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APPLICATION OF THE COEXISTENCE THEORY OF SLAG STRUCTURE TO MULTICOMPONENT SLAG SYSTEMS

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Synopsis: It is shown by the coexistence theory of slag structure that (1) $K'_{Mn}=N_{MnO}/N_{FeO}/[\%Mn]$ does not change with basicities and maintains constant at constant temperature; (2) the oxidizing capability of multicomponent slag systems expressed by $N_{Fe_tO}=N_{FeO}+6N_{Fe_2O_3}+8N_{Fe_3O_4}$ agree well with the measured a_{Fe_tO}; (3) the desulfurizing capabilities of various basic oxides in multicomponent slag systems are different and L_S calculated by

$$L_S=8(K_{CaS}N_{CaO}+K_{MgS}N_{MgO}+K_{FeS}N_{FeO})\ x\sum n/[\%O]$$

also agree well with the measured values.

Key words: coexistence theory, oxidizing capability, desulfurizing capability, manganese distribution

A lot of paper have already been published in the field for application of the coexistence theory of slag structure to the binary and ternary slag systems [1-6]. In this paper, some examples about application of the coexistence theory of slag structure to multicomponent slag systems are given. First of all, a brief introduction to the coexistence theory of slag structure is presented, then followed by examples about applications.

1. A brief introduction to the coexistence theory of slag structure

Fundamental facts the coexistence theory depends on are:

(1) Facts of crystal chemistry: The oxides in solid state, such as CaO, MgO, MnO, FeO etc. are of (face-centered cubic) ionic cells of NaCl type, therefore, they exist in the form of ions such as Ca^{2+}, Mg^{2+}, Mn^{2+}, Fe^{2+} and O^{2-} already in the solid state, in other words, the viewpoint that basic oxides dissociate into ions in the melting process is unreasonable.

(2) Difference in electric conductivities of slags: basic slags conduct electricity well, acid slags conduct poor and acid oxides don't conduct actually [7,8]. These facts show that not all slags can be regarded as electrolytes.

(3) In the slag systems of $CaO-SiO_2$, $MgO-SiO_2$ etc., two liquids are formed in liquid state at the SiO_2-rich end in the phase-diagram with the composition of one liquid phase nearly to be pure SiO_2[9]. Regarding these as phenomena of saturation, the above-mentioned facts indicate that SiO_2 can exist independently in the molten slags.

(4) Existence of molecules in slags is demonstrated by the congruent melting points in the phase diagrams of various slag systems.

(5) Remarkable difference between lattice energies(1.2-1.6 x 10^5 KJ/kg) and melting energies(2-4 x 10^2 KJ/kg) of silicates shows that melting process is not able to destroy the solid structures of slags completely [10].

(6) Absence of the complex ions SiO_3^{2-} and $Si_3O_9^{6-}$ as well as $Ca_3Si_3O_9$ in the molten slags: The congruent melting point of $CaSiO_3$ in the phase diagram of $CaO-SiO_2$, the ionic nature of $CaF_2(Ca^{2+}+2F^-)$ both in solid and liquid state and the linear relationship between viscosities and mole fractions of $CaSiO_3$ and $(Ca^{2+}+2F^-)$ in the slag system $CaSiO_3-CaF_2$ as shown in Fig.1 [11] tell us that the arguments about the presence of SiO_3^{2-}, $Si_3O_9^{6-}$ and $Ca_3Si_3O_9$ in molten slags are untenable.

(7) Consistency of thermodynamic data and the measured activities of various slag systems with their structures.

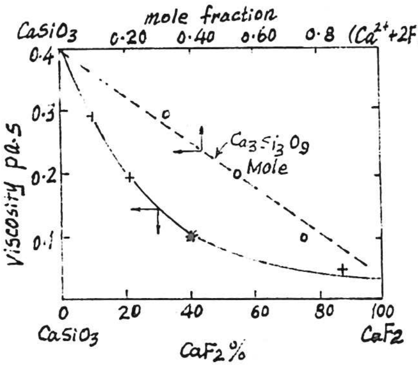

Fig.1 Effect of CaF_2 addition on viscosity of $CaSiO_3$

According to the above mentioned facts, viewpoints of the coexistence theory of slag structure can be summarized as follows:

(1) Molten slags are composed of simple ions such as Na^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Fe^{2+}, O^{2-}, S^{2-}, F^- etc. and molecules such as SiO_2, silicates, phosphates, aluminates etc.

