extent upon this operation, yet it is still

insufficient in some cases, the example of which can be the $CaO - SiO_2$ system. Figure 1 shows experimental results for the change of the free enthalpy of silica ($G^E_{SiO_2}$) in the $CaO - SiO_2$ system at a temperature of 1910 K, and relationships resulting from the model description.

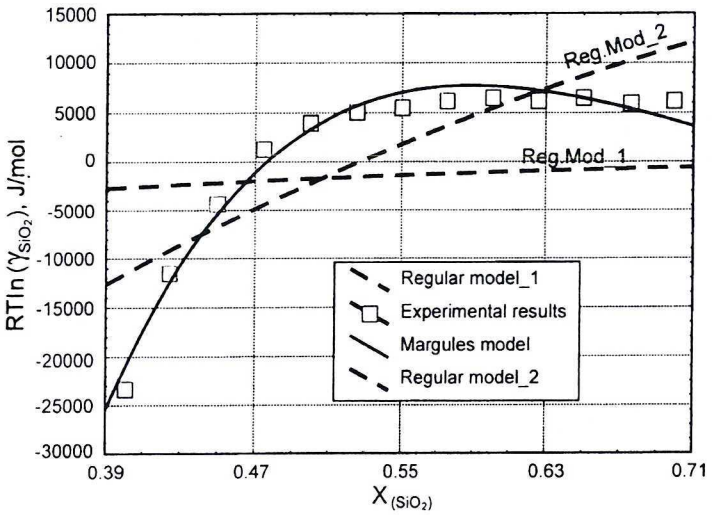

Fig. 1. Comparison of the description of the excess partial enthalpy of SiO_2 in $CaO - SiO_2$ slags using two models ($T = 1910$ K)

The line designated as "Reg.Mod_1" corresponds to the description using relationship (2), whereas "Reg.M_2" refers to relationship (3) that allows for the change in the free enthalpy of the reaction:

$$SiO_{2(liq.)} = SiO_{2(reg.solution)}. \tag{4}$$

It is clearly seen from Figure 1 that the application of the regular model to this type of system does not permit the thermodynamic properties resulting from the deviations of the real solution from the ideal solution to be represented sufficiently well. This situation improves substantially upon the application of a model based on the Margules polynomial.

3. Margules Model

The Margules model relies on using the expansion (to a specific degree) of the constituent concentrations polynomial for the description of the excess free enthalpy of solution, on the assumption that the expression for G^E reaches the value of zero when the mole fractions of that solution are equal to unity. This method is applied in geology for describing the thermodynamic properties of the liquid and solid solutions of various minerals [17 - 18].

3.1. Binary solutions

The form of the Margules polynomial should be a compromise between the precision of description and its complexity. To describe the excess free enthalpy of solution, a fourth-degree polynomial of the following form was used:

$$G^E_{1-2} = X_1 X_2 (W_{1112} X_1 + W_{1222} X_2 + W_{1122} X_1 X_2), \tag{5}$$

where: X_1, X_2 — mole fractions of solution constituents,
W_{ijkl} — Margules parameters fitting the model to experimental data.

Relationships for the partial mole enthalpies of particular constituents, as derived from formula (5) appear as follows:

$$\begin{aligned}\overline{G}^E_1 &= RT \ln \gamma_1 = X_2^2 (2 \cdot W_{1112} X_1 + (1 - 2 \cdot X_1) W_{1222} + X_1 (2 - 3 \cdot X_1) W_{1122}) = \\ &= X_2^2 \left(W_{1222} + 2(W_{1112} - W_{1222} + W_{1122}) X_1 - 3 \cdot W_{1122} X_1^2 \right), \end{aligned} \tag{6}$$

$$\begin{aligned}\overline{G}^E_2 &= RT \ln \gamma_1 = X_1^2 (2 \cdot W_{1222} X_2 + (1 - 2 \cdot X_2) W_{1112} + X_2 (2 - 3 \cdot X_2) W_{1122}) = \\ &= X_1^2 \left(W_{1112} + 2(W_{1222} - W_{1112} + W_{1122}) X_2 - 3 \cdot W_{1122} X_2^2 \right). \end{aligned} \tag{7}$$

