A Sub-regular Solution Model for $MnO-SiO_2-Al_2O_3-CaO$ Molten Slag and Its Applications

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ABSTRACT

A high order sub-regular solution model for predicting the component activities in a homogeneous region of a quaternary system was developed in the Shanghai Enhanced Lab of Ferrometallurgy, which is designated as SELF-SReM4.

SELF-SReM4 is composed of some polynomials of excess mole free energies vs content variable. A group of A_{jkl} parameters is included in the polynomials. Along with the reliable known thermodynamic properties associating the homogeneous region the A_{ikl} parameters can be evaluated. And then the component activities in that region are possible to be predicated.

This paper is devoted to illustrate the applications of SELF-SReM4 for molten slag of $MnO-SiO_2-Al_2O_3-CaO$. The results provide a basis for the optimization of the production of MnSi and the inclusion modification.

1. Introduction

It is emphasized that SELF-SReM4 is applicable to evaluate the thermodynamic properties of a homogeneous region of a random quaternary systems. As the matter of fact, in SELF, besides C-Fe based alloys an analysis of some Si alloys were involved [1]. The purpose of the present paper is to predict the component activities in the liquid region of the molten slag $MnO-SiO_2-Al_2O_3-CaO$ [2], and then to optimize some associated processes.

Certainly, SELF-SReM4 should be attributed to the category of thermodynamics parameter model. It does not concern with the bond structure of the slag, does not intend to link up its macroscopic properties with the features of its micro-structure. So, SELF-SReM cannot be used to substitute for the bond structure model of molten slag being developed in SELF. On the contrary, it can provide a series comparison to the later.

2. The prediction of component activities by means of SELF-SReM4

Take 1, 2, 3, 4 to denote MnO, SiO_2, Al_2O_3, CaO respectively. The final form of SELF-SReM4 is as follows:

$$f_1 = \sum_{2}^{j'}\sum_{0}^{k'}\sum_{0}^{l'} A_{jkl} Y^j Z^k T^l \tag{1}$$

$$f_2 = -\sum_{2}^{j'} A_{j00}/(1-j) + \sum_{2}^{j'}\sum_{0}^{k'}\sum_{0}^{l'} A_{jkl} Y^j Z^k T^l \{1+ (j-k)/Y(1-j)]\} \tag{2}$$

$$f_3 = -\sum_{2}^{j'}\sum_{0}^{k'} A_{jk0}/(1-j) + \sum_{2}^{j'}\sum_{0}^{k'}\sum_{0}^{l'} A_{jkl} Y^j Z^k T^l \{1+[(j-k)/Y(1-j)] + [(k-1)/YZ(1-j)]\} \tag{3}$$

$$f_4 = -\sum_{2}^{j'}\sum_{0}^{k'}\sum_{0}^{l'} A_{jkl} Y/(1-j) - \sum_{2}^{j'}\sum_{0}^{k'}\sum_{0}^{l'} A_{jkl} Y^j Z T^j \{1+[(j-k)/Y(1-j)] +[(k-1)/YZ(1-j)] + [1/YZT(1-j)]\} \tag{4}$$

$$f = -\sum_{2}^{j'} A_{j00} Y/(1-j) - \sum_{2}^{j'}\sum_{1}^{k'} A_{jk0} YZ/(1-j) - \sum_{2}^{j'}\sum_{1}^{k'}\sum_{1}^{l'} A_{jkl} YZT/(1-j) + \sum_{2}^{j'}\sum_{0}^{k'}\sum_{0}^{l'} A_{jkl} Y^j Z^k T^l /(1-j) \tag{5}$$

f_i is the partial molar free energy of the component i, and is the integral molar free energy of the quarternary system. The A_{jkl} involved in these equations are parameters which should be evaluated based on the known boundary conditions. j'+ k'+l' is the order of the sub-regular solution. In this paper, j', k', l ' all are taken to be 4. Xi is the molar fraction of the i component , and Y, Z ,T are the variables of the molar fractions.

$$Y = 1 - X_1 \tag{6}$$

$$Z = 1 - (X_2/Y) \tag{7}$$

$$T = 1 - (X_3/YZ) \tag{8}$$

If the standard of the activity of the component i is taken as its pure solid state, then

$$a_i = X_i \exp[(f_i - \Delta G_i^\circ)/RT] \tag{9}$$

X is the mole fraction. ΔG_i° is the free energy during the state transferring from liquid to solid. The values suggested by ISIJ[3] was adopted in this paper as follows.

$$MnO(l) = MnO(s)$$
$$\Delta G_1^\circ = -52752 + 25.67T \quad (J) \quad (10)$$

$$SiO_2(l) = SiO_2(s)$$
$$\Delta G_2^\circ = -10868 + 5.55T \quad (J) \quad (11)$$

$$Al_2O_3(l) = Al_2O_3(s)$$
$$\Delta G_3^\circ = -124882 + 53.63T \quad (J) \quad (12)$$

$$CaO(l) = CaO(s)$$
$$\Delta G_4^\circ = -99066 + 27.63T \quad (J) \quad (13)$$

Table 1 lists the adopted boundary properties for the evaluation in $MnO-SiO_2-Al_2O_3-CaO$.