(2) There are mobile equilibrium reactions between simple ions and molecules, taking silicate for example:

$$2(Me^{2+}+O^{2-})+(SiO_2) = (Me_2SiO_4)$$

As CaO, MgO etc. in solid state are of the ionic structure as that of NaCl, so the concentration of MeO should not be expressed in forms of ionic theory as

$$a_{MeO} = N_{MeO} = (N_{Me^{2+}}) \times (N_{O^{2-}})$$

but should be in the form as

$$N_{MeO} = (N_{Me^{2+}}) + (N_{O^{2-}})$$

(3) Chemical reactions in molten slags obey the mass action law.

2. Examples about application of the aforementioned theory

2.1 Manganese equilibrium between $FeO-MnO-MgO-SiO_2$ slags and molten iron

A lot of basic research work has been done to study manganese equilibria between molten slags and iron [12-14], though the authors are different, their results are similar, i.e. at constant temperature, $K'_{Mn} = N_{MnO}/N_{FeO}/[\%Mn]$ are not constant, but change with basicities and compositions of slag, these of course, are contrary to the mass action law, because according to the later, K'_{Mn} are dependent only on temperature. In order to clarify this contradiction, manganese equilibrium between slags and molten iron has been analyzed by means of the coexistence theory of slag structure as follows [1].

On the basis of phase diagrams $FeO-SiO_2$, $MgO-SiO_2$ [15, 16] and research work [2], considering that in $FeO-MnO-MgO-SiO_2$ slag system there isn't any complex compound formed from three or more oxides, structural units of this slag system are determined as Fe^{2+}, Mn^{2+}, Mg^{2+}, O^{2-} simple ions as well as SiO_2, Fe_2SiO_4, $MnSiO_3$, Mn_2SiO_4, $MgSiO_3$ and Mg_2SiO_4 molecules.

Assuming slag compositions $b_1 = \sum n_{FeO}$, $b_2 = \sum n_{MnO}$, $b_3 = \sum n_{MgO}$ and $a = \sum n_{SiO_2}$; mass actin concentrations $N_1 = N_{FeO}$, $N_2 = N_{MnO}$, $N_3 = N_{MgO}$, $N_4 = N_{SiO_4}$; equilibrium constants $K_1 = K_{Fe_2SiO_4}$, $K_2 = K_{MnSiO_3}$, $K_3 = K_{Mn_2SiO_4}$, $K_4 = K_{MgSiO_3}$, $K_5 = K_{Mg_2SiO_4}$ [17-19] and $\sum n$ = total number of moles of ions and molecules, the calculating model of mass action concentrations for this slag system can be deduced as

$$N_1+N_2+N_3+N_4+K_2N_2N_4+K_4N_3N_4+K_1N_1^2N_4+K_3N_2^2N_4+K_5N_3^2N_4-1 = 0 \qquad (1)$$

$$b_1[0.5+(K_2+2K_3N_2)N_4]N_2-b_2(0.5+2K_1N_1N_4)N_1 = 0 \qquad (2)$$

$$b_1[0.5+(K_4+2K_5N_3)N_4]N_3-b_3(0.5+2K_1N_1N_4)N_1 = 0 \qquad (3)$$

$$b_1(1+K_2N_2+K_4N_3+K_1N_1^2+K_3N_2^2+K_5N_3^2)N_4-a(0.5+2K_1N_1N_4)N_1 = 0 \qquad (4)$$

$$\sum n = b_1/(0.5+2K_1N_1N_4)/N_1 \qquad (5)$$

The reaction of manganese between molten slags and iron is

$$[Mn] + (Fe^{2+}+O^{2-}) = [Fe] + (Mn^{2+}+O^{2-}) \qquad (6)$$

$$K'_{Mn} = N_{MnO}/N_{FeO}/[\%Mn]\ ;\ [\%Mn] = N_{MnO}/K'_{Mn}/N_{FeO} \qquad (7)$$

$$L_{Mn} = (\%MnO)/[\%Mn] = 70.9375\sum n[0.5+(K_2+2K_3N_2)N_4]N_2/[\%Mn] \qquad (8)$$