If we assume that $W_{1122} = 0$ and $W_{1112} = W_{1222}$, then expressions (6) and (7) can be reduced to the formalism describing the classical model of regular solutions. For the performed calculations fitting the parameters W_{ijkl}, a uniform reference condition was assumed for the activities of particular solution constituents — in the form of a pure liquid constituent. The transition from one condition (a pure solid constituent) to another one (a pure liquid constituent) is defined by the following relationship:

$$a_i^{(\mathrm{liq})} = a_i^{(\mathrm{sol})} \Big/ \exp\left(-\frac{\Delta G^0_{i(m)}}{RT} \right), \tag{8}$$

where $G^0_{i(m)}$ — change of the standard free enthalpy of melting of a slag solution constituent.

3.2. $CaO-SiO_2$ system

To determine the parameters (W_{ijkl}) for $CaO-SiO_2$ system, the values of SiO_2 activity for the three temperatures: 1773 K, 1873 K and 1910 K were used, as reported in works [19–21]. The fitting of model parameters to experimental data was carried out using the "least squares" procedure. The obtained results are summarized in Table 1.

Assuming that there is a linear relationships between the parameters and the temperature, the following set of functional expressions for the parameters

TABLE 1

Results of the calculations of the parameters (W_{ijkl}) for the $CaO(1) - SiO_2(2)$ system

Temperature, K	Parameters (W_{ijkl}), J/mole		
	W_{1112}	W_{1222}	W_{1122}
1773	−50132	−402168	152394
1873	−116918	−644501	411021
1910	−140185	−711168	610038

(W_{ijkl}) have been determined for the temperature range 1773 – 1910 K:

$$W_{1112} = 683364 - 416.87 \cdot T, \tag{9}$$

$$W_{1222} = 1988795 - 1361.87 \cdot T, \tag{10}$$

$$W_{1112} = -3716533 + 2187.5 \cdot T. \tag{11}$$

The agreement of the fitting of experimental reslts (for the temperature 1910 K) with the model relationship represented by the Margules polynomial (7), as shown in Fig. 1, is sufficiently good — as opposed to the regular model.

3.3. $SiO_2 - MnO$ system

Rao and Gaskell [24] have determined the activities of MnO in $SiO_2 - MnO$ slags at the temperatures: 1673, 1773 and 1910 K. Using their data, the model parameters have been calculated. The calculation results are shown in Table 2.

TABLE 2

Results of the calculations of the parameters (W_{ijkl}) for the $SiO_2(1) - MnO(2)$ system

No.	Temperature, K	Parameters (W_{ijkl}), J/mole		
		W_{1112}	W_{1222}	W_{1122}
1	1673	28519	41402	−532330
2	1773	30100	402640	−517959
3	1873	−39734	150894	−226629
4	$f(T)$	$642427 - 359 \cdot T$	$2780794 - 1389 \cdot T$	$-3256716 + 1599 \cdot T$

In Figure 2, characteristics resulting from the thermodynamic models applied are shown as against the results of experimental examinations. Also in this case, the Margules model represents more accuratly the actual behaviour of the slag solution.

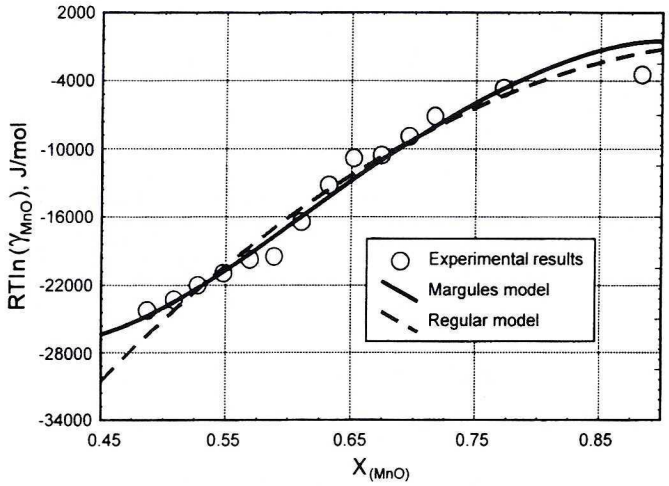

Fig. 2. Comparison of the description of the excess free enthalpy of MnO in $MnO-SiO_2$ slags using two models ($T = 1873\,K$)

