

UDC 541.122

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**THE THERMODYNAMIC PROPERTIES OF MELTS OF THE SYSTEM
MgO – Al₂O₃ – SiO₂, MgO – CaF₂ – SiO₂, Al₂O₃ – CaF₂ – SiO₂**

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Abstract. Method of forecasting thermodynamic properties of melts from the liquidus coordinates of phase diagram in the area of equilibrium of a solid component with a solution is presented. Gibbs mixing energies in the binary boundary MgO – Al₂O₃, MgO – SiO₂, MgO – CaF₂, Al₂O₃ – SiO₂, Al₂O₃ – CaF₂, SiO₂ – CaF₂ systems are calculated by this method.

Keywords: a activity, coordinates of liquidus, the diagrams of the state, the double and triple systems, the equalization of Hauffe-Wagner, the melts, the partial molar energy of Gibbs, the thermodynamics properties.

Introduction

Theoretical methods of forecasting thermodynamic properties of the multicomponent oxide alloys using the analogous data for binary boundary systems, compounds and phase equilibria are widely exploited for some time past.

In the work [1] we described a method for forecasting thermodynamic properties of alloys from the liquidus coordinates of the phase diagram in the concentration range of the pure solid component – solution equilibrium.

We calculated the mixing Gibbs energies of the binary boundary systems

MgO – Al₂O₃,MgO – SiO₂,MgO – CaF₂,Al₂O₃ – SiO₂,Al₂O₃ – CaF₂,SiO₂ – CaF₂ using that method [2].

The methodology of research

We used the Hauffe-Wagner equation for the ranges of the quasibinary compound (MgAl₂O₄, Mg₂SiO₄, Al₆Si₂O₁₃) – solution equilibrium.

The MgO – SiO₂, MgO – CaF₂, SiO₂ – CaF₂ systems, the phase diagrams of which have liquation regions, can be described with the following equations:

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

where x_1, x_2 are molar parts of the i component in the solutions which are in the equilibrium with each other;

$$\frac{da_i}{dx_i} = 0,$$

$$\frac{d^2a_i}{dx_i^2} = 0$$

for the liquation critical point.

Integral mixing Gibbs energies, which are obtained, can be recalculated onto the constant temperature, for example 1800 K.

Studying the thermodynamic properties of the ternary systems is even more complicated problem than for binary ones; however these systems have a wide practical use. So there are some methods developed to calculate the thermodynamic properties of ternary alloys from the analogous data for binary boundary subsystems.

The analysis of these methods showed: though the Kohler method doesn't always give maximal computation precision, but this method doesn't require any additional parameters of the boundary subsystems.

So we used this method to calculate the excess integral thermodynamic functions for the ternary alloys from the binary ones:

$$\Delta G^{exc} = \sum_A \sum_{B \neq A} (\Delta G^{exc}_{AB})_{\frac{x_A}{x_B}} (x_A + x_B)^2,$$

where A, B – all components of the ternary system.

Partial excess of Gibbs energies can be found by differentiation with the formula

$$\Delta \bar{G}_i^{exc} = \Delta G^{exc} - x_i \frac{d\Delta G^{exc}}{dx_i}.$$

Calculation was done with the special program which paints the excess Gibbs isoenergies or the isoactivities of components on the concentration triangle.

The isoactivities of SiO₂ calculated in three of the considered systems are presented on the fig.1.

