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MODELING METHOD OF PHASE EQUILIBRIUM IN METAL-SLAG SYSTEM

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This paper demonstrates a new modeling method of the complex heterogeneous processes between a metal and slag based on a pattern of formation of the crystallization fields of phases. The theoretical justification was provided for the using of the osmotic coefficients of Bjerrum-Guggenheim with the reduction reactions of elements from the liquid oxide melts into metal. As an example, the equilibrium procedure of a carbon-saturated Fe-Si melt with liquid CaO-SiO_2-Al_2O_3 slag was presented and a mathematical model of the complex phase equilibrium in a metal-slag system was provided.

Keywords: heterogeneous phase equilibrium, metal-slag system, Fe-Si/ CaO-SiO_2-Al_2O_3, crystallization surface of carbon, equilibrium constant

INTRODUCTION

In the melting of cast iron and ferroalloys, the distribution of elements between the metal and slag is significantly performed at the phase interface, and the degree of their transition to the metal is primarily determined by a temperature of the process and the thermodynamic properties of the components [1-4].

WAYS OF STUDY

The reduction reaction of the silicon from slag to a carbon-saturated metal is studied, which is significantly performed at the interface between these two phases:

$$(\mathrm{SiO_2})_{\mathrm{slag}} + 2(\mathrm{C})_{\mathrm{Me}} = (\mathrm{Si})_{\mathrm{Me}} + (\mathrm{CO})_{\mathrm{gas}} \qquad (1)$$

The equilibrium constant K_p is defined by a ratio:

$$\mathrm{K_p} = \frac{a_{(Si)} \cdot \mathrm{p}^2_{\mathrm{CO}}}{a_{(\mathrm{SiO_2})} \cdot a^2_{(C)satur.}} = \exp\left(-\frac{\Delta \mathrm{G}^0_{\mathrm{T}}}{\mathrm{RT}}\right) \qquad , (2)$$

where $a_{(Si)}$, $a_{(SiO_2)}$, - activities of components in the metal and slag; p^2_{CO}- the partial pressure of carbon oxide at equilibrium temperature (T); $a^2_{(C)satur.}$- a carbon activity in the liquid metal; T – the temperature equilibrium; R - an absolute gas constant;

ΔG^0_T - the change in the Gibbs energy of the reduction reaction from the liquid slag by the dissolved carbon in a metal.

By analogy with the monovariant “solid-liquid” phase equilibrium, the equilibrium transition of silicon at the metal-slag interface can be studied with using the osmotic coefficient of Bjerrum-Guggenheim of the reduction reaction of an element [5], which binds the thermodynamic equilibrium constant K_p to a composition of the equilibrium phases (i.e. the apparent reaction constant K_c) by a formula:

$$\Phi_{\mathrm{Si}} \cdot \ln \frac{x_{(Si)} \cdot \mathrm{p}^2_{\mathrm{CO}}}{x_{(\mathrm{SiO_2})} \cdot x^2_{(C)satur.}} = \Phi_{\mathrm{Si}} \cdot \ln \mathrm{K_C} = \ln \mathrm{K_p}, \qquad (3)$$

where Φ_{Si} – an osmotic coefficient of Bjerrum-Guggenheim for silicon reduction reaction; $x^2_{(C)satur.}$ - a concentration of carbon in the liquid metal; $x_{(Si)}$, $x_{(SiO_2)}$ - the concentrations of silicon in metal and silicon oxide in slag in the equilibrium phases in the mole units; K_p - a reaction equilibrium constant (1); K_C - an apparent reaction constant (1).

Thus, after the rearrangement of the equation (3), a formula can be received:

$$\ln \frac{x_{(Si)}}{x_{(SiO_2)}} = \frac{1}{\Phi_{(Si)}} \cdot \ln K_p - \ln \frac{p^2_{CO}}{x^2_{(C)satur}}. \qquad (4)$$

Equation (4) is an equation of a distribution coefficient of silicon between the metal and slag depending on a temperature and composition of the initial phases.

Using this equation (4), in the presence of an analytical dependence of the osmotic coefficient of Bjerrum-Guggenheim ($\Phi_{[Si]}$) on the temperature and composition of phases, two groups of the large equilibrium objectives in the complex systems can be solved.

The first objective is generally known experimentally. For known, arbitrarily chosen original compositions of the slag and metal, and for a preset temperature of the system, using a special program of an iterative method, it is possible to define the final compositions of the metal and slag [6-9].

The second objective is peculiar because a temperature of the system and the associated carbon saturation concentration are variable (i.e. a metal composition

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with the set Fe/Si ratio should not be detached from the crystallization surface of carbon).

The experiments should be performed in such a way that the partial pressure of carbon monoxide is constant with a continuous change in temperature. Under these conditions, the temperature value is fixed when the increase (or decrease) in a volume of the gas phase is reversed according to the equation (1). Thus, based on the equation (4), it is necessary to relate the equilibrium final concentrations of the components and CO pressure to an equilibrium constant using the osmotic coefficient of Bjerrum-Guggenheim of a silicon transition from the metal to slag.

