Thermodynamic Fundamentals of Deoxidation Equilibria

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Abstract: With the mass action law as the dominant principle, the coexistence theory of metallic melts involving compound formation (atoms and molecules), the coexistence theory of slag melts(molecules and ions) and the model of inseparable cations and anions of molten salts and mattes as well as the basic oxides solid solutions as the scientific basis for determination of the structural units of each solution, calculating models for a series of deoxiation equilibria have been formulated.without the use of classical Wagner interaction parameter formalism. Calculated results agree well with measured activities of corresponding deoxidation equilibria.At the same time using these models we can evaluate the content as well as the composition of inclusions in steel without the necessity for any assumption of associates M*O ,M_2*O etc.

Keywords: Calculating models, thermodynamics, deoxidation equilibria

1 Introduction

The steel production of our country has reached a great amount, but the quality level of steel is still not high enouph, the assortment of steel is not great，the energy consumption is too high and the task of CO_2 reduction is arduous etc. One of the crucial moments of steel quality is deoxidation and reduction as well as modification of inclusions. So the thermodynamics of deoxidation equilibria recently has become research hot spot for metallurgical workers. There are two measurements to solve it: One of them uses interaction parameter formalism of Wagner. the other uses associate model; the former brings little effect, the latter is effective, but still has something different with practice. In condition of publication《Computational thermodynamics of metallurgical melts and solutions》as original creative work by the government publication office as well as activities of metallic melts, slag melts, molten salts ,mattes, aqueous solutions and organic solutions can be evaluated under the guidance of mass action law, without any help from classi-cal interaction parameter formalism of Wagner, and again the results of evaluation are frequently in good agreement with measured values. Consequently at present, in the field of steelmaking careful solution of deoxidation and modification of inclusions are the most urgent task left.

1.1 Effect of using interaction parameter formalism of Wagner.

At present, in the field of solution theory, there is a forest of schools of thought，every school presents itself a system, and uses special emperical parameters, without any popular suitability, and in contradiction with the law of mass action. In case of application to multicomponent heterogeneous reactions, there are difficulties very hard to overcome. Taking deoxidation reaction as an example, H.Suito[1] using interaction parameters of Wagner during investigation on deoxidation by calcium, at 1873 K, with ［%Al］ ≤0.3 and [%Si]≤3, though he divided metal compositions into three regions as shown in table 1, K_{CaO} still does not keep constant, the interaction coef ficient e_o^{Ca} also varies violently, and the absolute value of which is astonishingly big. A little later, at 1873 K,, le t logK=-10.22， and[%Ca]+2.51[%O] has been divided into <0.005 and>0.005 two regions, as shown in table 2[2], It can be seen that though keep LogK=10.22,, variations of 1s t order and 2nd order interaction coefficient in two different regions are still terribly great.

Table 1 K_{CaO} and e_O^{Ca} at 1873 K and different regions of [%Ca]+2.51[%O]

[%Ca]+2.51[%O]	<0.0008	0.0008-0.0030	>0.0030
Log K_{CaO}	-10.34	-7.6±0.3	-5.8±0.3
e_O^{Ca}	-5000±400	-600±80	60±4

Table 2 Variation of first order and 2nd order interaction coefficient s at 1873 K as well as at [%Ca]+2.51[%O]< 0.005 and >0.005

[%Ca]+2.51[%O]	i	j	e_i^j	r_i^j	$r_i^{i.j}$
<0.005	O	Ca	-3600	5.7×10^5	2.9×10^6
	Ca	O	-9000	3.6×10^6	2.9×10^6
>0.005	O	Ca	-990	4.2×10^4	2.1×10^5
	Ca	O	-2500	2.6×10^5	2.1×10^5

Application of interaction parameters of Wagner to deoxidation by magnesium in liquid iron gave unsatisfactory result too at two compositions [%Mg] <0.003 and<0.04., variations of 1s t order and 2nd order interaction coefficients are shown in table 3[3]. It can be seen in the table ,that at constant temperature ,in case of variations of Mg in liquid iron , not only equilibrium constant changes,, but 1s t order and 2nd order interaction coefficients also alternate astonishingly great.This shows that the classical interaction parameter formalism of Wagner is incapable for treating deoxidation equilibria with Ca, Mg, Ba etc.

Table 3 $\log K_{MgO}$, as well as 1s t order and 2nd order interaction coefficients of equilibrium rea ction between[%Mg] and [%O] at 1873 K

e_O^{Mg}	e_{Mg}^{O}	r_O^{Mg}	r_{Mg}^{O}	$r_O^{Mg.O}$	$r_{Mg}^{Mg.O}$	$\log K_{MgO}$	[%Mg]
-280	-430	-20000	350000	462000	-61000	-6.80	<0.003[4]
-370	-560	5900	145000	191400	17940	-7.21	<0.04[3]

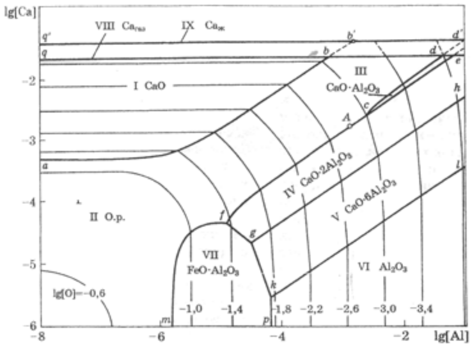


Fig. 1 Isothermal section of inclusions for Fe-Ca-Al-O system at 1873 K (by data [5])

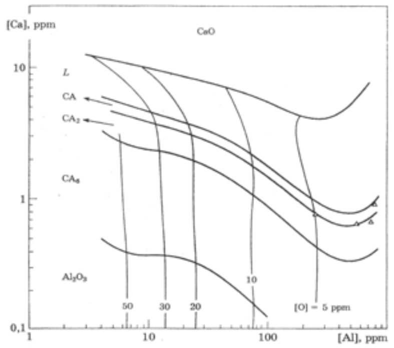


Fig.2 Isothermal section of inclusionsfor Fe-Ca-Al-O system at 1873 K (by data [6]])

As for inclusions in Fe-Ca-Al-O system at 1873 K, Russian scholar G.G.Mixailov using 1st order interaction parameters of Wagner evaluated variation of inclusions as shown in Fi.g.1[5].; While Japanese scholar H.Suito with help of 1st order and 2nd order interaction coefficients gave resulting inclusions for the same system as in Fog.2[6] . Only using different interaction parameters and in the equal thermodynamic condition leads to completely different results, how much usefulness the classical interaction parameter formalism of Wagner should have? It is necessary to study and discuss such a problem.

The weakness of classical interaction parameter formalism of Wagner is its supposition that the dissolved in liquid iron deoxidant and oxygen are independently and randomly distributed particles.. The above mentioned extremely great 1st order and 2nd order interaction coefficients testify that the affinity between deoxidant and oxygen is too great for explaining it by behavior of independently and randomly distributed particles, The proper way out lies in objective recognization of the fact about the formation in steelmaking process deoxidation products (chemical compounds) with different structure.

1.2 Effect of using associate model

Russian scholars E.H.Shahpazov，A.I.Zaitsev etc[7].in the same thermodynamic condition, applying associate model of Canadian scholars I.H.Jung，S.A.Decterev and A.D.Pelton[8,9] to metallic melts Fe-Ca-Al-O gave result as shown in Fig.3. It is seen in the figure, that the result is basically agree with practice, .but they used quasi-chemical model as basis to carry evaluation, which is unfavorable for acknowledgement of real structure of matter, secondly, they apply interaction parameter formalism of Wagner.

$$\underline{Al} + \underline{O} = \underline{Al^*O}$$

$$2\underline{Al} + \underline{O} = \underline{Al_2{}^*O}$$

Hence, associate model is not the highroad without any obstruction to investigation on thermodynamic properties of solutions.

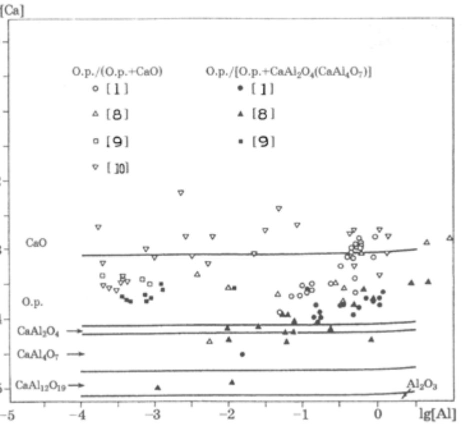


Fig.3 Isothermal section of inclusions for **Fe-Ca-Al-O system at 1873Ｋ(by data[7])**

1.3 First result about unification of computational theories for six solutions under the guidance of mass action law

First result about unification of computational theories for six solutions under the guidance of mass action law[8] are：

1) 191chemical reactions obey the mass action law, their equilibrium constant keep unchangeable:

metallic melts (2-4components)	9	slag melts(2-8components)	49
molten salts(2-3 components)	17	mattes(2-3 components)	5
aqueous solutions(2-3 components)	10	organic solutions(2-3 components)	13

2) The calculated mass action concentrations agree well with measured activities.