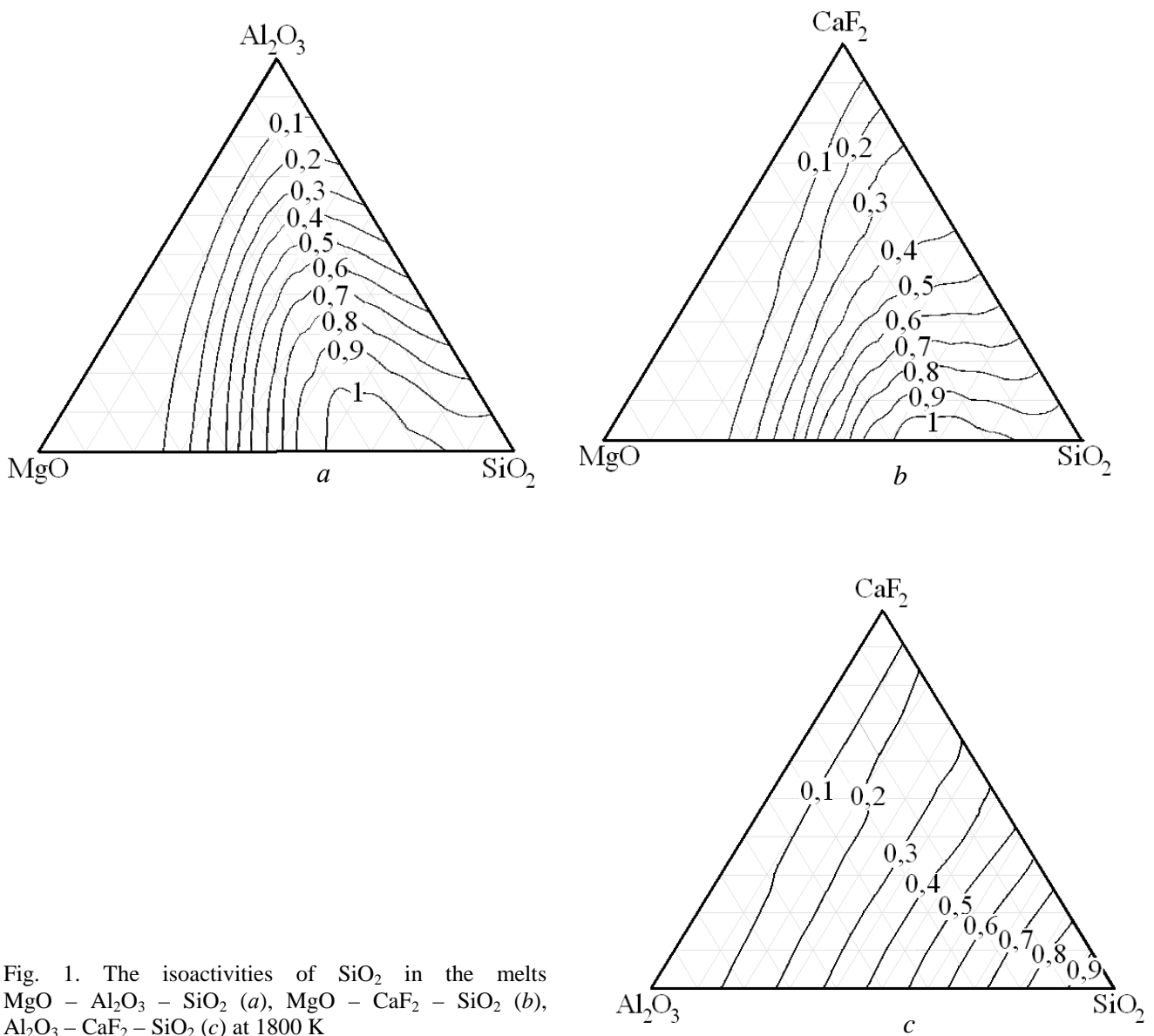


Fig. 1. The isoactivities of SiO₂ in the melts MgO – Al₂O₃ – SiO₂ (a), MgO – CaF₂ – SiO₂ (b), Al₂O₃ – CaF₂ – SiO₂ (c) at 1800 K

The melts of the binary MgO – SiO₂ system are characterized by the liquation in the range $0,6 < x_{\text{SiO}_2} < 0,99$.

So the isoactivities of SiO₂ look specifically and the precision of them is low.

But the negative deviations from the Raoult's law prevail in the range of low SiO₂ concentrations.

To verify the data obtained we compared them with the experimental ones by the authors [2-4].

Activities of SiO₂ in the MgO – Al₂O₃ – SiO₂ melts calculated in the work [4] (lines) and experimental (points) at various temperatures are presented on the fig. 2.

These data agree on the whole with the obtained by us.

For example, the alternating deviations from ideal solutions in the MgO – SiO₂ system, and the concentration dependence of the SiO₂ activity in the Al₂O₃ – SiO₂ system are confirmed.

We also calculated the integral excess Gibbs mixing energies of all ternary melts considered by us.

It was determined that the greatest absolute ΔG^{exc} values are observed in the MgO – Al₂O₃ – SiO₂(CaF₂) melts.

A minimum value of ΔG^{exc} which equals to – 21 kJ/mol is situated on the binary boundary MgO – Al₂O₃ subsystem, and in the melts enriched with SiO₂ they are small positive.

For the other systems small alternating ΔG^{exc} are observed.