The calculated K'_{Mn} by literature data [20] are shown in Fig.2. As seen in figure, K'_{Mn} are essentially constant and there isn't any relationship between K'_{Mn} and compositions(as well as basicities) of slag. Average $\bar{K}'_{Mn}$(= 3.69644) at 1550°C is in good agreement with K'_{Mn} obtained from manganese equilibrium between FeO+MnO slags and molten iron at 1550°C as given by the following equations.

$$\mathrm{Log}K'_{Mn}=7572/T-3.599 \quad (K'_{Mn}=3.58586 \text{ at } 1550^{\circ}C) \quad [21]$$

$$\mathrm{Log}K'_{Mn}=6440/T-2.95 \quad (K'_{Mn}=3.825 \text{ at } 1550^{\circ}C) \quad [22]$$

Therefore, it can be said that the arguments for K'_{Mn} increasing with the increase of acid oxides, and decreasing with that of basic oxides, as well as the presence of different values of K'_{Mn} in case of acid and basic slags still need further discussion and consideration.

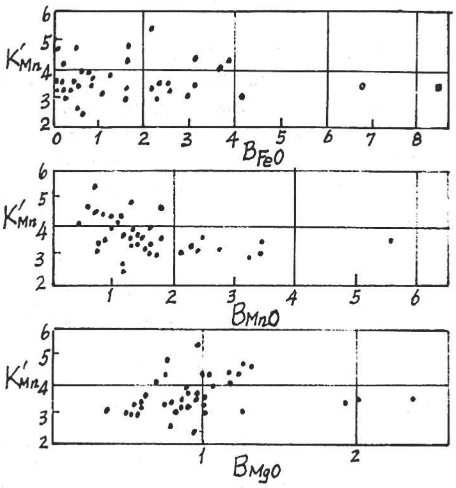

Fig.2 Relation between K'_{Mn} and B_{MeO}

Besides, as shown in Fig.3 and Fig.4, agreement between the calculated and measured [%Mn] as well as between those for L_{Mn} shows that the deduced calculating model of mass action concentrations for $FeO-MnO-MgO-SiO_2$ slags reflects actually the characteristics of this slag system.

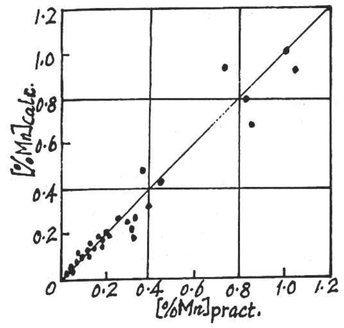

Fig.3 Comparison of calculated and measured [%Mn]

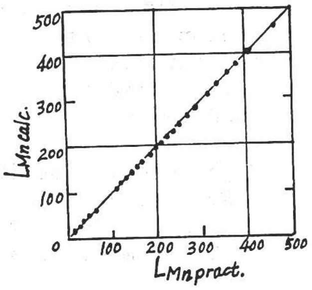

Fig.4 Comparison of calculated and measured L_{Mn}

Finally, it is necessary to point out, that there is a certain fluctuation of K'_{Mn} calculated, which may be mainly due to unconsidered Fe_2O_3 content in the above mentioned slag system.

