

THE DEVELOPMENT OF CALCULATION METHOD OF STRUCTURAL AND THERMODYNAMIC PROPERTIES OF THE MELTS FOR BINARY SYSTEMS WITH STRONG CHEMICAL INTERACTIONS

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Self-consistent of the one associate model (SCAM) [1] for calculation of miscibility gap of melts for the U-O system was used. According to of the SCAM, free energy of liquid phase for A - B system relatively pure components is

$$\Delta F^L(y, \lambda, T) = y_1 \cdot y_2 \cdot \Omega_{12} + y_1 \cdot y_3 \cdot \Omega_{13} + y_2 \cdot y_3 \cdot \Omega_{23} + \Delta F_{f, \lambda}^L(T) + R \cdot T \cdot \sum_{i=1}^3 y_i \cdot \ln(y_i) \quad (1)$$

where $n_0 = n_{A_1} + n_{B_1} + n_{A_p B_q}$, and $y_1 = n_{A_1} / n_0$, $y_2 = n_{B_1} / n_0$, $y_3 \equiv \lambda = n_{A_p B_q} / n_0$ - are mole fractions of A₁, B₁ and association A_pB_q. From conditions of conservation mass for the A_{1-x}B_x alloy of closed binary system we have $y_1 \equiv y_A = 1 - x - p\lambda$, $y_2 \equiv y_B = x - q\lambda$ $p + q = 1$; $\Omega_{ij} = E_{ij} - (E_{ii} + E_{jj}) / 2$ - are mixing parameters between structural elements (species) of melts, $i = 1, 2, 3$; $j = 1, 2$. The free energy formation of associate is

$$\Delta F_{f, \lambda}^L(T) = \Delta H_{f, \lambda}^L(0) - \int_0^T \Delta S_{f, \lambda}^L(T) dT, \text{ where } \Delta H_{f, \lambda}^L(0), \Delta S_{f, \lambda}^L(T) - \text{enthalpies for 0 K and}$$

entropies of formation associate. The equation (2) is allowed to find all structural elements. The equilibrium mole fraction of the associate λ was found from the Equation of State (EoS) (for T, x=constant): $d\Delta F / d\lambda = 0$; $\det \text{Ges} \Delta F(x, \lambda) > 0$ (2). And $\tilde{\lambda} = \tilde{\lambda}(x, T)$ is a solution of the EoS.

From the (2) - (1) was obtained the free energy minimized at $\tilde{\lambda}$ $\Delta \tilde{F}(x, T) = \Delta F \{x, \tilde{\lambda}(x, T), T\}$. Then allows to find the equilibrium composition at T=const

$$\left. \begin{aligned} \frac{d\Delta \tilde{F}(x)}{dx} \Big|_{(x_1, \tilde{\lambda}(x_1))} &= \frac{d\Delta \tilde{F}(x)}{dx} \Big|_{(x_2, \tilde{\lambda}(x_2))} \\ \Delta \tilde{F}(x_1) - x_1 \cdot \left(\frac{d\Delta \tilde{F}(x)}{dx} \right) \Big|_{(x_1, \tilde{\lambda}(x_1))} &= \Delta \tilde{F}(x_2) - x_2 \cdot \left(\frac{d\Delta \tilde{F}(x)}{dx} \right) \Big|_{(x_2, \tilde{\lambda}(x_2))} \end{aligned} \right\} (3)$$

The common methods of solution EoS is not exist (without initial condition). For solving this problem, were made special procedure for separation of roots for equation (2). For solve state system equation (3) was used U-algorithm [2]. The model's parameters was minimized the χ^2 function [2]. The temperature dependence of mixing energy is $\Omega_{ij}(T) = \Omega_{ij}^0 + \Omega_{ij}^1 \cdot T + \Omega_{ij}^2 \cdot T \cdot \ln(T)$. The this model and development software were applying to modeling structural and thermodynamic properties of melts of the U-O system, as well as area immiscibility gap of melts by solution of the inverse problem for calculation optimized values of model's parameters. It was calculated thermodynamic and structural properties of melts depending on composition and the temperature, as well as miscibility gap of melts of the U-O system.

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1. A.L.Udovsky. Proc. of Science-Practical Conf. "Development of Materials with predicted Properties: Methodology and Modeling. Nov.22-26, 2004, Ershovo, Moscow Region. 2004, p.106-107.

2. A.L.Udovsky. Russian Metally, 1990, № 2, p.136-157.