PREDICTION OF THERMODYNAMIC PROPERTIES OF MELTS OF $MgO–Al_2O_3–SiO_2–CaF_2$ SYSTEM

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The calculation procedure is proposed for prediction of thermodynamic properties of simple slag melts, allowing for liquidus coordinates of constitutional diagrams. Excess integral functions calculated for more complex systems are given. The possibility of controlling the thermodynamic activity of SiO_2 in slag and, hence, silicon reduction process is shown.

Keywords: *arc welding, high-strength steels, fused flux, slag melts, thermodynamic properties, SiO_2 activity*

Step-by-step implementation of new high-strength steels has been taking place in the recent years. High requirements are made to toughness and strength of welded joints manufactured from these steels. For their fulfillment it is necessary to have a possibility for control of a content of oxygen and sulfur in weld metal, processes of microalloying, formation of non-metallic inclusions and structure in a process of solidification and cooling of a weld.

Silicon oxide are to be included in a flux for providing the necessary welding-technological properties (for pipes, for example, defect-free formation of the welds in multiarc welding with speed higher than 100 m/h are to be provided). However, presence of the latter in the flux during welding of modern steels results in silicon reduction in the weld metal and formation of non-metallic silicate inclusions, which is the reason of deterioration of mechanical properties of the weld metal. A slag system and flux composition, providing combination of optimum technological and metallurgical indices, are, in particular, the aim of our investigations.

Thermodynamic properties of welding consumables are to be known for prediction of metallurgical and technological characteristics. The experimental investigations of oxide melts are complex due to their aggressive behavior and refractoriness. Therefore, the calculation methods for prediction of thermodynamic properties of such melts are widely used in the recent years using similar data for solid compounds and phase equilibriums [1–3]. Present paper proposes a procedure for prediction of thermodynamic properties of melts by liquidus coordinates of constitutional diagrams in area of solid component–solution equilibriums which being described by the following equations:

$$(\mu_1^1)_{T_{eq}} = (\mu_1^{So})_{T_{eq}}, \tag{1}$$

$$\mu_1^{1_0} + RT_{eq} \ln a_1^1 = (\mu_1^{So})_{T_{eq}}, \tag{2}$$

$$RT_{eq} \ln \gamma_1^1 = (-\Delta G_{melt})_{1,\,T_{eq}} - RT_{eq} \ln x_1^1, \tag{3}$$

$$\Delta\bar{H}_1 - T\Delta\bar{S}_1^{ex} = -\Delta G_{melt,\,1} - RT \ln x_1^1, \tag{4}$$

where μ is the chemical potential of component; T_{eq} is the temperature at which solid component–solution equilibrium is considered; ΔS^{ex} is the excess entropy of solution mixing.

Investigations of thermodynamic properties were carried out applicable to $MgO–Al_2O_3–SiO_2–CaF_2$ slag system. These equations were used, however, areas of indicated equilibriums for double oxide and oxide-fluoride melts $MgO–Al_2O_3$, $MgO–SiO_2$, $MgO–CaF_2$, $Al_2O_3–SiO_2$, $Al_2O_3–CaF_2$, $SiO_2–CaF_2$ are not large. Partial molar Gibbs energies of the components from constitutional diagrams in area of pure component–liquid solution equilibrium in $MgO–Al_2O_3$, $MgO–SiO_2$, $MgO–CaF_2$, $Al_2O_3–SiO_2$, $Al_2O_3–CaF_2$, $SiO_2–CaF_2$ binary boundary systems were calculated by equation, obtained from formulae (3) and (4):

$$\Delta\bar{G}_i = \Delta S_{melt}(T_L - T_{melt}),$$

where $\Delta\bar{G}_i$ is the partial molar Gibbs energy of component; ΔS_{melt} is the entropy of melting of pure component; T_{melt} is the temperature of pure component melting; T_L is the liquidus temperature.

Activities of the second component can be found through integration of Gibbs–Dugem equation

$$x_{Al} d \ln (a_{Al}) + x_Y d \ln (a_Y) = 0.$$

Hauffe–Wagner equation was used for area of solid quasibinary compound ($Mg_2Al_2O_4$, Mg_2SiO_4, $Al_6Si_2O_{13}$)–liquid solution equilibrium:

$$\Delta\mu_1(T, x_2) = \Delta S_{melt} \left\{ -\frac{x_2}{x_2 - y_2} \Delta T - y_2 \int_{y_2}^{x_2} \frac{\Delta T}{(x_2 - y_2)^2} dx_2 \right\},$$

where $\Delta\mu_1(T, x_2)$ is the measurement of chemical potential of the component 1 at temperature T and concentration of the component 2 in x_2 melt (standard condition — component in quasibinary compound); ΔS_{melt} is the entropy of compound melting; y_2 is the mole fraction of component 2 in quasibinary compound; $\Delta T = T_{melt} - T_L$.