2 Calculating models for Deoxidation and Inclusion Formation

2.1 The coexistence theory of metallic melts involving compound formation and the present state of deoxidation products

The carrier of deoxidation reactions is molten steel ,i.e metallic melt, in chapter 1 of our book[8] ,the coexistence theory of metallic melt's structure had been testified in detail, the chief points of which are:

（1）Metallic melts involving compound formation consist of atoms and molecules.

（2）The coexistence of atoms and molecule is continuous in the whole composition range.

（3）There are mobile dynimic equilibrium reactions between atom and molecule,，for example：

$x\mathrm{A}+y\mathrm{B}=\mathrm{A}_x\mathrm{B}_y$

（4）Chemical reactions in metallic melts obey the law of mass action。

In order to study deoxidation and inclusion formation in metallic melts, it is necessary to add fifth point:, i.e

（5）The deoxidation products in metallic melts(molten steel), are all present as molecules.

For the sake of explanation of why the deoxidation products in molten steel are present in molecule state, first of all we talk about cations and anions in solid solution CaO.MgO and molten salts behaving themselves in what state.. Both have face centered crystal structure of NaCl in solid state, hence they present as ions Ca^{2+}，Mg^{2+}，O^{2}，Na^{+}，K^{+}，Cl^{-} already in solid state, the former is solid solution,its activities haven't any deviation with respect to Raoult's law; the latter is solid solution with low melting point, the activities of which at 1073～1223 K have symmetrical negative deviations relative to Raoultian behavior, in case of. these two kinds of solid solutions, as pointed in literature[9] . Applying only two phase calculating model can give result having good agreement with practice.

Ftrstly , take solid solution CaO.MgO as an example..putting it′s composition as $b=\Sigma x_{CaO}$,$a=\Sigma x_{MgO}$;the equilibrium mole fraction of every structural unit as $x=x_{CaO}$，$y=x_{MgO}$，$z=x_{CaO.MgO}$.；mass actiuon concentrations of every structural unit.$N_1=N_{CaO}$ ，$N_2=N_{MgO}$，，$N_3=N_{CaO.MgO}$ ， and formed two solutions $Ca^{2+}+O^{2-}$ +CaO.MgO and $Mg^{2+}+O^{2-}$+CaO.MgO.$\sum x_1$ represents total mole fraction of solution $Ca^{2+}+O^{2-}$+CaO.MgO .,$\sum x_2$ represents total mole fraction of solution $Mg^{2+}+O^{2-}$+CaO.MgO. Then the real deoxidation condition is testified by the model of separable cations and anions as well as the model of inseparable cations and anions respectively as follows:

In case of model for separable cations and anions, the chemical equilibrium is:

$$(Ca^{2+}+O^{2-})+(Mg^{2+}+O^{2-})=CaO.MgO \qquad K=\frac{N_3}{N_1N_2}, \qquad N_3=KN_1N_2 \tag{1}$$

The equilibrium constant is

$$K=2b(1-N_1)/(2-N_1)N_1N_2 \quad \text{or } K=2a(1-N_2)/(2-N_2)N_1N_2 \tag{2}$$

Applying the same symbols of preceding binary melts, and considering that there have been two solutios.$Ca^{2+}O^{2-}$+CaO.MgO and $Mg^{2+}O^{2-}$+ CaO.MgO formed,.$\sum x_1$ represents the equilibrium mole fraction of solution $Ca^{2+}O^{2-}$+CaO.MgO., while $\sum x_2$ represents the equilibrium mole fraction of solution $Mg^{2+}O^{2-}$+CaO.MgO. In condition of inseparable cations and anions, both ions behave together without any difference as single atom or molecule, hence we have

Chemical eqilibrium: （$Ca^{2+}O^{2-}$）+($Mg^{2+}O^{2-}$)=CaO.MgO $K=\frac{N_3}{N_1N_2}$, $N_3=KN_1N_2$ (3)

The equilibrium constant is: $K=ab(2-N_1-N_2)/(a+b)N_1N_2$ (4)

Eqs.(14)、(15) and (16) are the the model of inseparable anions and cations of binary melts involving solid solution. Similarly ，for binary molten salt NaCl.KCl，using the same symbols of preceding example., In case of separable cations and anions as well as inseparable cations and anions we could also obtain equilibrium constant respectively as Eqs.(2) and (4).

Comparison of equilibrium constants from two models about the behaviors of cations and anions in the solution is shown in Tab.4.

Table.4 Comparison of equilibrium constants from two models about the behaviors of cations and anions in the solution

State of ions	The cations and anions are separable				The cations and anions are inseparable	
Calculating equations	$K=2b(1-N_1)/(2-N_1)N_1N_2$		$K=2a(1-N_2)/(2-N_2)N_1N_2$		$K=ab(2-N_1-N_2)/(a+b)N_1N_2$	
Calculated K b a	$K_{CaO.MgO.}$ 1200^{0}C	$K_{NaCl.KCl..}$ 950^{0}C	$K_{CaO.MgO.}$ 1200^{0}C	$K_{NaCl.KCl.}$ 950^{0}C	$K_{CaO.MgO.}$ 1200^{0}C	$K_{NaCl.KCl.\ 950}$ ^{0}C
0.1 0.9	1.818181	2.157329	1.052632	1.236686	1	1.184027
0.2 0.8	1.666667	1.944671	1.111111	1.284930	1	1.171498
0.3 0.7	1.538462	1.763280	1.176471	1.367605	1	1.174683
0.4 0.6	1.428571	1.639150	1.250000	1.431670	1	1.164604
0.5 0.5	1.333333	1.509263	1.333333	1.509263	1	1.149304
0.6 0.4	1.250000	1.435548	1.428571	1.649454	1	1.169997
0.7 0.3	1.176471	1.364921	1.538462	1.799232	1	1.180818
0.8 0.2	1.111111	1.323344	1.666667	1.980077	1	1.206030
0.9 0.1	1.052632	1.266167	1.818181	2.186591	1	1.212061

From the comparison of two models, it can be seen , that the equilibrium constants from the model of inseparable anions and cations are considerably unchangeable, While the equilibrium constants from the model of separable cations and anions are changeable with varying melt compositions.Why in solid solution CaO.MgO of tppical face centered crystal structure of NaCl and in salts with typical electric conductivity appeared phenomenon about solutions of inseparable cations and anions?. One of the reasons is, that there should be certain condition to separate cations and anions, presence of outside electric field, may lead to electrolysis of the solution is one of such important conditions; In the absence of outside electric field, as we had pointed in reference[10] there should be somethings present with high dielectric constant: silicates,phosphates, aluminates etc are just such things; Why in melts CaF_2-$CaSiO_3$, CaF_2 appears as three ions Ca^{2+} + $2F^-$? because $CaSiO_3$ with high dielectric constant is present; Why the calculating models of slag melts can evaluate the mass action concentrations in good agreement with measured activities? Because in slag melts, both cations and anions as well as silicates、phosphates etc.with high dielectric constant are present.

2.2 Ternary Metallic Melts

2.2.1 Fe-Ca-O

Calcium is the extremly powerful deoxidatiuon agent,In addition to use it as deoxidation agent, it can be used to modify configuration of inclusions so as to reduce nozzle blockage in continuous casting，therefore, study on deoxidation equilibrium with calcium is very important.

(1) Calculating Model

As this paper uses pure element as standard state, and mole fraction as concentration unit, when met with the 1 wt pct standard state, their standard free energy of formation ΔG^{θ} should be transformed into ΔG^{θ} with pure element as standard state, and with mole fraction as concentration unit.

Taking two equilibrium constants as examples ; $K_{FeO(l)}=K_{(1\%)}\times M_{Fe}\times M_{O}/M_{FeO}$; $K_{CaO(S)}=K_{(1\%)}\times M_{Ca}\times M_{O}$, then two equilibrium constants obtained should be transformed into corresponding free energy of formation respectively by ΔG^{θ}=-RTLn K. Where M represents atomic or molecular weight, the bracketed (l)and (S) represent liquid and solid respectively.

