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http://www.nas.gov.ua/pwj
State Registration Certificate
KV 4790 of 09.01.2001

Subscriptions:

\$324, 12 issues per year,
postage and packaging included.
Back issues available.

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PREDICTION OF THERMODYNAMIC PROPERTIES OF MELTS OF MgO–Al₂O₃–SiO₂–CaF₂ 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 SiO₂ in slag and, hence, silicon reduction process is shown.

Keywords: arc welding, high-strength steels, fused flux, slag melts, thermodynamic properties, SiO₂ 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 equilibria [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 equilibria which being described by the following equations:

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

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

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

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

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–Al₂O₃–SiO₂–CaF₂ slag system. These equations were used, however, areas of indicated equilibria for double oxide and oxide-fluoride melts MgO–Al₂O₃, MgO–SiO₂, MgO–CaF₂, Al₂O₃–SiO₂, Al₂O₃–CaF₂, SiO₂–CaF₂ are not large. Partial molar Gibbs energies of the components from constitutional diagrams in area of pure component–liquid solution equilibrium in MgO–Al₂O₃, MgO–SiO₂, MgO–CaF₂, Al₂O₃–SiO₂, Al₂O₃–CaF₂, SiO₂–CaF₂ binary boundary systems were calculated by equation, obtained from formulae (3) and (4):

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

where $\bar{\Delta G}_i$ 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

$$x_A d \ln(a_A) + x_Y d \ln(a_Y) = 0.$$

Hauffe–Wagner equation was used for area of solid quasibinary compound (Mg₂Al₂O₄, Mg₂SiO₄, Al₆Si₂O₁₃)–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; $\Delta T = T_{melt} - T_L$.