For MgO–SiO$_2$, MgO–CaF$_2$, SiO$_2$–CaF$_2$ systems, which have areas of delamination of melts on constitutional diagram, used a relation

$$a_i(x_1) = a_i(x_2),$$

where x_1, x_2 are the mole fractions of the component i in the solutions which being in equilibrium to each other as well as $da_i/dx_i = 0$, $d^2a_i/dx_i^2 = 0$ for critical point of delamination.

$\Delta\overline{G}_i^{\text{ex}}$ can be found for binary boundary systems in all concentration interval knowing that $\Delta\overline{G}_i^{\text{ex}} + RTx_i \ln x_i = \Delta\overline{G}_i = RT \ln a_i$, and from them the integral excessive Gibbs energies are determined as $\Delta\overline{G}^{\text{ex}} = \Delta\overline{G}_i^{\text{ex}} x_i$.

Figure 1 shows obtained integral Gibbs energies of mixing recalculated for 1800 K temperature.

It can be seen from the Figure that significant negative values (on absolute value) of Gibbs energy of mixing are character for MgO–Al$_2$O$_3$ and MgO–SiO$_2$ systems in accordance to our calculations, that is proved by formation of stable compounds in these systems. Difference of thermodynamic properties of the solutions from ideal ones is sufficiently small for other systems. Comparison of the predicted Gibbs energies of mixing of melts of Al$_2$O$_3$–SiO$_2$ and MgO–SiO$_2$ binary systems with that which were determined by method of mass spectrometry in works [4, 5] showed that they have good agreement.

Study of thermodynamic properties of three- and four-component systems is more complex problem than of binary ones, however, they often have wide application. Therefore, the methods allowing calculation of thermodynamic properties of three-component melts using data similar for binary boundary sub-systems (method of Bonnier–Caboz, Toop, Li, Colinet, Kohler, Muggianu and etc.) [6] are developed in the last decades. Analysis of these methods showed that Kohler method has no need in additional data on the boundary sub-systems thought not always provide the maximum accuracy. Therefore, the following method was chosen for calculation of excess integral functions in the melts of three- and four-component systems among used by us boundary binary systems:

$$\Delta G^{\text{ex}} = \sum_{A} \sum_{B \neq A} (\Delta\overline{G}^{\text{ex}}AB)_{x_A/x_B}(x_A + x_B)^2,$$

where A, B are all components of three- or four-component system.

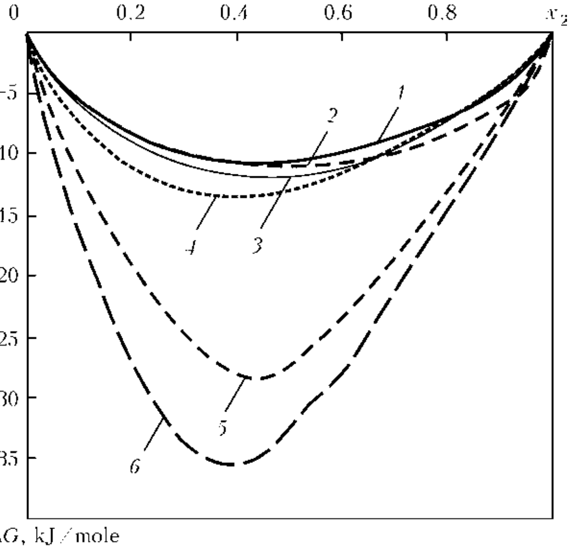

Figure 1. Gibbs energies of mixing of melts of binary systems at 1800 K: *1* — SiO$_2$–CaF$_2$; *2* — Al$_2$O$_3$–SiO$_2$; *3* — Al$_2$O$_3$–CaF$_2$; *4* — MgO–CaF$_2$; *5* — MgO–Al$_2$O$_3$; *6* — MgO–SiO$_2$

Partial excessive Gibbs energies of the components are taken from integral ones through differentiation on formula

$$\Delta\overline{G}_i^{\text{ex}} = \Delta G^{\text{ex}} - x_i \frac{d\Delta G^{\text{ex}}}{dx_i}.$$

Calculation was performed on a special program drawing isolines of excessive Gibbs energies or activities of components over concentration triangular diagrams of the ternary system or section with constant concentration of fourth component for the tetrad system.