Now，giving the compositions of ternary melt as $b_1=\Sigma x_{Fe,}$,$b_2=\Sigma x_{Ca}$,$a=\Sigma x_{O}$;the equilibrium mole fractions of every component evaluated from compositions of the melt as $x_1=x_{Fe}$,, $x_2=x_{Ca}$, $y=x_O$, $z_1=x_{FeO}$,$z_2=x_{CaO;}$ the normalized mass action concentrations of every structural unit as. $N_1=N_{Fe}$, $N_2=N_{ca}$, $N_3=N_O$,$N_4=N_{FeO}$,$N_4=N_{CaO}$; Σx=sum of equilibrium mole fractions.then we have Chemical equilibria[11]：

$Fe_{(l)}+[O]=FeO_{(l)}$ $K_1=N_4/N_1N_3, N_4=K_1N_1N_3, \quad z_1=K_1x_1 y/\Sigma x$ (5)

$\Delta G^{\theta}=-109467+24.46T$ J/mol

$Ca_{(l)}+[O]=CaO_{(s)}$ $K_2=N_5/N_2N_3, N_5=K_2N_2N_3, \quad z_2=K_2x_2 y/\Sigma x$ (6)

$\Delta G^{\theta}=-630930+91.222T$ J/mol

Mass balance：

$$N_1+N_2+N_3+K_1N_1N_3+K_2N_2N_3=1 \quad (7)$$

$$b_1=x_1+z_1=\Sigma x(N_1+K_1N_1N_3) \quad (8)$$

$$b_2=x_2+z_2=\Sigma x(N_2+K_2N_2N_3) \quad (9)$$

$$a=y+z_1+z_2=\Sigma x(N_3+K_1N_1N_3+K_2N_2N_3) \quad (10)$$

$$[1+(a-1)(N_1+N_2)-(1+b_1+b)N_3]/(1+b_1+b_2-a)=K_1N_1N_3+K_2N_2N_3 \quad (11)$$

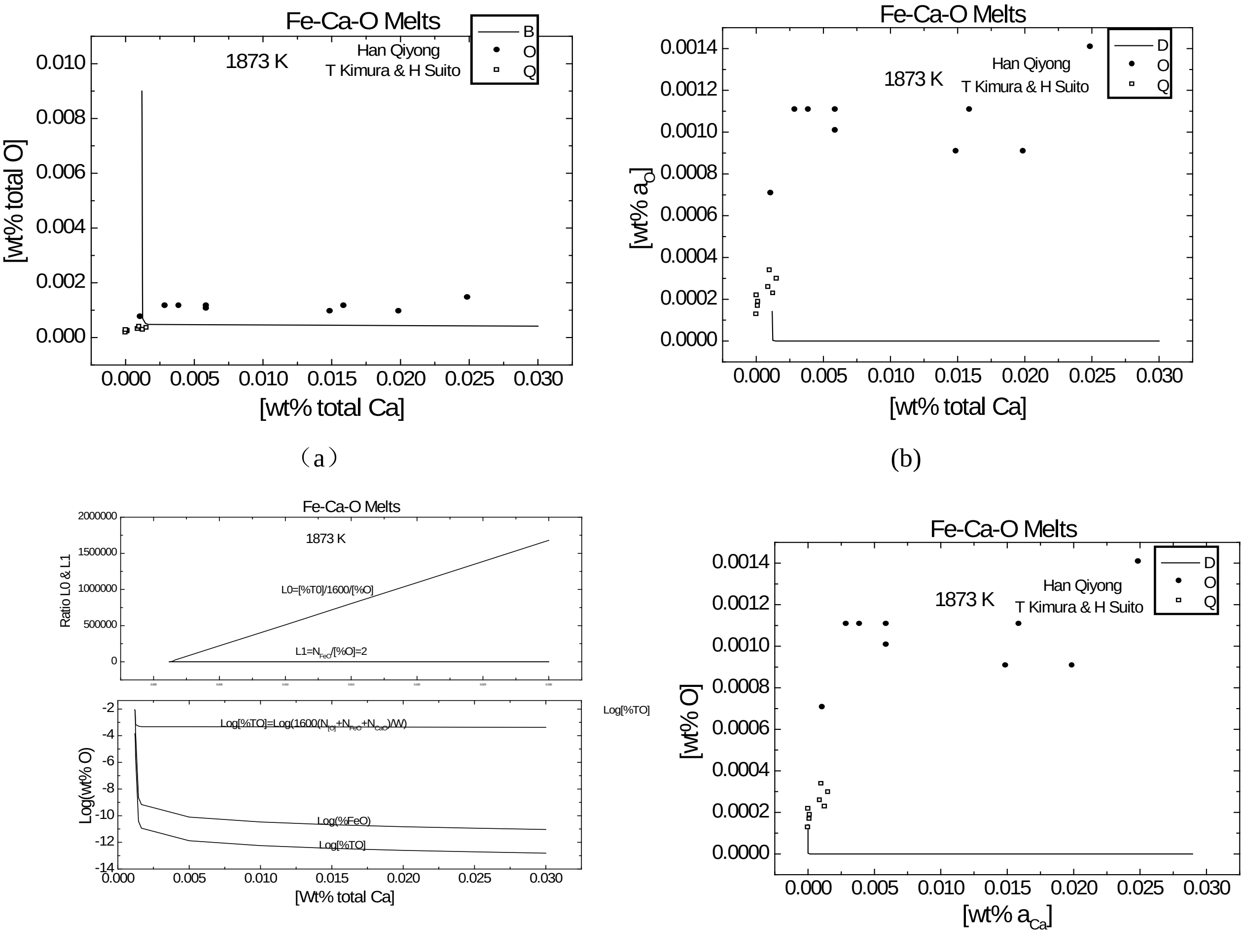
Above mentioned Eqs(5)~(11) are the universal calculating model for deoxidation equilibria pertaining to this kind of ternary metallic melt Fe-Ca-O, Fe-Ba-O, Fe-Mg-O and Fe-Mn-O. In which, after using Eqs(5）and（6）in combination with Eqs（8）（9）and（10）to evaluate the initial results, which should be transformed in the following way into mass action concentrations：$N_1=x_1/\Sigma x$, $N_2=x_2/\Sigma x$,$N_3=y/\Sigma x$,$N_4=z_1/\Sigma x$,$N_5=z_2/\Sigma x$。Eqs (7)and(11) are used to regress equilibrium constants K_1 and K_2 in condition of known measured activities N_1、N_2 and N_3.

(2) Calculated Result:

The evaluated curves of deoxidation by calcium are shown in Fig.4. As can be seen in the figures, the extremely difficult problem of deoxidation equilibrium Ca-O annoying many metallurgical scholars has been easily acomplished as regular curves（the upper part of hyperbola xy=K）by the calculating model formulated on the basis of mass action law and the coexistence theory of metallic melt′s structure without the use of interaction parameters formalism of Wagner.

There are regular functional relationships for [%TO] and [%TCa]，[%a_O] and [%TCa]，（%FeO）and [%TCa] as well as [%O] and [%a_{Ca}]，as they are all under equilibrium state., the regularities between them are controlled by equilibrium constants, so there isn”t any necessity to modify them by interaction parameter formalism of Wagner.

At the same time, what the measured oxygen represents ? disolved oxygen, oxygen activity or sum of oxygen content in inclusions is also problem to talk about. It can be seen from Fig.4(a) that［％ＴＯ］represents sum of oxygen content in inclusions，the evaluated curve is comparatively nearer to the measured oxygen contents of Han Qiyong[12] as well as T Kimura & H.Suito[13]，Which confirms that the transformed thermodynamic parameters are apllicable. The oxygen activity［％ a_o］in Fig.4(b)is considerably less than［％ＴＯ］，hence，it represents dissolved oxygen, The.（%FeO）in Fig. 4 (c)is less than［％ＴＯ］,but greater than [%O]，so it is a_{FetO}, The distribution coefficitnt L1=a_{FetO}/[%O]≈2; L0=($N_{[O]}$+N_{FeO}+N_{CaO})/[%O]>0, may reach very big value, as calcium is a very strong deoxidation.



（a） （b）

（c） （d）

Fig 4 The relationship between different oxygen content and concentration of calcium in liquid iron.

It is seen from Fig.5 that contents of [%O] and (%FeO) decrease gradually, while that of (%CaO) and sum of total Inclusions are basically invariable with increasing the calcium content.

Fig.6 shows that compositions of [%O] and (%FeO) decrease gradually, while that of (%CaO) and sum of total Inclusions are basically invariable with increasing the calcium content.

Having Fig.5 and Fig.6 in mind, we are able to reduce and modify inclusions according to the requirement of production.

