A thermodynamic model for evaluation of mass action concentrations of Ce_2O_3-contained slag systems based on the ion and molecule coexistence theory

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Abstract: According to the ion and molecule coexistence theory (IMCT) for molten slags and corresponding phase diagrams, a thermodynamic model for the evaluation of mass action concentrations (designated by N_i for structure unit i) for Ce_2O_3-Al_2O_3, CaO-Al_2O_3-Ce_2O_3 and CaO-Al_2O_3-SiO_2-Ce_2O_3 slag systems has been formulated. The results show that when the mole fraction of Ce_2O_3 is at 0.49 in the binary slag, the mass action concentration of $Ce_2O_3 \bullet Al_2O_3$ achieves its maximum value 0.90. In a composition area of CaO/Al_2O_3 (mass fraction ratio) from 0.7 to 1.5 and Ce_2O_3 content (mass fraction) from 0 to 45% of the ternary slag at 1773K, the results show that trends of calculated $N_{Al_2O_3}$ are in good agreement with reported measured trends of $a_{Al_2O_3}$. The iso-curves of $N_{Ce_2O_3}$ and N_{CaO} are also drawn from the calculated results. The thermodynamic model application to the equilibrium between 55.83%CaO-23%Al_2O_3-11.17%SiO_2- 10%Ce_2O_3 quaternary slag and molten steel containing aluminum has been further discussed. Results indicate that certain content of Ce would be dissolved in steel, which increases with the increasing of temperature and aluminum content, and when the aluminum content is 0.02%, the corresponding cerium content is in the range of 1.87 to 13.30ppm at 1873K. In summary, using Ce_2O_3 to replace Al_2O_3 can effectively reduce $N_{Al_2O_3}$, certain content of Ce can dissolved in steel.

Keywords: CaO-Al_2O_3-Ce_2O_3, CaO-Al_2O_3-SiO_2-Ce_2O_3, coexistence theory, mass action concentration, thermodynamic model

1. Introduction

In Al-killed steel, Al_2O_3 is one of the main inclusions which deteriorate steel performance as well as result in the submerged entry nozzle clogging during continuous casting [1]. In the process of steel refining, these harmful Al_2O_3 inclusions can be removed by the absorption of the molten covering slag and are also usually modified to form low melting complex inclusions to reduce the harmfulness of alumina inclusions.

Studies have shown that reducing the activity of Al_2O_3 and improve the fluidity properties of refining slag can effectively promote the refining slag absorption ability for Al_2O_3 inclusions [2, 3]. Shigeru UEDA et al. [4] have found that the activity coefficient of Al_2O_3 decreases with the increasing concentration of Ce_2O_3 to the CaO-Al_2O_3-Ce_2O_3 system. In addition, the equilibrium of refining slag containing Ce_2O_3 and molten steel containing Al would have a small amount of Ce dissolved in steel [5] which plays an important role in the modification of fine Al_2O_3 inclusions and micro-alloying in steel. Long Hu et al. [6] investigated on the melting and fluidity properties of refining slag containing Ce_2O_3. They have found that the high basicity refining slag with appropriate content of Ce_2O_3 has good melting and fluidity properties. The above investigations show that the activity of Al_2O_3 in the slag is reduced with the addition of Ce_2O_3 to traditional refining slag used for absorption Al_2O_3 inclusions, as a result of formation of xCe_2O_3•yAl_2O_3 compounds. Meanwhile the equilibrium between refining slag containing Ce_2O_3 and molten steel containing Al would have certain Ce dissolved in steel.

Therefore, it is of great significance that the research on Al_2O_3-Ce_2O_3, CaO-Al_2O_3-Ce_2O_3 and CaO-Al_2O_3-SiO_2-Ce_2O_3 slags which attained from the addition of Ce_2O_3 to traditional refining slags (CaO-Al_2O_3, CaO-Al_2O_3-SiO_2). At present, only Shigeru UEDA et al. [4] have measured the activity of Al_2O_3 in CaO-Al_2O_3-Ce_2O_3 ternary system at 1773 K. Enough detailed data, systematic research and the thermodynamic calculation model of the Ce_2O_3-contained slag have not yet been reported in the literature so far.