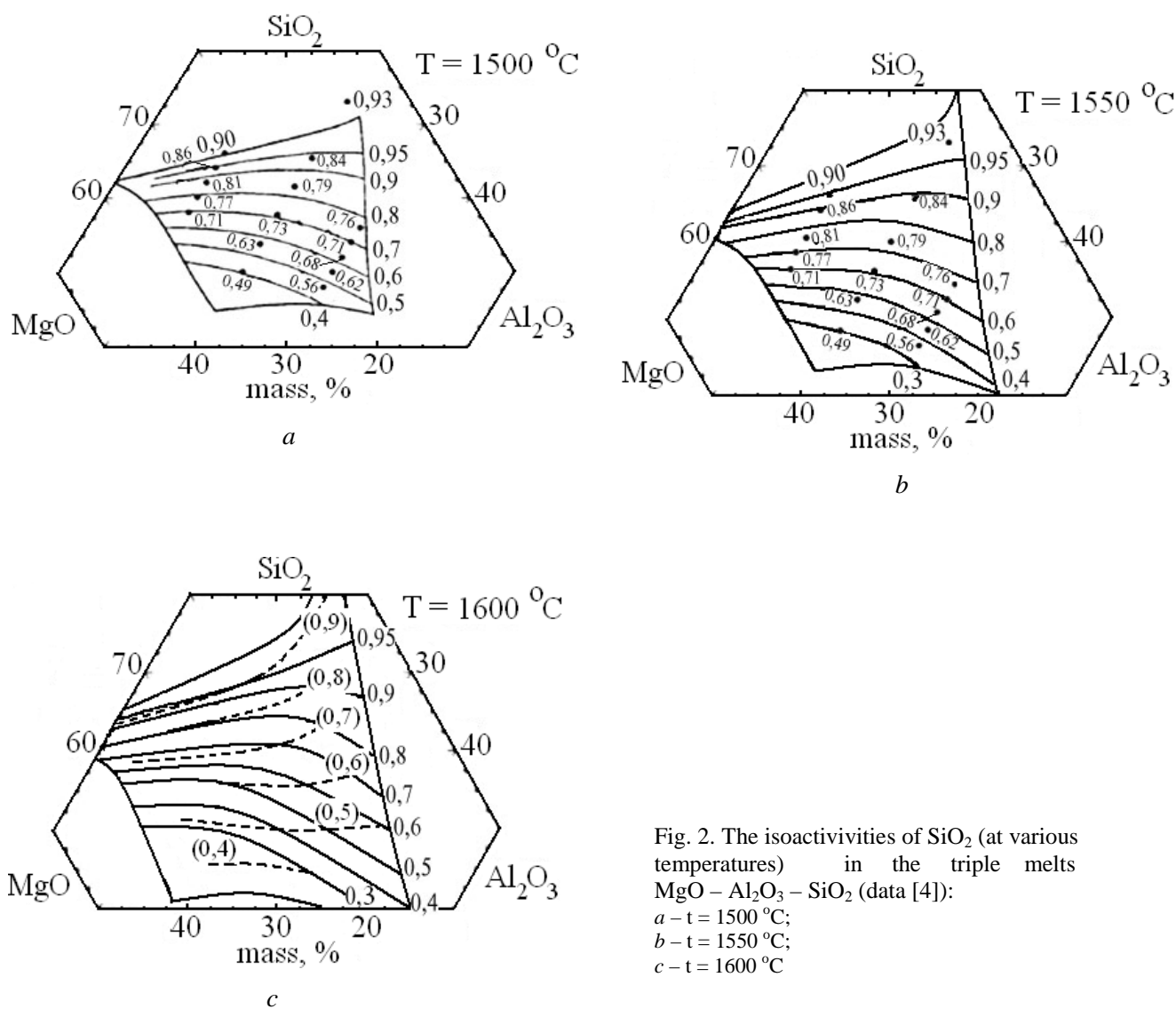


Fig. 2. The isoactivities of SiO₂ (at various temperatures) in the triple melts MgO – Al₂O₃ – SiO₂ (data [4]):
 a – t = 1500 °C;
 b – t = 1550 °C;
 c – t = 1600 °C

Conclusions

From data for the binary boundary systems after equalization of Hauffe-Wagner the mixing Gibbs energies of melts and the activities of components in the ternary MgO – Al₂O₃ – SiO₂, MgO – CaF₂ – SiO₂, Al₂O₃ – CaF₂ – SiO₂ systems at 1800 K are calculated.

It was found that the expected and experimental activities of SiO₂ in the MgO – Al₂O₃ – SiO₂ melts correlate with each other.

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Received 16 March 2011.