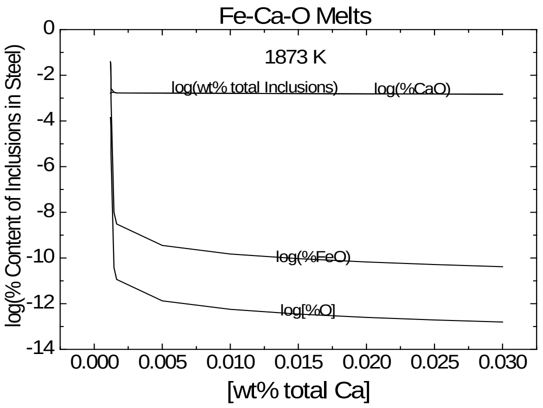


Fig. 5 The relationship between content of inclusions and sum of total inclusions with respect to calcium content of liquid iron

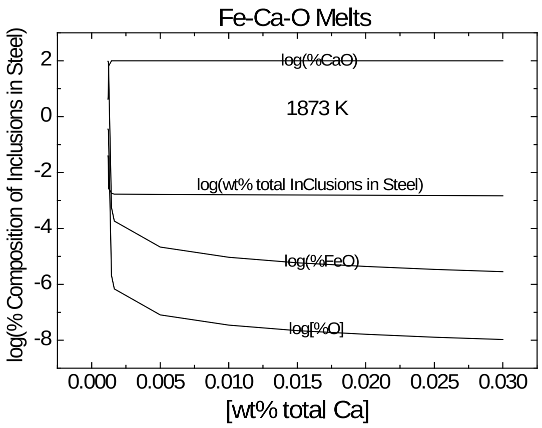


Fig.6 The relationship between composition of and sum of total inclusions with respect to calcium content of liquid iron

2.2.2 Fe-Ba-O

Barium is also an extremely strong deoxidation agent, which is used to reduce oxygen content of steel, change the properties of inclusions, reduce the globular inclusions and increase the fatigue life of stee. Hence it encourages metallurgical workers to study deoxidation by barium with strong interest.

(1) Calculating model

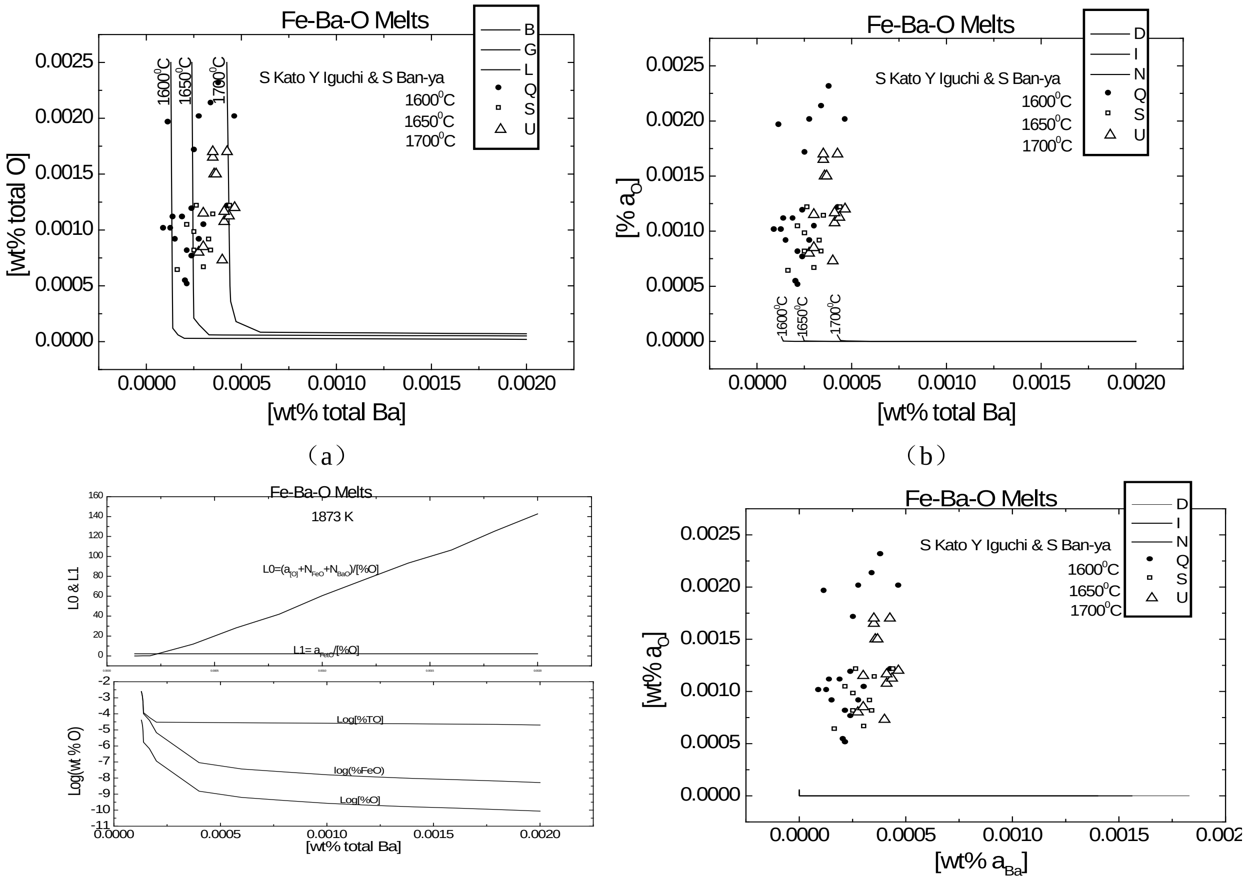
This ternary system applies same calculaing model as ternary system. Fe-Ca-O i.e. Eqs.(5)~(11), and uses thermodynamic parameter a little different from the preceding paragraph, with Eq.(12) being added.

$Fe_{(l)}+[O]=FeO_{(l)}$ $\Delta G^{\theta}=-109467+24.46T$ J/mol[11] (5)

$Ba_{(l)}+[O]=BaO_{(S)}$ $\Delta G^{\theta}=-191000-98.91T$ J/mol[14] (12)

(2) Calculated Results

Fig.7 is the calculated deoxidation curves by barium. It is seen from the figures, that using same calculating model and thermodynamic parameters of ternary metallic melt Fe-Ba-O is also able to make regular curves like the upper part of hyperbola xy=K.,i.e.There are regular functional relationships for [%TO] and [%TBa], [%a_O] and[%TBa], (%FeO) and [%TBa]as well as [%O] and [%a_{Ba}], which are also controlled by equilibrium constants, and have no relation with interaction parameters formalism of Wagner. Fig.7(a) shows the relationship between oxygen content of inclusions and concentration of barium, which is basically agree with measured results of Japanese scholars S Kato Y Iguchi and S.Ban-ya[14], testifying that the transformed thermodynamic parameters are reasonable for application..Fig. 7 (b) is the relationship between oxygen activities and concentrations of barium；Fig.7(c) represents the relationship between[%TO], （%FeO）and [%O] as well as distribution coefficients L0 and L1 with increasing the concentrations of barium in liquid Iron；The distribution coefficient $L1=a_{FetO}/[\%O]\approx 2$; $L0=(N_{[O]}+N_{FeO}+N_{BaO})/[\%O]>0$, may reach very big value, as barium is a very strong deoxidant. While Fig.7(d) is the relationship between oxygen activities and barium activities.



(a)　　(b)

(c)　　(d)

Fig. 7 Relationship between different calculated oxygen content and concentration of barium in liquid iron.

Fig.8 shows the relationship between content of inclusions and sum of total inclusions with respect to barium concentrations of liquid iron, while Fig.9 is the relationship between composition of inclusions and sum of total inclusions with respect to barium concentrations of liquid iron. It is seen from Fig.8 that contents of [%O] and (%FeO) decrease gradually, while that of (%BaO) and sum of total Inclusions are basically invariable with increasing barium concentrations.

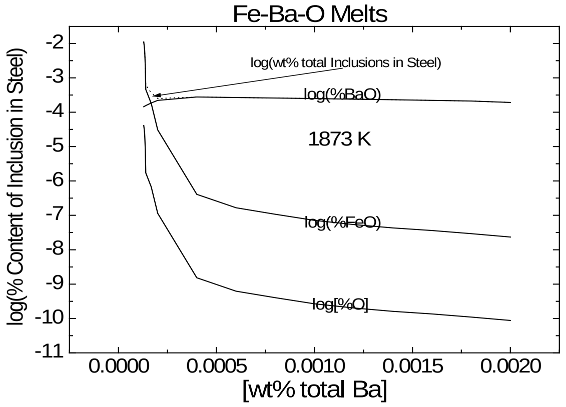


Fig.8 The relationship between content of inclusions and sum of total inclusions with respect to the barium concentration of liquid iron

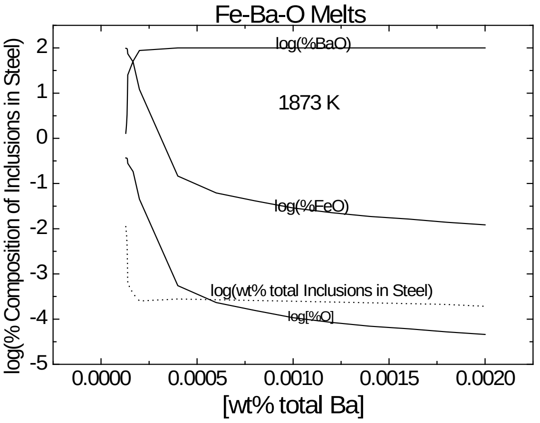


Fig.9 The relationship between composition of inclusions and sum of total inclusions with respect to barium concentration of liquid iron

Fig.9 shows that compositions of [%O] and (%FeO) decrease gradually, while that of (%BaO) and sum of total Inclusions are basically invariable with increasing barium concentrations.