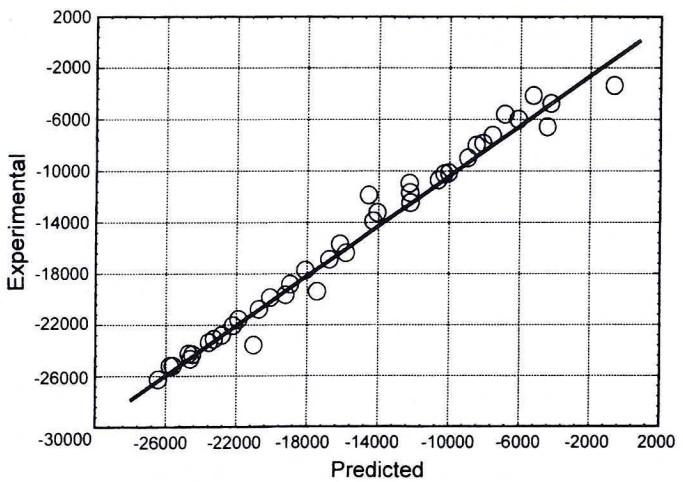

Fig. 3. Comparison of the experimental results ($RT \ln \gamma_{MnO}$) with the values calculated from the model (a temperature relationship) for slags of $MnO-SiO_2$ type

Figure 3 represents a summary and a comparison of experimental results for three temperatures (1673, 1773 and 1873) with the results as obtained from the Margules model while using the parameters given in pos. 4 of Table 2.

3.4. CaO – FeO system

The activities of FeO, as determined for the temperatures: 1667 K [22], 1833 K [23] and 1873 K [22], were a basis for determining the coefficients of Margules

polynomials in a isothermal system and as a function of temperature. The calculation results are summarized in Table 3.

TABLE 3

Results of the calculations of the parameters (W_{ijkl}) for the CaO(1) – FeO(2) system

No.	Temperature, K	Parameters (W_{ijkl}), J/mole		
		W_{1112}	W_{1222}	W_{1122}
1	1673	−13611	24261	−49360
2	1833	−84223	−292040	129339
3	1873	−12555	29894	−58362
4	$f(T)$	$-57394 + 27.03 \cdot T$	$-90378 + 70.2 \cdot T$	$176935 - 139.0 \cdot T$

3.5. $FeO - SiO_2$ system

Data for the $FeO - SiO_2$ system, drawn from work [2], comprise sets of activity values for FeO and SiO_2 for the temperature 1873 K. Using the "least squares" procedure, the following model parameters have been evaluated, (J/mole): $W_{1112} = 22057$, $W_{1222} = -397$, $W_{1122} = -17121$.

3.6. Ternary slags

Excess free enthalpy in ternary solution can be expressed by means of the following relationship:

$$G^E = G^E_{1-2} + G^E_{1-3} + G^E_{2-3} + G^E_{1-2-3}, \tag{12}$$

where: G^E_{1-2}, G^E_{1-3}, G^E_{2-3} — denote contributions of 1 – 2, 1 – 3, 2 – 3 pairs interactions in the description of the excess free enthalpy of ternary solution, G^E_{1-2-3} denote contribution of 1 – 2 – 3 components interactions in the description of the excess free enthalpy of ternary solution.

Frequently, in the absence of data for certain system, it is assumed that the last member of expression (12) takes on the value $G^E_{1-2-3} = 0$. This represents, however, some approximation of the thermodynamic description.