Table 1. The used boundary conditions in $MnO-SiO_2-Al_2O_3-CaO$.

Boundary	Information	Ref.
$MnO-SiO_2$	$a_{(MnO)}$ (1923K)	4
$MnO-Al_2O_3$	$a_{(MnO)}$ (1923K)	5
$SiO_2-Al_2O_3$	$a_{(Al2O3)}$ (1923K)	6
SiO_2-CaO	$a_{(SiO2)}$ (1873 K)	7
Al_2O_3-CaO	$a_{(CaO)}$ (1773 K)	8
$MnO-SiO_2-Al_2O_3$	$a_{(MnO)}$ (1923 K)	6
$MnO-SiO_2-CaO$	$a_{(MnO)}$ (1923 K)	9
$MnO-Al_2O_3-CaO$	$a_{(MnO)}$ (1923 K)	9
$SiO_2-Al_2O_3-CaO$	$a_{(SiO2)}$ (1873 K)	7
$MnO-SiO_2-Al_2O_3-CaO$	$a_{(MnO)}$ (1923 1773 K)	9 10

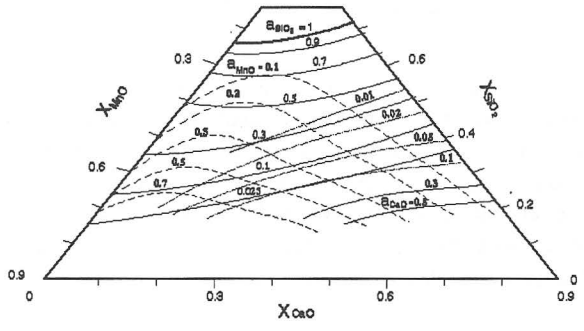

Fig.1a Activities of components in $MnO-SiO_2-Al_2O_3-CaO$ at 1873K and $X_{Al_2O_3} = 0.1$

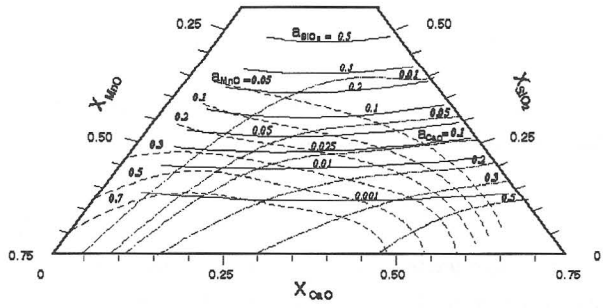

Fig. 1b Activities of components in $MnO-SiO_2-Al_2O_3-CaO$ at 1873K and $X_{Al_2O_3}=0.25$

The evaluated A_{jkl} parameters of the liquid region of $MnO-SiO_2-Al_2O_3-CaO$ under 1873 K in Table 2. The total of A_{jkl} parameters is 55.

Fig.1 is the curves of a_1, a_2 and a_4 under the restriction of 1873 K and X_{Al2O3}= 0.1, 0.25.

Table 2. The A_{jkl} parameters of $MnO-SiO_2-Al_2O_3-CaO$

j	k	l= 0	l= 1	l= 2	l= 3	l= 4
	0	**20364.18**	**0**	**0**	**0**	**0**
	1	**51407.31**	**-1512478**	**53486.7**	**2374882**	**-964271.4**
2	**2**	**-312982.2**	**7932143**	**-4701225**	**-4136081**	**1277958**
	3	**604647.7**	**-12416530**	**10802550**	**-498074.1**	**1137433**
	4	**-330015.9**	**5948135**	**-5991563**	**1788065**	**-1091908**
	0	**-155654**	**0**	**0**	**0**	**0**
	1	**-154730**	**11904010**	**-14831350**	**3753345**	**-462286**
3	**2**	**1207316**	**-44265340**	**41896160**	**4337970**	**-2895840**
	3	**-2297821**	**61696790**	**-56723820**	**-2520007**	**0**
	4	**1179604**	**-28243810**	**26295560**	**0**	**0**
	0	**151995.1**	**0**	**0**	**0**	**0**
	1	**96188.2**	**-13304270**	**22119150**	**-12790780**	**3601156**
4	**2**	**-894208.3**	**42869880**	**-48971320**	**6432668**	**0**
	3	**1645870**	**-55915010**	**55255200**	**0**	**0**
	4	**-775411.4**	**24992650**	**-24240480**	**0**	**0**