Having Figs.8 and 9 in hand, we can reduce and modify inclusions as required from the steelmaking production.

2.2.2 Fe-Mg-O

The research work on deoxidation and modification by magnesium is very little, nevertheless, the reaction equilibrium of Mg-O, annoying many steelmaking scholars still should be answered.

(1) Calculating Model

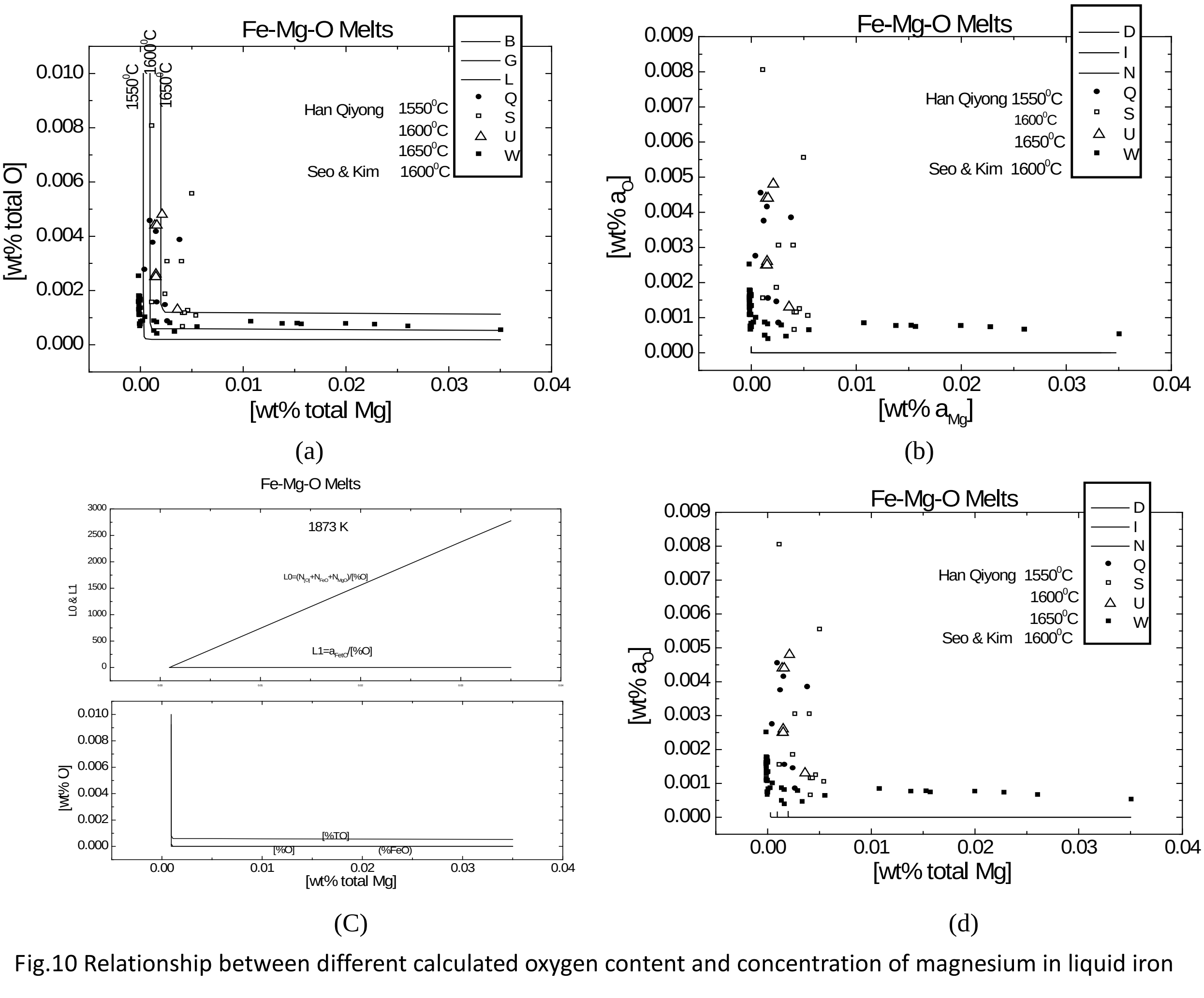
This ternary system applies same calculating model as ternary system Fe-Ca-O i.e. Eqs.(5)~(11), and uses thermodynamic parameter a little different from the preceding paragraph with Eq.(13) being added.

$Fe_{(l)}+[O]=FeO_{(l)}$ $\Delta G^{\theta}=-109467+24.46T$ J/mol[11] (5)

$Mg_{(l)}+[O]=MgO_{(S)}$ $\Delta G^{\theta}=-728600+188.79T$ J/mol[15] (13)

(2) Calculated Results

Fig.10 Shows the relationship between different calculated oxygen content and concentration of magnesium in liquid iron.



(a) (b)

(C) (d)

Fig.10 Relationship between different calculated oxygen content and concentration of magnesium in liquid iron

As it has been shown in the preceding example, that using transformed thermodynamic parameters of ternary metallic melt is able for reproduee the measured data regularly:as the upper part:of hyperbola xy=K: Fig.10(a) for[%TO] and [%TMg], Fig.10(b) for [%a_O] and [%TMg], Fig.10(c) for（%FeO）and [%TMg] as well as Fig.10.(d) for[%O] and [%a_{Mg}]. The calculated curve of Fig.10(a) is basically agree with the experimental results of scholars Han Qiyong[16] and Seo & Kim[17].,testifying that the transformed thermodynamic parameters are suitable for application.Measured [%TO] represents the oxygen content of total inclusions, (%FeO)) represents a_{FetO}, while [%O] represents $a_{[\%o]}$.L0>0, it may increase to very big value with increasing the concentration of magnesium in liquid iron. L1 is generally a little greater than 2.

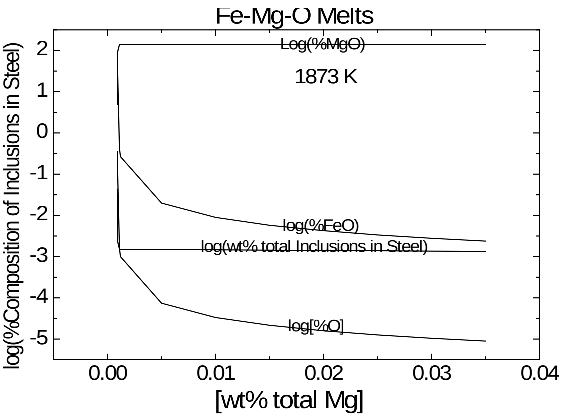


Fig.11 The relationship between content of inclusions and sum of total inclusions with respect to magnesium concentrations of liquid iron

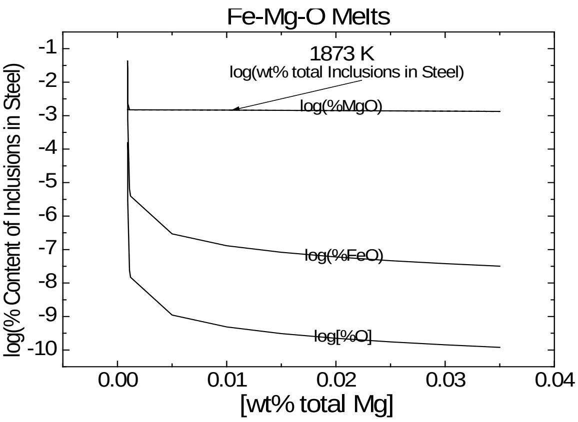


Fig.12 The relationship between composition of inclusions and sum of total inclusions with respect to magnesium concentrations of liquid iron

Fig.11 shows the relationship between content of inclusions and sum of total inclusions with respect to magnesium concentrations of liquid iron It can be seen from Fig.11, that the content of［%O］and（%FeO）decreases gradually with increasing the concentrations of magnesium, while the content of（%MgO）and the sum of total inclusions are basically maintain unchangeably. It is also seen from Fig.12, that the composition of［%O］and（%FeO）drops gradually with increasing the concentration of magnesium, while the compositions of（%MgO）and the sum of total inclusions are basically maintain unchangeably.

Of course, having Fig.11 and Fig 12 in mind, it is helpful for reducing and modification of inclusion

2.3 Quarternary metallic melt Fe-Ca-Al-O

This quarternary metallic melt is very important for globular inclusions control and prevention of nozzle blockage during continuous casting. In this melt, in addition to deoxidation equilibria[11], there are also intermetallic chemical reactions between Fe and Al as well as Ca and Al[8], hence the calculating model is considerably complex.