Since expressions for excess enthalpy were assumed for binary systems in the form of a fourth-degree polynomial, then a similar expression can be employed for a ternary system, namely:

$$G^E_{1-2-3} = X_1 X_2 X_3 (W_{1123} X_1 + W_{1223} X_2 + W_{1233} X_3). \tag{13}$$

The relationship describing the effect of the chemical composition on the change of the activity coefficient in ternary solution is obtained by using the dependence

that relates the total value and the partial values of excess enthalpy

$$\overline{G}_i^E = RT \ln \gamma_i = G^E + \sum_{j=2}^{3} (\delta_{ij} - X_j) \frac{\partial G^E}{\partial X_j}, \tag{14}$$

where: δ_{ij} — is the Kronecker symbol ($\delta_{ij} = 0$ for $i \neq j$ and $\delta_{ij} = 1$ for $i = j$).

Starting from formula (12), while considering Margules polynomials ((5) and (13)) for the $FeO - SiO_2 - CaO$ system and making use of relationship (14), the following expression is obtained for the activity coefficient of ferrous oxide:

$$\begin{aligned} RT \ln \gamma_{FeO} = {} & X_{SiO_2}^2 \left(2 \cdot W_{1112}^{FeO-SiO_2} X_{FeO} + (1 - 2 \cdot X_{FeO}) W_{1222}^{FeO-SiO_2} + \right. \\ & \left. X_{FeO}(2 - 3 \cdot X_{FeO}) W_{1122}^{FeO-SiO_2}\right) + \\ & X_{CaO}^2 \left(2 \cdot W_{1112}^{FeO-CaO} X_{FeO} + (1 - 2 \cdot X_{FeO}) W_{1222}^{FeO-CaO} + \right. \\ & \left. X_{FeO}(2 - 3 \cdot X_{FeO}) W_{1122}^{FeO-CaO}\right) + \\ & X_{SiO_2} X_{CaO} \left(-(2 \cdot W_{1112}^{SiO_2-CaO} X_{SiO_2} + 2 \cdot X_{CaO} W_{1222}^{SiO_2-CaO} + \right. \\ & 3 \cdot X_{CaO} X_{SiO_2} W_{1122}^{SiO_2-CaO}) + X_{FeO}(2 - 3 \cdot X_{FeO}) W_{1123}^{FeO-SiO_2-CaO} + \\ & \left. (1 - 3 \cdot X_{FeO})(X_{SiO_2} W_{1223}^{FeO-SiO_2-CaO} + X_{CaO} W_{1133}^{FeO-SiO_2-CaO})\right). \end{aligned} \tag{15}$$

Using the data for FeO activity in $FeO - SiO_2 - CaO$ slags [25], the missing model parameters were determined for excess free enthalpy in the ternary system. Applying a similar fitting procedure the following parameter values were evaluated for the temperature 1873 K (J/mole): $W_{1123} = -890847$, $W_{1223} = 309330$, $W_{1233} = -1099734$. Having these data available, the remaining values of activity coefficients in the $FeO - SiO_2 - CaO$ system can be easily calculated. Extending formula (12) with additional expressions for binary and ternary solutions, an expression can be obtained which describes the thermodynamic state of a multi-constituent slag system. The members expressing the excess free enthalpies of quaternary and higher systems can be neglected in the conducted calculations, and so obtained results will describe the actual state of slags still better than the regular solutions model does.

4. Summary

From among numerous models for the thermodynamic description of slags in the domain of iron metallurgy the regular solutions model, as being partially modified by S. Ban-ya and co-workers, is used. One of the reasons for it being widespread is that the model parameter base worked out embraces a large scope the chemical compositions of slags, and obtained results are the effect of the statistical processing of a considerable number of experimental examinations.

This model has, however, the drawback of not being able to represent sufficiently well the changes of the activity coefficient within a broad range of solution concentrations for slags that are characterized by strong and asymmetric interactions of the constituents.

This situation can be rectified by using more mathematically complex a model of thermodynamic interactions in solutions. One of the methods is to employ Margules polynomials of an appropriate order. It has been found that polynomials of IV order can be used for the description of binary and multi-constituent solution more successfully than regular solutions models either in their classical formulation or as corrected by S. Ban-ya.

The presented in the article method of proceeding for obtaining the parameters of the model based on Margules polynomials will be a basis for developing a new and alternative variant of thermochemical database for the computer system aiding the calculations of equilibrium states in heterophasic systems.

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