In the present work, according to the ion and molecule coexistence theory (IMCT) of slag structure and corresponding phase diagrams, the thermodynamic model for the evaluation of mass action concentration for Ce_2O_3-Al_2O_3, CaO-Al_2O_3- Ce_2O_3 and CaO-Al_2O_3-SiO_2-Ce_2O_3 are formulated. Mass action concentrations of each structure units were gained with Matlab software. And the mass action concentration of Al_2O_3 was compared with reported experimental activity of Al_2O_3 in CaO-Al_2O_3-Ce_2O_3 slag system. Influencing factors of mass action concentration for Al_2O_3, Ce_2O_3 and CaO were investigated. On this basis, the equilibrium between CaO-Al_2O_3-SiO_2-Ce_2O_3 and steel was also calculated from the view point of thermodynamics to study the probability of reduction of Ce_2O_3 to metals by aluminum and the probability of modification of Al_2O_3 inclusions by the cerium reduced from Ce_2O_3 in Al-killed steel. The results will provide scientific basis for further study and exploitation on the application of rare earth oxides in steelmaking refining slag.

2. Thermodynamic model

2.1 Hypotheses

According to the classic hypotheses of IMCT described in detail elsewhere [7], the main assumptions in the developed thermodynamic model for calculating the mass action concentrations of structural units or ion-pair inclusions in Ce_2O_3-Al_2O_3, CaO-Al_2O_3-Ce_2O_3 and CaO-Al_2O_3-SiO_2-Ce_2O_3 slags can be simply summarized as follows:

(a) Structural units in the studied slags are composed of Ca^{2+}, Ce^{3+} and O^{2-} as simple ions, SiO_2 and Al_2O_3 as simple molecules, silicates, and aluminates and so on as complex molecules. Each structural unit has its independent position in the slags. Every cation and anion generated from the same component will take part in reactions of forming complex molecules in the form of ion-pair as $(Ca^{2+}+O^{2-})$ or $(2Ce^{3+}+3O^{2-})$.

(b) Reactions of forming complex molecules are under chemically dynamic equilibrium between the generated ion-pair from simple ions and simple molecules by taking $(2Ce^{3+}+3O^{2-})$ and Al_2O_3 to form $Ce_2O_3{\cdot}Al_2O_3$ as an example as $(2Ce^{3+}+3O^{2-}) + Al_2O_3 = (Ce_2O_3{\cdot}Al_2O_3)$.

(c) Chemical reactions of forming complex molecules obey the mass action law. This implies that the chemical reaction equilibrium constant can be represented by the defined mass action concentrations in the following text.

Table 1 Expression of structural units, their mole numbers and mass action concentrations of Ce_2O_3-Al_2O_3, CaO-Al_2O_3-Ce_2O_3 and CaO-Al_2O_3-SiO_2-Ce_2O_3 slags at metallurgical temperature based on the ion and molecule coexistence theory.

Slag system			Structural units	No	Mole number of structural units	Mass action concentration
CaO-Al_2O_3-SiO_2-Ce_2O_3	CaO-Al_2O_3-Ce_2O_3	Ce_2O_3-Al_2O_3	$2Ce^{3+}+3O^{2-}$	2	$n_2 = n_{Ce_2O_3}$	$N_2 = 5n_2/\sum n_i$
			Al_2O_3	4	$n_4 = n_{Al_2O_3}$	$N_4 = n_4/\sum n_i$
			$Ce_2O_3 \cdot Al_2O_3$	13	$n_{13} = n_{Ce_2O_3 \bullet Al_2O_3}$	$N_{13} = n_{13}/\sum n_i$
			$Ce_2O_3 \cdot 11Al_2O_3$	14	$n_{14} = n_{Ce_2O_3 \bullet 11Al_2O_3}$	$N_{14} = n_{14}/\sum n_i$
			$Ca^{2+}+O^{2-}$	1	$n_1 = n_{CaO}$	$N_1 = 2n_1/\sum n_i$
			$CaO \cdot Al_2O_3$	5	$n_5 = n_{CaO \bullet Al_2O_3}$	$N_5 = n_5/\sum n_i$
			$CaO \cdot 2Al_2O_3$	6	$n_6 = n_{CaO \bullet 2Al_2O_3}$	$N_6 = n_6/\sum n_i$
			$CaO \cdot 6Al_2O_3$	7	$n_7 = n_{CaO \bullet 6Al_2O_3}$	$N_7 = n_7/\sum n_i$
			$3CaO \cdot Al_2O_3$	8	$n_8 = n_{3CaO \bullet Al_2O_3}$	$N_8 = n_8/\sum n_i$
			$12CaO \cdot 7Al_2O_3$	9	$n_9 = n_{12CaO \bullet 7Al_2O_3}$	$N_9 = n_9/\sum n_i$
			SiO_2	3	$n_3 = n_{SiO_2}$	$N_3 = n_3/\sum n_i$
			$CaO \cdot SiO_2$	10	$n_{10} = n_{CaO \bullet SiO_2}$	$N_{10} = n_{10}/\sum n_i$
			$2CaO \cdot SiO_2$	11	$n_{11} = n_{2CaO \bullet SiO_2}$	$N_{11} = n_{11}/\sum n_i$
			$3CaO \cdot SiO_2$	12	$n_{12} = n_{3CaO \bullet SiO_2}$	$N_{12} = n_{12}/\sum n_i$
			$2CaO \cdot Al_2O_3 \cdot SiO_2$	15	$n_{15} = n_{2CaO \bullet Al_2O_3 \bullet SiO_2}$	$N_{15} = n_{15}/\sum n_i$
			$CaO \cdot Al_2O_3 \cdot 2SiO_2$	16	$n_{16} = n_{CaO \bullet Al_2O_3 \bullet 2SiO_2}$	$N_{16} = n_{16}/\sum n_i$
			$3Al_2O_3 \cdot 2SiO_2$	17	$n_{17} = n_{3Al_2O_3 \bullet 2SiO_2}$	$N_{17} = n_{17}/\sum n_i$