(1) Calculating Model

Assuming the composition of the melt as $b_1=\Sigma x_{Fe,,}$ $b_2=\Sigma x_{Ca}$,$b_3=\Sigma x_{Al}$,$a=\Sigma x_O$;the equilibrium mole fraction evaluated from the composition of the melt as $x_1=x_{Fe}$, $_2=x_{Ca}$, $_3=x_{Al}$, $=x_O$, $_1=x_{Fe3Al}$, $z_2=x_{FeAl}$,$z_3=x_{FeAl2}$, $z_4=x_{Fe2Al5}$, $z_5=x_{FeAl6}$,

$z_6=x_{CaAl4}$, $z_7=x_{CaAl2}$, $z_8=x_{CaAl,}$ $z_9=x_{FeO}$, $z_{10}=x_{Al2O3}$, $z_{11}=x_{CaO}$, $z_{12}=x_{FeAl2O4,}$ ${}_3=x_{3CaO.Al2O3}$, ${}_{14.}=x_{12CaO.7Al2O3,}$ $z_{15}=x_{CaO.Al2O3}$, ${}_{16}=x_{CaO.2Al2O3}$, $z_{17.}=x_{CaO.6Al2O3;}$ the normalized mass action concentrations as $N_1=N_{Fe}(=x_1/\Sigma x)$,$N_2=N_{Ca}$, $N_3=N_{Al}$,$N_4=N_O$, $N_5=N_{Fe3Al}$, $N_6=N_{FeAl}$, $N_7=N_{FeAl2}$,$N_8=N_{Fe2Al5}$,$N_9=N_{FeAl6}$,$N_{10}=N_{CaAl4}$,$N_{11}=N_{CaAl2}$,$N_{12}=N_{CaAl,}$ $N_{13}=N_{FeO}$,$N_{14}=N_{Al2O3}$, $N_{15}=N_{FeAl2O4,}$ $N_{16}=N_{CaO}$,$N_{17}=N_{3CaO.Al2O3}$, $N_{18}=N_{12CaO.7Al2O3,}$ $N_{19}=N_{CaO.Al2O3}$,$N_{20}=N_{CaO.2Al2O3}$, $N_{21}=N_{CaO.6Al2O3}$; Σx=Sum of equilibrium mole fractions, then we have

Chemical Equilibria[8]:

$3Fe_{(l)}+Al_{(l)}=Fe_3Al_{(l)}$ $K_1=N_5/N_1^3N_3,N_5=K_1N_1^3N_3,\quad z_1=K_1x_1^3x_3/\Sigma x$ (14)

$\Delta G^{\theta}_{Fe3Al}=-120586.85+48.61T$ J/mol

$Fe_{(l)}+Al_{(l)}=FeAl_{(l)}$ $K_2=N_6/N_1N_3,N_6=K_2N_1N_3,\quad z_2=K_2x_1\,x_3/\Sigma x$ (15)

$\Delta G^{\theta}_{FeAl}=-47813.287+7.893T$ J/mol

$Fe_{(l)}+2Al_{(l)}=FeAl_{2(l)}$ $K_3=N_7/N_1N_3^2,N_7=K_3N_1N_3^2,\quad z_3=K_3x_1\,x_3^2/\Sigma x$ (16)

$\Delta G^{\theta}_{FeAl2}=130186.64-84.582T$ J/mol

$2Fe_{(l)}+5Al_{(l)}=Fe_2Al_{5(l)}$ $K_4=N_8/N_1^2N_3^5,N_8=K_4N_1^2N_3^5,\quad z_4=K_4x_1^2\,x_3^5/\Sigma x$ (17)

$\Delta G^{\theta}_{Fe2Al5}=-165372.213+43.05T$ J/mol

$Fe_{(l)}+6Al_{(l)}=FeAl_{6(l)}$ $K_5=N_9/N_1N_3^6,N_9=K_5N_1N_3^6,\quad z_5=K_5x_1\,x_3^6/\Sigma x$ (18)

$\Delta G^{\theta}_{FeAl6}=-14710.17-18.712T$ J/mol

$Ca_{(l)}+4Al_{(l)}=CaAl_{4(l)}$ $K_6=N_{10}/N_2N_3^4,N_{10}=K_6N_2N_3^4,\quad z_6=K_6x_2\,x_3^4/\Sigma x$ (19)

$\Delta G^{\theta}_{CaAl4}=-260400.72+143.31T$ J/mol

$Ca_{(l)}+2Al_{(l)}=CaAl_{2(l)}$ $K_7=N_{11}/N_2N_3^2,N_{11}=K_7N_2N_3^2,\quad z_7=K_7x_2\,x_3^2/\Sigma x$ (20)

$\Delta G^{\theta}_{CaAl2}=-193406.58+103.71T$ J/mol

$Ca_{(l)}+Al_{(l)}=CaAl_{(l)}$ $K_8=N_{12}/N_2N_3,N_{12}=K_8N_2N_3,\quad z_8=K_8x_2\,x_3/\Sigma x$ (21)

$\Delta G^{\theta}_{CaAl}=-94082.19+42.87T$ J/mol

$Fe_{(l)}+[O]=FeO_{(l)}$ $K_9=N_{13}/N_1N_4,N_{13}=K_9N_1N_4,\quad z_9=K_9x_1\,y/\Sigma x$[11] (5)

$\Delta G^{\theta}=-109467+24.46T$ J/mol

$2Al_{(l)}+3[O]=Al_2O_{3(S)}$ $K_{10}=N_{14}/N_3^2N_4^3,N_{14}=K_{10}N_3^2N_4^3,z_{10}=K_{10}x_3^2y^3/\Sigma x$ (22)

$\Delta G^{\theta}=-1225000+269.772T$ J/mol

$Ca_{(l)}+[O]=CaO_{(S)}$ $K_{11}=N_{15}/N_2N_4,N_{15}=K_{11}N_2N_4,\quad z_{11}=K_{11}x_2\,y/\Sigma x$ (6)

$\Delta G^{\theta}=-630930+91.222T$ J/mol

$FeO_{(l)}+Al_2O_{3(S)}=FeAl_2O_{4(l)}$ $K_{12}=N_{16}/N_{13}N_{14},N_{16}=K_{12}N_{13}N_{14},z_{12}=K_{12}\,z_9\,z_{10}/\Sigma x$ (23)

$\Delta G^{\theta}=-33272.8+6.1028T$ J/mol

$3CaO_{(S)}+Al_2O_{3(S)}=3CaO.Al_2O_{3,}$ $K_{13}=N_{17}/N_{15}^3N_{14},N_{17}=K_{13}N_{15}^3N_{14}\;z_{13}=K_{13}z_{11}^3z_{10}/\Sigma x$ (24)

$\Delta G^{\theta}=-17000-32.0T$ J/mol

$12CaO_{(S)}+7Al_2O_{3(S)}=12CaO.7Al_2O_{3,}$ $K_{14}=N_{18}/N_{15}^{12}N_{14}^7,N_{18}=K_{14}N_{15}^{12}N_{14}^7,\;z_{14}=K_{14}\,z_{11}^{12}z_{10}^7/\Sigma x$ (25)

$\Delta G^{\theta}=-86100-205.1T$J/mol

$CaO_{(S)}+Al_2O_{3(S)}=CaAl_2O_4$ $K_{15}=N_{19}/N_{15}N_{14},N_{19}=K_{15}N_{15}N_{14},z_{15}=K_{15}\,z_{11}z_{10}/\Sigma x$ (26)

$\Delta G^{\theta}=-18120-18.62T$ J/mol

$CaO_{(S)}+2\,Al_2O_{3(S)}=CaAl_4O_7$ $K_{16}=N_{20}/N_{15}N_{14}^2,N_{20}=K_{16}N_{15}N_{14}^2,z_{16}=K_{16}\,z_{11}z_{10}^2/\Sigma x$ *(27)*

$\Delta G^{\theta}=-16400-26.8T$ J/mol

$CaO_{(S)}+6\,Al_2O_{3(S)}=CaAl_{12}O_{19}$ $K_{17}=N_{21}/N_{15}N_{14}^6,N_{21}=K_{17}N_{15}N_{14}^6,z_{17}=K_{17}\,z_{11}z_{10}^6/\Sigma x$ (28)

$\Delta G^{\theta}=-17430-37.2T$ J/mol

Mass balance:

$N_1+N_2+N_3+N_4+K_1N_1^3N_3+K_2N_1N_3+K_3N_1N_3^2+K_4N_1^2N_3^5+K_5N_1N_3^6+K_6N_2N_3^4+K_7N_2N_3^2+K_8N_2N_3+$

$$K_9N_1N_4+K_{10}N_3^2N_4^3+K_{11}N_2N_4+K_{12}N_{13}N_{14}+K_{13}N_{15}^3N_{14}+K_{14}N_{15}^{12}N_{14}^7+K_{15}N_{15}N_{14}+K_{16}N_{15}N_{14}^2+K_{17}N_{15}N_{14}^6=1 \quad (29)$$

$$b_1=x_1+3z_1+z_2+z_3+2z_4+z_5+z_9+z_{12}=\Sigma x(N_1+3K_1N_1^3N_3+K_2N_1N_3+K_3N_1N_3^2+2K_4N_1^2N_3^5+K_5N_1N_3^6+K_9N_1N_4+K_{12}N_{13}N_{14}) \quad (30)$$

$$b_2=x_2+z_6+z_7+z_8+z_{11}+3z_{13}+12z_{14}+z_{15}++z_{16}+z_{17}=\Sigma x(N_2+K_6N_2N_3^4+K_7N_2N_3^2+K_8N_2N_3+K_{11}N_2N_4+3K_{13}N_{15}^3N_{14}+2K_{14}N_{15}^{12}N_{14}^7+K_{15}N_{15}N_{14}+K_{16}N_{15}N_{14}^2+K_{17}N_{15}N_{14}^6) \quad (31)$$

$$b_3=x_3+z_1+z_2+2z_3+5z_4+6z_5+4z_6+2z_7+z_8+2z_{10}+2z_{12}+2z_{13}+14z_{14}+2z_{15}+4z_{16}+12z_{17}=\Sigma x(N_3+K_1N_1^3N_3+K_2N_1N_3+2K_3N_1N_3^2+5K_4N_1^2N_3^5+6K_5N_1N_3^6+4K_6N_2N_3^4+2K_7N_2N_3^2+K_8N_2N_3+2K_{10}N_3^2N_4^3+2K_{12}N_{13}N_{14}+2K_{13}N_{15}^3N_{14}+14K_{14}N_{15}^{12}N_{14}^7+2K_{15}N_{15}N_{14}+4K_{16}N_{15}N_{14}^2+12K_{17}N_{15}N_{14}^6) \quad (32)$$

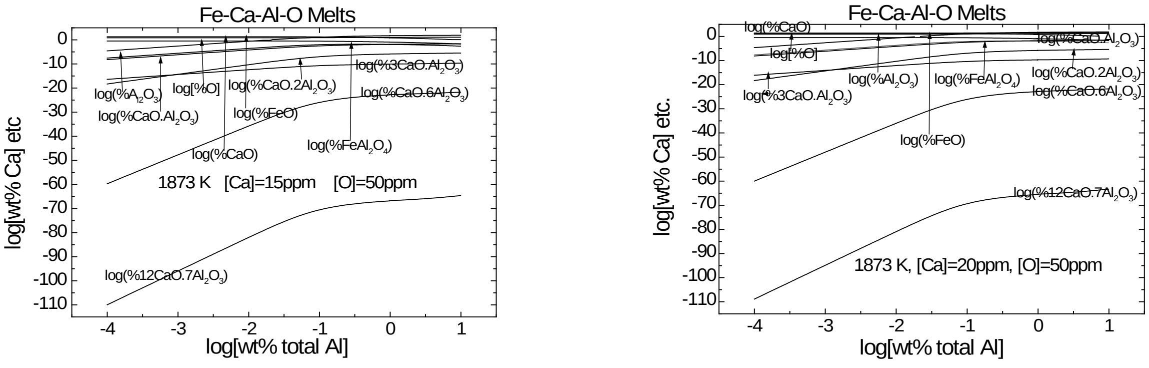
$$a=x_4+z_9+3z_{10}+z_{11}+4z_{12}+6z_{13}+33z_{14}+4z_{15}+7z_{16}+19z_{17}=\Sigma x(N_4+K_9N_1N_4+3K_{10}N_3^2N_4^3+K_{11}N_2N_4+4K_{12}N_{13}N_{14}+6K_{13}N_{15}N_{14}+33K_{14}N_{15}^{12}N_{14}^7+4K_{15}N_{15}N_{14}+7K_{16}N_{15}N_{14}^2+19K_{17}N_{15}N_{14}^6) \quad (33)$$

$$[1+(a-1)(N_1+N_2+N_3)-(1+N_1+N_2+N_3)N_4-[(1-4a)K_1N_1^3N_3+(1-2a)(K_2N_1N_3+K_8N_2N_3)+(1-3a)(K_3N_1N_3^2+K_7N_2N_3^2)+(1-7a)(K_4N_1^2N_3^5+K_5N_1N_3^6)+(1-5a)K_6N_2N_3^4]=(1+b_1+b_2+b_3-a)(K_9N_1N_4+K_{11}N_2N_4)+(1+3b_1+3b_2+3b_3-2a)K_{10}N_3^2N_4^3+(1+4b_1+4b_2+4b_3-3a)(K_{12}N_{13}N_{14}+K_{15}N_{15}N_{14})+(1+6b_1+6b_2+6b_3-5a)K_{13}N_{15}^3N_{14}+(1+7b_1+7b_2+7b_3-5a)K_{16}N_{15}N_{14}+(1+33b_1+33b_2+33b_3-26a)K_{14}N_{15}^{12}N_{14}^7+(1+19b_1+19b_2+19b_3-13a)K_{17}N_{15}N_{14}^6 \quad (34)$$

The above mentioned Eq.(5) ,(6) and Eqs.(14）～（34）are the calculating model of inclusion content for this quarternary metallic melt, which can be resolved by simultaneous equations.(5)), (6) and Eqs.（14）～（28）as well as Eqs.(30), (31), (32) and (33). While Eqs.(29) and (34) are used to regress equilibrium constants by measured activities N_1,N_2,$N_3$and N_4.

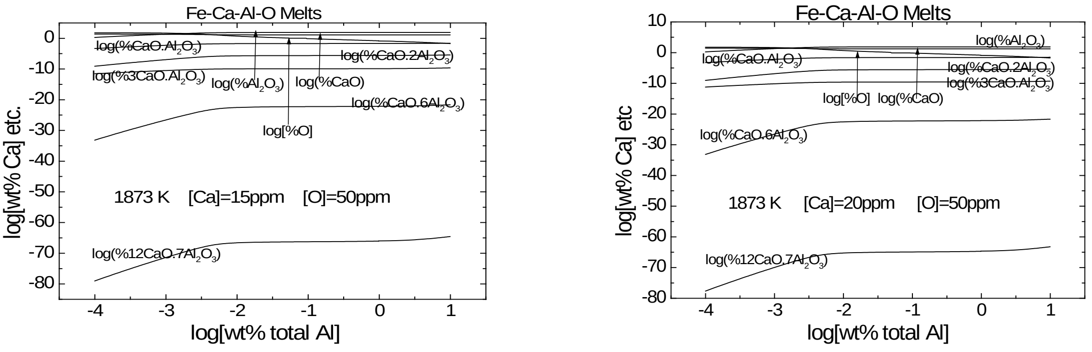
(2) Calculated results

Fig.13 Shows the variation of inclusions content in case of considering two components of metallic melt (%FeO and %$FeAl_2O_4$)。It is seen from the figure，that there isn't any calculated inclusion curve behaved parallelly with increasing the concentration of aluminium.At the same time, there aren′t any region of Iso-oxygen content lines with respect to log[wt% total Al] appeared in the figure, as pointed by the reference [34,35] ,so it should be studied farther. It is seen from Fig.13(a) and (b) that，applying the above calculating model without any help of the interaction parameters of Wagner. It is completely capable to evaluate the relationship between the content variation of inclusions and concentration increment of aluminum.



（a） (b)

Fig.13The relationship between Composition of inclusions and Concentration of Aluminum (including %FeO and %$FeAl_2O_4$)



（a） (b)

Fig.14 The relationship between Composition of inclusions and concentration of Aluminum (Without %FeO and %$FeAl_2O_4$)

Fig.14 shows the relationship between composition of inclusions and concentration of aluminum (not including %FeO and %$FeAl_2O_4$).It can be seen from the figure, that there are certainly a number of calculated inclusion curves behaved more or less parallelly with increasing the concentration of aluminum. But there aren′t any region of Iso-oxygen content lines with respect to log[wt%total Al] appeared in the figure, as pointed by the reference[18,19], aren′t there any quaternary Fe-Ca-Al-O metallic melt without %FeO and %$FeAl_2O_4$? so these should be studied farther.

It is shown in figure 15, that there are three kinds of oxygen contents in metallic melts:

1) Oxygen activity $a_{[O]}$ or dissolved oxygen[%O];
2) Oxygen of ferrous and ferric oxides, $a_{FetO}= N_{FeO}+3N_{Fe2O3;}$
3) Oxygen content of inclusions.$[\%TO]=1600(N_{[O]}+N_{FeO}+3N_{Fe2O3}+N_{CaO}+3N_{Al2O3}+4N_{FeAl2O4}etc)/W$; L0>［%TO］/1600/[%O]>0 and may reach a value greater than 4, where W=weight of metallic melt. L1 generally is a little greater than 2

Fig.13（b）Shows the variation of inclusion content in low carbon steel after LF refining and killed by aluminum finally. It′s T=1873 K ,［% O］=0.0013,$a_{[O]}$= 0.0013/16=8.125exp-05.