Thus, Figure 2 shows calculated isoactivities of SiO$_2$ in three systems among considered ternary systems.

Delamination in area $0.60 < X_{\text{SiO}_2} < 0.99$ is character for melts of MgO–SiO$_2$ system. In this connection isoactivities of SiO$_2$ calculated in this and close to it areas have complex appearance and calculation accuracy is not high. However, reduction of SiO$_2$ concentration promotes negative deviations from Raoult's law.

Isoactivities of SiO$_2$ for section $C_{(\text{CaF}_2)} = 0.25$ of tetrad system MgO–Al$_2$O$_3$–SiO$_2$–CaF$_2$ are given in Figure 3. Data calculated were compared with given in literature [7]. Thus, calculation (lines) and experimental (points) of SiO$_2$ activity in MgO–Al$_2$O$_3$–SiO$_2$ melts at different operating temperatures [7] are given in Figure 4.

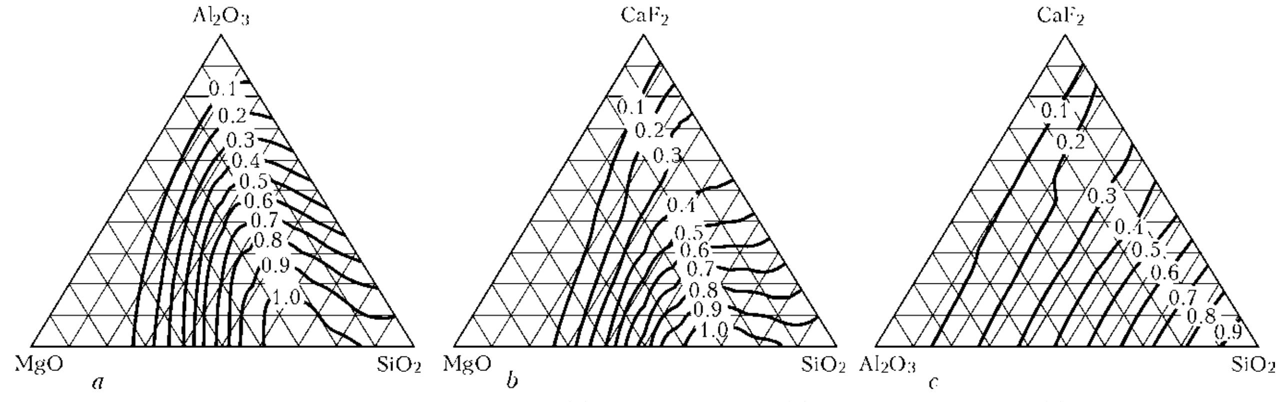

Figure 2. Isoactivities of SiO$_2$ in MgO–Al$_2$O$_3$–SiO$_2$ (*a*), MgO–CaF$_2$–SiO$_2$ (*b*) and Al$_2$O$_3$–CaF$_2$–SiO$_2$ (*c*) melts at 1800 K

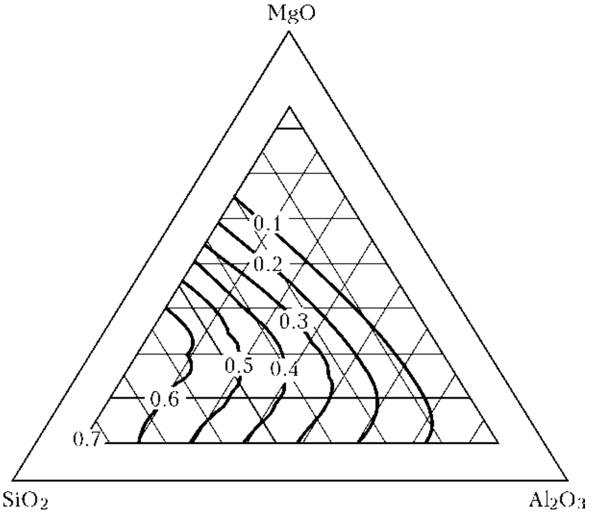

Figure 3. Isoactivities of SiO_2 in $MgO-Al_2O_3-SiO_2-CaF_2$ melt at 1800 K for $C_{(CaF_2)} = 0.25$

It was determined that these data as a whole agree with calculated by us. Thus, predicted alternating deviations from ideal melts for $MgO-SiO_2$ system as well as concentration dependence of SiO_2 activity in $Al_2O_3-SiO_2$ system are proved.