2.2 Structural units in Ce_2O_3-Al_2O_3, CaO-Al_2O_3-Ce_2O_3 and CaO-Al_2O_3-SiO_2-Ce_2O_3 slags

According to the reported binary phase diagram of Ce_2O_3-Al_2O_3 slag [8], it can be reasonably obtained that there are two simple ions Ce^{3+} and O^{2-}, one simple molecule Al_2O_3 and two kinds of complex molecules $Ce_2O_3 \cdot Al_2O_3$ and $Ce_2O_3 \cdot 11Al_2O_3$, in the Ce_2O_3-Al_2O_3 slag, as listed in Table 1, at metallurgical temperature based on IMCT. Additionally, according to the ternary phase diagram of CaO-Al_2O_3-Ce_2O_3 slag [4], as compared with Ce_2O_3-Al_2O_3 slag, there were added one simple ion $Ca^{2+}$and five kinds of complex molecules, such as: $CaO \cdot Al_2O_3$, $CaO \cdot 2Al_2O_3$, $CaO \cdot 6Al_2O_3$, $3CaO \cdot Al_2O_3$ and $12CaO \cdot 7Al_2O_3$ in the CaO-Al_2O_3-Ce_2O_3 slag, as listed in Table 1, at refining temperature based on IMCT.

From above mentioned hypotheses, it can be obviously deduced that there are three simple ions, including Ca^{2+}, Ce^{3+} and O^{2-}, and two simple molecules as SiO_2 and Al_2O_3 in CaO-Al_2O_3-SiO_2-Ce_2O_3 slag at metallurgical temperature with respect to the ion and molecule coexistence theory. According to the reported binary phase diagram of Ce_2O_3-Al_2O_3 and Ce_2O_3-SiO_2 [9,10] slags, ternary phase diagrams of CaO-Al_2O_3-Ce_2O_3 and CaO–Al_2O_3–SiO_2 slags [11], in a refining temperature range from 1873 K to 1973 K, 16 kinds of complex molecules such as: $CaO \cdot Al_2O_3$, $CaO \cdot 2Al_2O_3$, $CaO \cdot 6Al_2O_3$, $3CaO \cdot Al_2O_3$, $12CaO \cdot 7Al_2O_3$, $CaO \cdot SiO_2$, $2CaO \cdot SiO_2$, $3CaO \cdot SiO_2$, $Ce_2O_3 \cdot Al_2O_3$,

$Ce_2O_3 \cdot 11Al_2O_3$, $Ce_2Si_2O_7$, $Ce_{4.47}(SiO_4)_3O$, $CeSi_2O_5$, $2CaO \cdot Al_2O_3 \cdot SiO_2$, $CaO \cdot Al_2O_3 \cdot 2SiO_2$ and $3Al_2O_3 \cdot 2SiO_2$, can be formed in CaO-Al_2O_3-SiO_2-Ce_2O_3 slag. However, the Gibbs free energy of three complex molecules among them such as: $Ce_2Si_2O_7$, $Ce_{4.47}(SiO_4)_3O$ and $CeSi_2O_5$ are unknown. Therefore, this model manly takes into account 13 kinds of complex molecules, as listed in Table 1.

Finally, as listed in Table 1, the structural units of Ce_2O_3-Al_2O_3, CaO-Al_2O_3-Ce_2O_3 and CaO-Al_2O_3-SiO_2-Ce_2O_3 slag systems were determined, and the corresponding numbers are 4, 10 and 17, respectively. The total equilibrium mole number of all structural units can be expressed as $\sum n_i$ (mol).