2.2 Oxidizing capability of multicomponent slag systems

2.2.1 $CaO-FeO-Fe_2O_3-SiO_2$ melts (1258-1370°C)

According to the phase diagrams [15], there should be Ca^{2+}, Fe^{2+}, O^{2-} simple ions as well as Ca_3SiO_5, Ca_2SiO_4, Fe_2SiO_4, $Ca_2Fe_2O_5$, $CaFe_3O_5$, $3CaO\cdot 2SiO_2$, $CaSiO_3$, $CaFe_2O_4$, Fe_3O_4, SiO_2, Fe_2O_3 molecules in this slag system. As for $CaFeSiO_4$, presence of it in the melts in the range of 1258-1370°C can be demonstrated in the course of calculation as shown later.

Assuming $b_1 = \sum n_{CaO}$, $b_2 = \sum n_{FeO}$, $a_1 = \sum n_{SiO_2}$, $a_2 = \sum n_{Fe_2O_3}$; $N_1 = N_{CaO}$, $N_2 = N_{FeO}$, $N_3 = N_{SiO_2}$, $N_4 = N_{Fe_2O_3}$; $K_0 = K_{Ca_3SiO_5}$, $K_1 = K_{Ca_2SiO_4}$, $K_2 = K_{Fe_2SiO_4}$, $K_3 = K_{CaFeSiO_4}$, $K_4 = K_{Ca_2Fe_2O_5}$, $K_5 = K_{CaFe_3O_5}$, $K_6 = K_{3CaO\cdot 2SiO_2}$, $K_7 = K_{CaSiO_3}$, $K_8 = K_{CaFe_2O_4}$, $K_9 = K_{Fe_3O_4}$ [3, 4, 18, 23, 24] and $\sum n$=total number of ions and molecules, the calculating model of mass action concentrations for this slag system can be formulated as:

$$N_1+N_2+N_3+N_4+K_0N_1^3N_3+K_1N_1^2N_3+K_2N_2^2N_3+K_3N_1N_2N_3+K_4N_1^2N_4+K_5N_1N_2N_4+K_6N_1^3N_3^2+K_7N_1N_3+K_8N_1N_4+K_9N_2N_4-1 = 0 \qquad (9)$$

$$0.5(b_1N_2-b_2N_1)+b_1(2K_2N_2N_3+K_9N_4)N_2+(b_1-b_2)(K_3N_3+K_5N_4)N_1N_2-b_2[3K_0N_1^2+2K_1N_1+3K_6N_1^2N_3+K_7)N_3+(2K_4N_1+K_8)N_4]N_1 = 0 \qquad (10)$$

$$0.5a_1N_2-b_2N_3-b_2(K_0N_1^2+K_1N_1+2K_6N_1^2N_3+K_7)N_1N_3+[(2a_1-b_2)K_2N_2+(a_1-b_2)K_3N_1]N_2N_3+a_1(K_5N_1+K_9)N_2N_4 = 0 \qquad (11)$$

$$a_1[1+(K_4N_1+K_5N_2+K_8)N_1+K_9N_2]N_4-a_2[1+(K_0N_1^2+K_1N_1+K_3N_2+2K_6N_1^2N_3+K_7)N_1+K_2N_2^2]N_3 = 0 \qquad (12)$$

$$\sum n = b_2/(0.5+2K_2N_2N_3+K_3N_1N_3+K_5N_1N_4+K_9N_4)/N_2 \qquad (13)$$

As (FeO), (Fe_2O_3), (Fe_3O_4) are all oxidizing agent with respect to liquid iron, according to the following reactions.

$$(Fe_2O_3)+[Fe] = 3(Fe^{2+}+O^{2-}), \qquad (Fe_3O_4)+[Fe] = 4(Fe^{2+}+O^{2-}) \qquad (14)$$

the oxidizing capability of slag with respect to liquid iron can be given as:

$$N_{Fe_tO} = N_{FeO}+6N_{Fe_2O_3}+8N_{Fe_3O_4} \qquad (15)$$

The actual oxidizing capability of slag is

$$a_{Fe_tO} = [\%O]/[\%O]_{sat.} = [\%O]/10^{(-6320/T+2.734)} \qquad (16)$$

Supposing $K_3 = C\sqrt{K_1K_2}$, and using trial and error method, it is shown that when C=20, the agreement between N_{Fe_tO} and a_{Fe_tO} is most satisfactory, as shown in Fig.5. This fact shows that, in the temperature range of 1258 — 1370°C, the formation reaction of $CaFeSiO_4$ is really going on in the molten slag. The relation between $K_3(\Delta G^o_{CaFeSiO_4})$ and temperature can be given as.