It can be seen from Figures 2, *a*, *b* and 3 that increase of magnesium oxide content in $MgO-Al_2O_3-SiO_2$, $MgO-CaF_2-SiO_2$, $MgO-Al_2O_3-SiO_2-CaF_2$ melts results in reduction of thermodynamic activity of SiO_2 in the melt. Therefore, it is possible to suppress processes of silicon reduction and formation of non-metallic silicate inclusions unnecessary from point of view of metallurgy of welding of low-alloyed high-strength steels and preserve, at that, melt structure and its physical-chemical properties favorable from point of view of providing of necessary technological properties of welding fluxes.

CONCLUSIONS

1. The procedure is proposed for prediction of thermodynamic properties of slag melts by liquidus coordinates of constitutional diagrams in area of solid component–solution equilibrium.

2. Thermodynamic properties of $MgO-Al_2O_3$, $MgO-SiO_2$, $MgO-CaF_2$, $Al_2O_3-SiO_2$, $Al_2O_3-CaF_2$, SiO_2-CaF_2 binary oxide and oxide-fluoride melts were calculated. Significant negative values of Gibbs energies of mixing for $MgO-Al_2O_3$ and $MgO-SiO_2$ systems were found that is proved by formation of stable compounds in these systems. The difference of thermodynamic properties of solutions from ideal ones is sufficiently small for other systems.

3. Calculation of excess integral functions from binary boundary systems was made using Kohler method in the melts of three- and four-component systems. Special program was developed for drawing isolines of excessive Gibbs energies or activities of components on concentration triangular diagram of the ternary system or section with constant concentration of fourth component for the tetrad system.

4. It is determined that increase of magnesium oxide content in $MgO-Al_2O_3-SiO_2$, $MgO-CaF_2-SiO_2$, $MgO-Al_2O_3-SiO_2-CaF_2$ melts results in reduction of thermodynamic activity of SiO_2 in the melt that allows controlling the processes of silicon reduction and formation of silicate non-metallic inclusions.

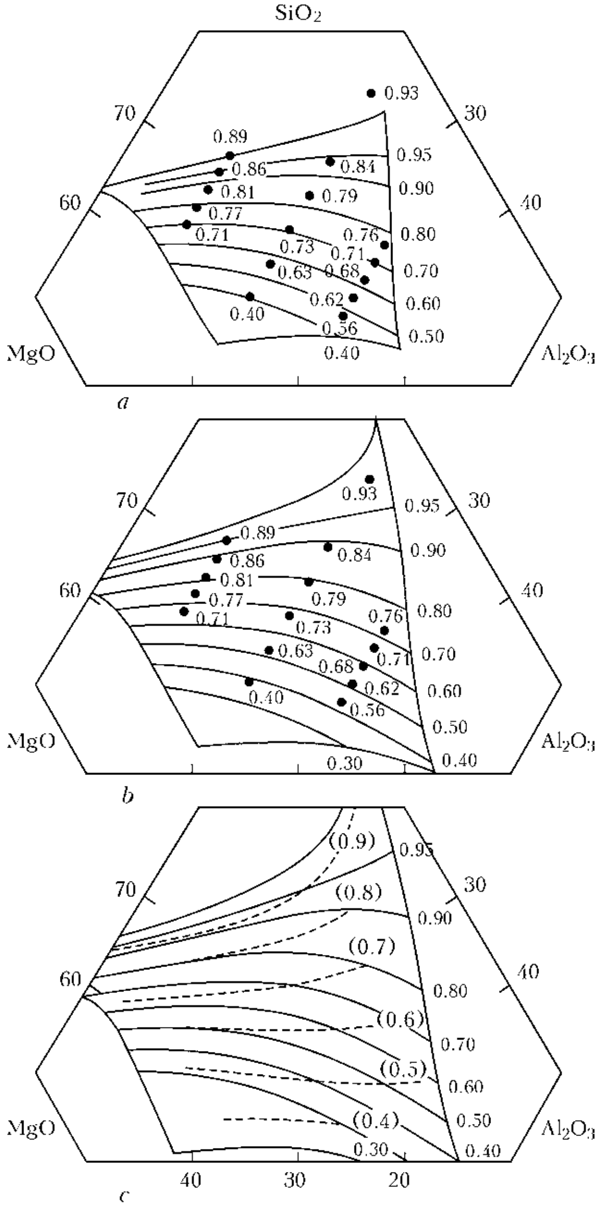

Figure 4. SiO_2 activities at temperature 1500 (*a*), 1550 (*b*) and 1600 (*c*) °C

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