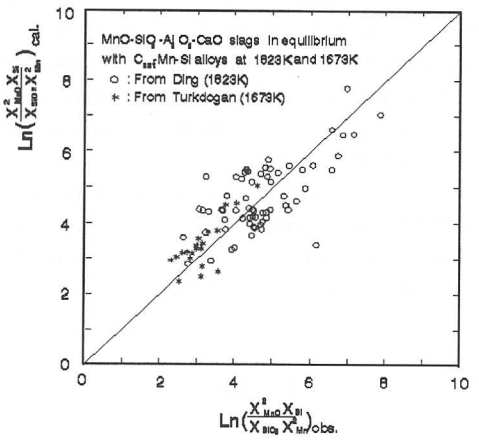

Fig. 2 Comparision of calculated and observed $\frac{X^2_{MnO} X^2_{Si}}{X^2_{SiO_2} X^2_{Mn}}$ in equilibrium at 1823K

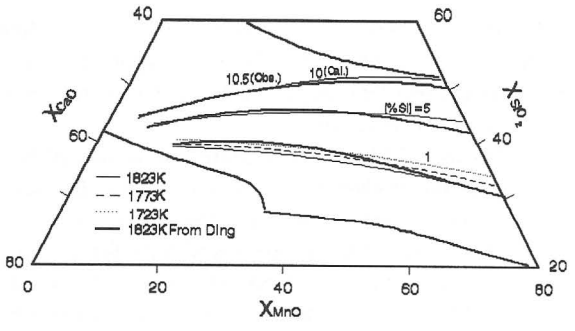

Fig. 3 Equilibrium relations in $MnO-SiO_2-CaO$ saigs in contact with C_{sat} Mn-Si alloys

3. The comparison of the predicted equilibrium state with that of the experiment

The apparent equilibrium constant is

$$K_c = X^2_{MnO} X_{Si} / X_{SiO2} X^2_{Mn} \quad (14)$$

$$\ln(K_c \cdot \Gamma) = \exp(-\Delta G_{SiMn}^{\circ} / RT) \quad (15)$$

$$\Gamma = \gamma_{MnO}^2 \gamma_{Si} / \gamma_{SiO2} \gamma^2_{MnO} \quad (16)$$

The γ_{Si} and γ_{Mn} were calculated based on SELF-SReM4 [11], the standard state of them was taken as the pure liquid. Here, ΔG_{SiMn}° denotes the standard free energy of the following reaction,

$$SiO_2(s) + 2Mn(l) = 2(MnO)(s) + Si(l)$$
$$\Delta G^{\circ} = -138300 + 23.62\,T \quad (17)$$

Fig.2 indicates that K_c observed by Ding (1823K) [12] and Turkdogan(1673K) [13] is in a reasonable agreement with that calcaulated by this model. Moreover, Fig.3 displays three groups of equilibrium curves, for a comparison under three different temperature of 1723, 1773, 1823K and three various [%Si] as 1, 3, 10. Every point on these curves represents the value of a [%Mn] for a given temperature and a given [%Si]. Especially, the case of 10% [Si] and 1823K leads to a clearly evident that the curve resulted from SELF-SReM4 and the experimental curve of Ding are almost overlap each other.

4. The prediction of inclusion modification by means of SELF-SReM4

The modification of inclusions is a key problem in the production of so called clean steel. An investigation on this kind of topic concerns with the variation of inclusions during steel solidification. Arising from the vital difficulty of sampling during steel solidification process, the estimation as shown by Key and Jiang [14], Morales [15], and this paper are quite significant for correct modification of inclusions.

Fig.4 is an estimation for the deoxidization by means of Al-Si-Mn.It indicates the composition of deoxidization products for various [%Si] in the case of $a_o = 70 \cdot 10^{-4}$ % and under 1873K. The a_{Al}, a_{Si}, a_{Mn}, a_o were calculated along with the frequently used method of interaction coefficient. The standard of them was taken as 1% dilute solution. The slag component activities were calculated based on SELF-SReM4.

Usually the compound of $3MnO \cdot Al_2O_3 \cdot SiO_2$ is thought to be the most suitable inclusion. Fig.5 exhibits the region of [%Mn] / [%Si] corresponding to the formation of this kind compound under various temperatures and oxygen potentials.