$$\mathrm{Log}K_3 = 3811/T+1.53 \qquad (r = 1) \qquad (17)$$

$$\Delta G^o_{CaFeSiO_4} = -72996.8-29.3169T \quad \mathrm{J/mol} \qquad (18)$$

Hence the argument about $CaFeSiO_4$ decomposition above 1230°C still needs further discussion and consideration.

2.2.2 $CaO-MgO-FeO-Fe_2O_3-SiO_2-S$ melts (1550-1650°C)

Similarly, assuming $b_1 = \sum n_{CaO}$, $b_2 = \sum n_{MgO}$, $b_3 = \sum n_{FeO}$, $a_1 = \sum n_{SiO_2}$, $a_2 = \sum n_{Fe_2O_3}$; $N_1 = N_{CaO}$, $N_2 = N_{MgO}$, $N_3 = N_{FeO}$, $N_4 = N_{SiO_2}$, $N_5 = N_{Fe_2O_3}$, $N_{20} = N_{S^{2-}}$, the calculating model of mass action concentrations for this slag system can be derived as:

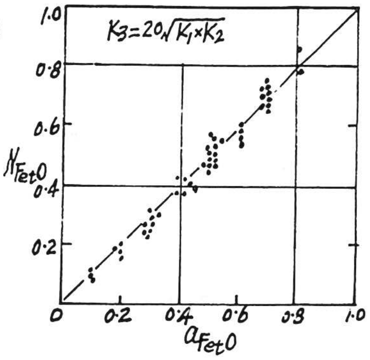

Fig.5 Comparison of N_{Fe_tO} with a_{Fe_tO} (using Bodsworth's data [25])

$$N_1+N_2+N_3+N_4+N_5+K_0N_1N_4+K_1N_2N_4+K_2N_1N_5+K_3N_2N_5+K_4N_3N_5+K_5N_1^2N_4+K_6N_2^2N_4+K_7N_3^2N_4+ \\ +K_8N_1N_2N_4+K_9N_1^2N_5+K_{10}N_1^3N_4+K_{11}N_1N_2N_4^2+K_{12}N_1^2N_2N_4^2+K_{13}N_1^3N_2N_4^2+N_{20}-1 = 0 \tag{19}$$

$$0.5(b_1N_3-b_3N_1)+b_1(K_4N_3N_5+2K_7N_3^2N_4)-b_3[(K_0N_4+K_2N_5+K_8N_2N_4+K_{11}N_2N_4^2)N_1+ \\ 2(K_5N_4+K_9N_5+K_{12}N_2N_4^2)N_1^2+3(K_{10}+K_{13}N_2N_4)N_1^3N_4] = 0 \tag{20}$$

$$0.5(b_2N_3-b_3N_2)+b_2(K_4N_5+2K_7N_3N_4)N_3-b_3[K_3N_5+(K_1+2K_6N_2+K_8N_1)N_4+(K_{11}+ \\ K_{12}N_1+K_{13}N_1^2)N_1N_4^2]N_2 = 0 \tag{21}$$

$$0.5a_1N_3-b_3N_4+a_1(K_4N_5+2K_7N_3N_4)N_3-b_3[(K_0+K_5N_1+K_8N_2+K_{10}N_1^2)N_1+2(K_{11}+ \\ K_{12}N_1+K_{13}N_1^2)N_1N_2N_4]N_4 = 0 \tag{22}$$

$$0.5a_2N_3-b_3N_5+[(a_2-b_3)K_4N_5+2a_2K_7N_3N_4]N_3-b_3[K_3N_2+(K_2+K_9N_1)N_1]N_5 = 0 \tag{23}$$

$$\sum n = b_3/(0.5+K_4N_5+2K_7N_3N_4)/N_3 \tag{24}$$

Meanwhile, the calculated and actual oxidizing capabilities of this slag system are also expressed by equations (15) and (16) respectively.