The order of the analysis of the state change of the system is determined with a rule of the Gibbs phase: C=K-F+2. Thus, to describe the equilibrium state of the system in the studied case, it is necessary to use six parameters.

It is known for any slag composition:

1) the content of SiO_2;
2) the ratio of CaO / Al_2O_3;
3) the ratio of Fe/Si in the metal is constant;
4) the carbon content in a liquid metal from a preset mathematical equation of the liquidus surface of carbon in the Fe-Si-C system;
5) the equilibrium constant K_p for the reaction (1);
6) a number of moles of the arising (during reduction) or disappearing (during oxidation) silicon; despite the direction of the reaction, the number of moles is always equal to number of moles of silica.

Thus, if the slag composition (ratio of CaO/Al_2O_3 and content of SiO_2, i.e. 2 parameters) and a ratio of Fe/Si in the metal are specified, then, to find the final composition of the metal and temperature where the metal-slag-gas system will be in equilibrium, two equations of connection are required. These are the equations of liquidus surface for carbon in the Fe-Si-$C_{satur.}$ system and equilibrium constants for reaction (1).

The equation of crystallization surface of carbon (5) can be found as a consequence of the connection an equilibrium concentration between the equilibrium saturation concentration of carbon with its activity and the osmotic coefficient of Bjerrum-Guggenheim of the carbon melting:

$$\ln x_{(C)satur.} = \frac{\ln a_{(C)satur.}}{\Phi_{(C)satur.}}. \qquad (5)$$

where $\ln a_{(C)satur.}$ - a carbon activity (saturated) in liquid metal; $x_{(C)satur.}$ - a molar concentration of carbon, an activity of carbon (saturated) in a liquid metal is calculated using the Le Chatelier - Shreder equation; $\Phi_{(C)satur.}$ - the osmotic coefficient of Bjerrum-Guggenheim of the carbon melting in the generalized form for the carbon crystallization region of the ternary system of Fe-Si-C_{satur}. Since the reaction involves the dissolved carbon in the metal which is simultaneously in equilibrium with the solid graphite (reaction is performed in a graphite crucible at p_{co}=1), the pure liquid components are taken as a standard state.

In this case, the carbon activity in the liquid metal ($a^{L}_{(C)satur.}$) (6) will be not equal to unity and calculated using the Le Chatelier – Shreder equation:

$$\ln a^{L}_{(C)satur.} = \frac{\Delta H_{fus,C}}{R}\left(\frac{1}{T_{m,c}} - \frac{1}{T}\right) + \\ + \int_{T_{fus,\ C}}^{T} \frac{1}{RT^{2}} \int_{T_{m,C}}^{T} \Delta C^{S \to L}_{p,C} \cdot dT, \qquad (6)$$

where $\Delta H_{fus,c}$, $T_{m,c}$ – an enthalpy and melting point of pure graphite; R – n absolute gas constant; $\Delta C^{S\to L}_{p,c}$ - change in heat capacity of pure graphite during the melting; T – a current equilibrium temperature for the preset liquid metal and slag compositions.

The osmotic coefficient of Bjerrum-Guggenheim of the carbon melting in generalized form (7) for the carbon crystallization region of the Fe-Si-$C_{satur.}$ system can be expressed through the carbon activity and the Fe/Si ratio in the liquid metal as follows:

$$\Phi_{(C)satur.} = \frac{Z_{Fe}}{Z_{Fe}+Z_{Si}} \cdot \Phi^{C-Fe}_{C} + \frac{Z_{Si}}{Z_{Fe}+Z_{Si}} \cdot \Phi^{C-Si}_{C} + \\ + \frac{Z_{Si} \cdot Z_{Fe}}{(Z_{Fe}+Z_{Si})^{2}} \cdot \Phi_{A} \qquad (7)$$

where Φ^{C-Fe}_{C}, Φ^{C-S}_{C} - a mathematical equations of the osmotic coefficients of carbon in the liquid phase for systems of C-Fe and C-Si obtained with the method of the mathematical processing of the crystallization lines of phases of these systems based on the Bjerrum-Guggenheim concept; $\Phi = (\Phi_{aver.} - Z_{Fe} \cdot \Phi^{C-Fe}_{C} - Z_{Si} \cdot \Phi^{C-Si}_{C})/Z_{Fe} \cdot Z_{Si}$, - an equation of the osmotic coefficient of carbon in the liquid phase along liquidus line for a certain beam of Fe-Si-C system; $\Phi_{aver.}$ – an equation of the osmotic coefficient of carbon for the arbitrary chosen beam; Z_{Fe} and Z_{Si} - a ratio of iron to silicon, for the beam coming out of the carbon peak to a side of Fe-Si of the Fe-Si-C_{satur}. system, i.e. F:Si = Z_{Fe}:Z_{Si} in mole units or $Z_{Fe} = Z_{Fe}/(Z_{Fe}+Z_{Si})$; $Z_{Si} = 1-Z_{Fe}$.