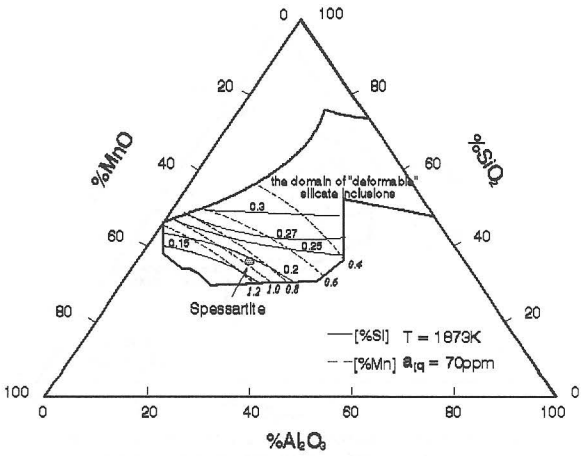

Fig. 4 Iso-content lines of silicon and manganese for $MnO\text{-}SiO_2\text{-}Al_2O_3$ for Al-Si-Mn killed steel at $a_{[o]}$ = 70ppm

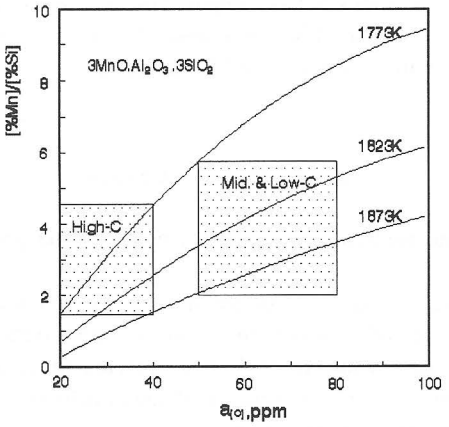

Fig.5 Effect of $a_{[o]}$ and temperture on the critial [%Mn]/[%Si] to spessartite

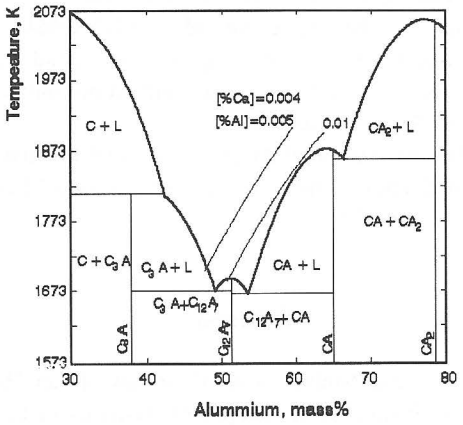

Fig. 6 Effect of temperature on the equilbria for $CaO\text{-}Al_2O_3$ system with Fe-O-Ca-Al

The purpose of calcium treatment is to eliminate Al_2O_3. Fig.6 resulted from the similar way as that used for Fig.4 and 5 expresses the variation of the composition of the treated product vs. the temperature in the cases of different [%Al] and [%Ca]. If it is necessary to acquire a product of ($12\,CaO_7 \cdot Al_2O_3$) under quite lower temperature, then the [%Al] and [%Ca] should be controlled according to the curve "4".

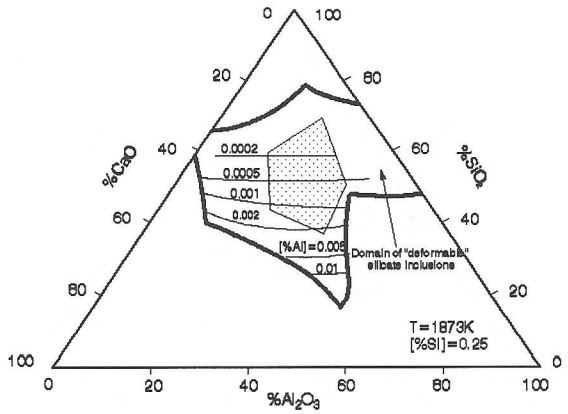

Fig.7 Iso-activitues of alumium in the composition domains of "deformable" silicate inclusins for Si-Mn killed steels with aluminium at 1873K

For the service performance of bearing steel, the spherical inclusions mainly composed of SiO_2, Al_2O_3 and CaO are most harmful. Fig.7 indicates the steel composition associating the composition of the inclusion.

5. Discussion and conclusion

(1) The application of SELF-SReM4 to the prediction of slag ispossible. Comparing the use foralloy, the choose of boundary conditions are more difficult. On the other hand, inside the homogeneous space there are more available information, though the better to check their accuracy before use it.

(2) Inside the polynary slag, where are the boundaries separating liquidand solid, this is a significant research task. By the application of SELF-SReM4 to the homogeneous liquid region and solid region respectively seems to be an interesting approach to solve the mentioned task.

(3) The optimization of the production of MnSi and the modification of inclusions can be successful based on SELF-SReM4.

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