As shown in Fig.6, calculated N_{Fe_tO} is in good agreement with a_{Fe_tO}. So it can be concluded that the coexistence theory of slag structure is applicable to calculate the oxidizing capability for multicomponent slag systems.

2.3 Distribution of sulfur between molten slags and liquid iron

Desulfurization reactions between CaO-MgO-FeO-Fe$_2$O$_3$-SiO$_2$ slag melts and liquid iron can be written as:

$$\left.\begin{aligned} &(Ca^{2+}+O^{2-})+[S] = (Ca^{2+}+S^{2-})+[O] \\ &K_{CaS}=N_{CaS}N_{[O]}/N_{CaO}N_{[S]}=(\%S)_{CaS}[\%O]/8N_{CaO}[\%S]\sum n \\ &L_{CaS} = (\%S)_{CaS}/[\%S] = 8K_{CaS}N_{CaO}\times\sum n/[\%O] \end{aligned}\right\} \tag{25}$$

$$\left.\begin{aligned} &(Mg^{2+}+O^{2-})+[S] = (Mg^{2+}+S^{2-})+[O] \\ &L_{MgS} = (\%S)_{MgS}/[\%S] = 8K_{MgS}N_{MgO}\times\sum n/[\%O] \end{aligned}\right\} \tag{26}$$

$$\left.\begin{aligned} &(Fe^{2+}+O^{2-})+[S] = (Fe^{2+}+S^{2-})+[O] \\ &L_{FeS} = (\%S)_{FeS}/[\%S] = 8K_{FeS}N_{FeO}\times\sum n/[\%O] \end{aligned}\right\} \tag{27}$$

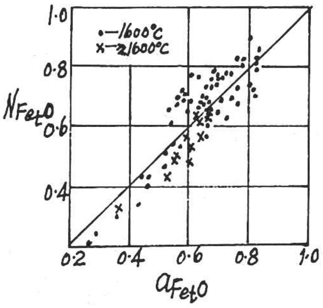

Fig.6 Comparison of N_{Fe_tO} with a_{Fe_tO} (using data [26])

Hence, distribution of sulfur between these slag melts and liquid iron is

$$L_S = [(\%S)_{CaS}+(\%S)_{MgS}+(\%S)_{FeS}]/[\%S] = 8(K_{CaS}N_{CaO}+K_{MgS}N_{MgO}+K_{FeS}N_{FeO})\times\sum n/[\%O] \tag{25}$$

Using data from different sources [26-28], calculated L_{SC} are compared with the measured L_{SP} as shown in Fig.7 and Fig.8.

As can be seen from the figures, the agreements are well.

3. Conclusions

The coexistence theory of slag structure is applicable to the calculation of manganese distribution, oxidizing capability as well as desulfurizing capability for multicomponent slag systems.

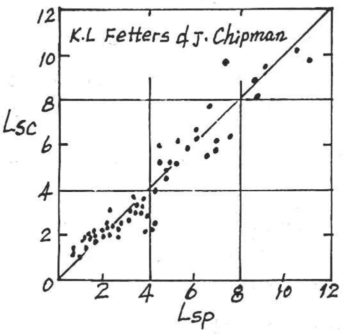

Fig.7 Comparison of calculated and measured L_S [28]

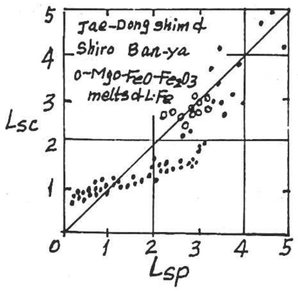

Fig.8 Comparison of calculated and measured L_S [26]

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