Consider that just after killing by aluminum, the Al_2O_3 formed is solid, hence a_{Al2O3}=1.in this case, the aluminum activity can be evaluated by the above mentioned Eq.(22) as follows：

$$2Al_{(l)}+3[O]=Al_2O_{3(S)} \quad \Delta G^{\theta}=-1225000+269.772T \text{ J/mol or } LgK_{CaO}=-32938.8/T+4.762. \qquad (22)$$

$$K_{Al2O3(S)}= N_{Al2O3}/(N_{Al}^{2}\times N_{O}^{3}) , \quad N_{Al}=1/(K_{Al2O3}\times N_{[O]}^{3})^{1/2} \quad a_{Al}= N_{Al}\times 27=0.00344$$

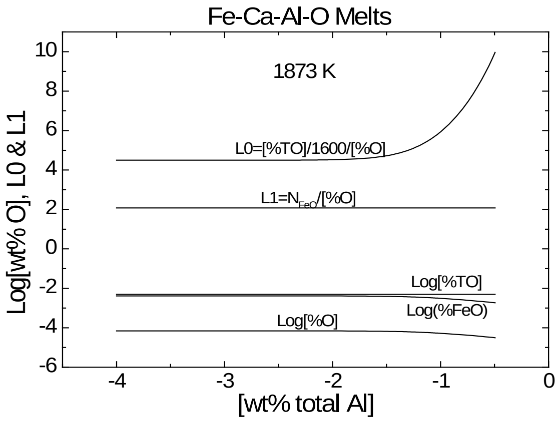


Fig 15 Relationship between different oxygen contents L0 & L1 with increasing the concentration of aluminum in liquid iron

Table5 Activities of CaO-Al_2O_3 binary slag melt[20]

Equilibrium on phase bonders	a_{CaO}	a_{Al2O3}
C/L	1.000	0.017
12C.7A	0.340	0.064
L/C.A	0.150	0.275
C.A/C.2A	0.100	0.414
C.2A/C.6A	0.043	0.631
C.6A/A	0.003	1.000

For such aluminium contents, the lower and upper oxygen activity value can be evaluated by Eq.(22) according to C/L and L/C.A phase borders in table 5[40] as follows:

$$N_{[O]}^3=a_{Al2O3}/(K_{Al2O3}\times N_{Al}^2)\ ,\quad N_{[O]}=a_{Al2O3}^{1/3}/(K_{Al2O3}\times N^2)^{1/}$$

At phase border C/L, (a_{CaO}=1,a_{Al2O3}=0.017), $a_{\{O\}}$=0.000334

At phase border L/C.A, (a_{CaO}=0.15,a_{Al2O3}=0.275), $a_{\{O\}}$ =0.000844

When the oxygen activity is between 3.34ppm and 8.44ppm in liquid steel, it′s inclusions would be liquid modified calcium-aluminates without any possibility of solid inclusions precipitation, hence occurrence possibility of nozzle blockage in continuous casting would be little. Further, in order to obtain ideal mayanite 12CaO.7Al_2O_3(a_{CaO}=0.340, a_{Al2O3}=0.064) composition, calcium necessary for evaluated aluminium after final killing of steel can be calculated by the above mentioned Eqs.(6) and (22) in the following way:

$$Ca_{(l)}+[O]=CaO_{(s)}\quad \Delta G^{\theta}=-630930+91.222T\ J/mol\ or\ LgK_{CaO}=-32938.8/T+4.762 \qquad (6)$$

$$N_{[O]}^3=a_{Al2O3}/(K_{Al2O3}\times N_{Al}^2)\ ,\quad N_{[O]}==a_{Al2O3}^{1/3}/(K_{Al2O3}\times N_{Al}^2)^{1/3}$$

$$K_{CaO(S]}=a_{CaO}/(N_{Ca}\times N_{[O]}),\qquad N_{Ca}=a_{CaO}/(K_{CaO}\times N_{[O]\times})$$

At mayanite composition a_{Ca}==6.3exp-08

At phase border C/L，a_{Ca}=2.91exp-07

At phase border L/C.A，a_{Ca}=1.706exp-08

Not only inclusions containing calcium aluminates cause nozzle blockage, but CaS also does so. In order to prevent nozzle blockage by solid CaS, it is necessary to limit sulfur content according to the conditions of 12CaO.7Al_2O_3 formation as well as two phase borders L/C and l/C.A by Eq.(35)：

$$[Ca]+[S]=CaS_{(S)}\quad logK_{CaS}=log(-28300/T+7)\ J/mol^{[20]} \qquad (35)$$

At composition of 12CaO.7Al_2O_3, $a_{[Ca]}$= 6.3exp-08, $a_{[S]}=1/(K_{CaS}\times(a_{[Ca]}/40.08))=4.945\times32=158.9$

At phase border C/L，$a_{[Ca]}$= 2.91exp-07, $a_{[S]}=1/(K_{CaS}\times(a_{[Ca]}/40.08))=1.0705\times32=34.2$

At phase border L/C.A，$a_{[Ca]}$= 1.706exp-08, $a_{[S]}=1/(K_{CaS}\times(a_{[Ca]}/40.08))=18.26\times32=584.2$

Finally comparison of effects for modifying inclusions after aluminium killing of low carbon steel with different oxygen activities at 1873 K is given in table 6.

It can be seen from Tab.6, that whether the thermodynamic parameters are accurate or not plays very important role for inclusions modification. Thermodynamic parameters from refferennce [40] are suitable to use, while those from refference [11] are not convenient to apply. Hence, uninterruptedly improve the accuracy of thermodynamic parameters pertaining metallurgical melts is one of urgent tasks of metallurgists.

Table 6 Comparison of effects for modifying inclusions after aluminium killing of low carbon steel with different oxygen activities at 1873 K

$[Ca]+[O]=CaO_{(S)}$ $2[Al]+3[O]=Al2O3_{(S)}$ $[Ca]+[S]=CaS_{(S)}$	$LgK_{CaO}=25655/T-4.843$[20] $\Delta G^{\theta}=-491411.52+92.765T$ $LgK_{Al2O3}=61304/T-13.895$ $\Delta G^{\theta}=-1174254.211+266.152T$ $LgK_{CaS}=28300/T-7$		$\Delta G^{\theta}=-630930+91.222T$ J/mol[11] $LgK_{CaO}=-32938.8/T+4.762.$ $\Delta G^{\theta}=-1225000+269.772T$ J/mol $LgK_{Al2O3}=63953.3/T-14.08$ $LgK_{CaS}=28300/T-7$	
$a_{[1\%O]}$ after aluminium killing	0.0013	0.0009	0.0013	0.0009
$a_{[1\%Al]}$ after Al killing	0.01393	0.0242	0.000344	0.0059
$a_{[1\%O]}$ at phase border C/L	0.000337	0.000233	0.000332	0.000229
$a_{[1\%O]}$ at phase border L/C.A	0.000853	0.00059	0.00084	0.000581
$a_{[1\%Ca]}$at composition12CaO.7Al_2O_3	0.000581	0.00084	6.3exp-08	9.15exp-08
$a_{[1\%Ca]}$ at phase border C/L	0.00286	0.00384	2.91exp-07	4.19exp-07
$a_{[1\%Ca]}$ at phase border L/C.A	0.00015	0.000228	1.725exp-08	2.48exp-08
$a_{[1\%S]}$atcomposition12CaO.7Al_2O_3	0.0172	0.0119	158.9	109.4
$a_{[1\%S]}$ at phase border C/L	0.00376	0.00261	34.2	23.9
$a_{[1\%S]}$ at phase border L/C.A	0.0634	0.0439	577.9	402

The above mentioned calculation is only an priliminary example for prevention of nozzle blockage during continuous casting. There are large amount of problems for modification of inclusions，This example is only serve to explain that the possibility of applying coexistence theory of metallic melt structure as well as of slag melt structure is considerably great

3 Conclusions

(1) With the coexistence theory of metallic melts involving compound formation (atoms and molecules), the coexistence theory of slag melts(molecules and ions) and the model of inseparable cations and anions of molten salts and mattes as well as the basic oxides solid solutions as the scientific basis for determination of the structural units of each solution and with the mass action law as the dominant principle, calculating models for a series of deoxidation equilibria have been formulated without the use of classical interaction parameter formalism of Wagner.

(2) Calculating model can be used to evaluate the content, composition and sum of total inclusions.

(3) The problem of nozzle blockage in continuous casting were discussed initially.

(4) Uninterruptedly improve the accuracy of thermodynamic parameters pertaining metallurgical melts is one of urgent tasks of metallurgists.

(5) There are three kinds of oxygen content in metallic melt:
   1) oxygen activity or dissolved oxygen $a_{[\%O]}=[\%O]$

2) $a_{FetO}=N_{FeO}+3N_{Fe2O3}$; L1= a_{FetO}/[%O]=≈2

3) Oxygen content of inclusions [%TO]=1600($N_{[O]}+N_{FeO}+3N_{Fe2O3}+N_{CaO}+3N_{Al2O3}+4N_{FeAl2O4}$etc)/W; L0＝［％TO］/1600/[%O]>0 and may reach a value greater than 4, where W=weight of metallic melt.

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