In order to improve the accuracy, it is necessary to study several beams. Having the experimental data from the Fe-Si-C_{satur}. diagram as a dependence of temperature on the carbon concentration for each beam (beams are passed from the figurative carbon point to the Fe-Si side and given by a ratio of iron to silicon concentration).

Further, the data of each beam are processed to find the dependence of the osmotic coefficient on activity by the least squares method. Since the metal is saturated with carbon, its composition at any temperature is always located on the crystallization surface of the carbon of the Fe-Si-$C_{satur.}$ system, and in the CaO-SiO_2-Al_2O_3 system for the equilibrium temperature, there is a single slag composition equilibrium with a preset metal, provided that the Fe/Si ratio in the alloys should be unchanged.

On the left side of equation (4) there are two unknown: $x_{(Si)}$, $x_{(SiO_2)}$ - the molar concentrations of silicon and silica in the metal and slag after the achieving of equilibrium. They can be linked to the original compositions of the metal and slag. For this purpose, reference is made again to reaction (1), thus despite the direction of the reaction, the number of moles of the arising (or disappearing) silicon during reduction (or oxidation) is always equal to number of moles of silica.

Initially the metal has Z_{Si} - moles of silicon. As a result of its restoration from a preset slag, during the achieving of equilibrium, α_{Si} - moles of silicon in the metal can be observed. By the same amount, silica decreases in slag up to $Z_{(SiO2)}$ - $a_{(SiO2)}$ moles. Since the number of moles of (Z_{Fe}, Z_{CaO}, $Z_{(Al_2O_3)}$) -Fe, CaO, Al_2O_3 in metal and slag was not changed, then after equilibrium, the metal and slag will contain (8-10):

$$x_{\mathrm{Si}} = \frac{Z_{[\mathrm{Si}]} + \alpha_{[\mathrm{Si}]}}{Z_{([\mathrm{Fe})]} + Z_{(Si)} + \alpha_{(Si)} + x_{(C)satur.}} = \frac{Z_{(Si)} + \alpha_{(Si)}}{\sum \mathrm{Me}}, \quad (8)$$

$$x_{(\mathrm{SiO_2})} = \frac{Z_{(\mathrm{SiO_2})} - \alpha_{(\mathrm{SiO_2})}}{Z_{(\mathrm{CaO})} + Z_{(\mathrm{Al_2O_3})} + Z_{(\mathrm{SiO_2})} - \alpha_{(\mathrm{SiO_2})}} = \frac{Z_{(\mathrm{SiO_2})} - \alpha_{(\mathrm{SiO_2})}}{\sum Slag} \quad (9)$$

$$x_{(\mathrm{CaO})} = \frac{Z_{(\mathrm{CaO})}}{\sum Slag}; \quad x_{(\mathrm{Al_2}O_3)} = \frac{Z_{(\mathrm{Al_2O_3})}}{\sum Slag}, \quad (10)$$

where $Z_{(Si)}$, $Z_{(Fe)}$, - the number of moles of components in the metal; $Z_{(SiO_2)}$, $Z_{(CaO)}$, $Z_{(Al_2O_3)}$ - number of moles of components in slag; $\alpha_{(Si)}$ - number of moles of silicon in metal reduced from preset slag; $\alpha_{(SiO_2)}$ - the number of moles of silicon oxide lost from a reset slag; $\sum \mathrm{Me}$ - the total number of moles of components in the metal; $\sum Slag$ - the total number of moles of components in the slag. Adding these ratios in formula (4) and, transferring P^2_{CO} and $X^2_{[C]satur.}$ to the left, there will be received:

$$\ln \frac{\left[\frac{Z_{(Si)} + \alpha_{(Si)}}{Z_{(Fe)} + \alpha_{(Si)} + Z_{(Fe)} + X_{(C)satur.}}\right] \cdot P^2_{CO}}{\left[\frac{Z_{(\mathrm{SiO_2})} - \alpha_{(\mathrm{SiO_2})}}{Z_{(\mathrm{SiO_2})} - \alpha_{(SiO_2)} + Z_{(\mathrm{CaO})} + Z_{(\mathrm{Al_2O_3})}}\right] \cdot X^2_{[C]satur.}} = \frac{\ln K_p}{\Phi_{Si}}. \quad (11)$$

In this formula, only one variable is $\alpha_{[Si]}$, i.e. $a_{(Si)} = a_{(SiO_2)}$. This value is also included in the equation of the crystallization surface of graphite (5) through $\Phi_{©satur.}$ and the expressing of the osmotic coefficient of Bjerrum-Guggenheim (Φ_{Si}) of the silicon transition process from slag to metal under the equation (3).

CONCLUSIONS

Equation (11) is fundamental, since it is possible to uniquely determine the final state of the metal-slag system with using the some combinations of the initial data. The system should have only one single solution for a preset state. Equation (11) is calculated by numerical methods on a computer relative to α_{Si} in an iterative way using a special program "Equilibrium".

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