2.3 Model formulation of mass action concentrations

The components of molten slag were defined respectively as follows: $b_1 = \sum n_{CaO}$, $b_2 = n_{Ce_2O_3}$, $a_1 = n_{SiO_2}$, $a_2 = n_{Al_2O_3}$. The symbols of the mass action concentrations for all structure units were listed as following: $N_1 = N_{CaO}$, $N_2 = N_{Ce_2O_3}$, $N_3 = N_{SiO_2}$, $N_4 = N_{Al_2O_3}$, $N_5 = N_{CaO\bullet Al_2O_3}$, $N_6 = N_{CaO\bullet 2Al_2O_3}$, $N_7 = N_{CaO\bullet 6Al_2O_3}$, $N_8 = N_{3CaO\bullet Al_2O_3}$, $N_9 = N_{12CaO\bullet 7Al_2O_3}$, $N_{10} = N_{CaO\bullet SiO_2}$, $N_{11} = N_{2CaO\bullet SiO_2}$, $N_{12} = N_{3CaO\bullet SiO_2}$, $N_{13} = N_{Ce_2O_3\bullet Al_2O_3}$, $N_{14} = N_{Ce_2O_3\bullet 11Al_2O_3}$, $N_{15} = N_{2CaO\bullet Al_2O_3\bullet SiO_2}$, $N_{16} = N_{CaO\bullet Al_2O_3O\bullet 2SiO_2}$, $N_{17} = N_{3Al_2O_3\bullet 2SiO_2}$.

The chemical equations in the temperature range of 1600-1700℃ can be defined as follows [12, 13]:

$$(\mathrm{Ca}^{2+}+\mathrm{O}^{2-})_{(s)}+\mathrm{Al_2O}_{3(s)}=\mathrm{CaO}\cdot\mathrm{Al_2O}_{3(s)} \quad \Delta G^{\theta}=-18120-19.62T \quad N_5=K_1\cdot N_1\cdot N_2 \tag{1}$$

$$(\mathrm{Ca}^{2+}+\mathrm{O}^{2-})_{(s)}+2Al_2O_{3(s)}=\mathrm{CaO}\cdot 2Al_2\mathrm{O}_{3(s)} \quad \Delta G^{\theta}=-16400-26.8T \quad N_6=K_2\cdot N_1\cdot N_2^2 \tag{2}$$

$$(\mathrm{Ca}^{2+}+\mathrm{O}^{2-})_{(s)}+6\mathrm{Al_2O}_{3(s)}=\mathrm{CaO}\cdot 6\mathrm{Al_2O}_{3(s)} \quad \Delta G^{\theta}=-17430-37.2T \quad N_7=K_3\cdot N_1\cdot N_2^6 \tag{3}$$

$$3(\mathrm{Ca}^{2+}+\mathrm{O}^{2-})_{(s)}+\mathrm{Al_2O}_{3(s)}=3\mathrm{CaO}\cdot\mathrm{Al_2O}_{3(s)} \quad \Delta G^{\theta}=-17000-32.0T \quad N_8=K_4\cdot N_1^3\cdot N_2 \tag{4}$$

$$12(\mathrm{Ca}^{2+}+\mathrm{O}^{2-})_{(s)}+7\mathrm{Al_2O}_{3(s)}=12\mathrm{CaO}\cdot 7\mathrm{Al_2O}_{3(s)} \quad \Delta G^{\theta}=-86100-205.1T \quad N_9=K_5\cdot N_1^{12}\cdot N_2^7 \tag{5}$$

$$(\mathrm{Ca}^{2+}+\mathrm{O}^{2-})_{(s)}+\mathrm{SiO}_{2(s)}=\mathrm{CaO}\cdot\mathrm{SiO}_{2\ (s)} \quad \Delta G^{\theta}=-81416-10.498T \quad N_{10}=K_6\cdot N_1\cdot N_3 \tag{6}$$

$$2(\mathrm{Ca}^{2+}+\mathrm{O}^{2-})_{(s)}+\mathrm{SiO}_{2(s)}=2\mathrm{CaO}\cdot\mathrm{SiO}_{2\ (s)} \quad \Delta G^{\theta}=-160431+4.016T \quad N_{11}=K_7\cdot N_1^2\cdot N_3 \tag{7}$$

$$3(\mathrm{Ca}^{2+}+\mathrm{O}^{2-})_{(s)}+\mathrm{SiO}_{2(s)}=3\mathrm{CaO}\cdot\mathrm{SiO}_{2(s)} \quad \Delta G^{\theta}=-93366-23.03T \quad N_{12}=K_8\cdot N_1^3\cdot N_3 \tag{8}$$

$$(2\mathrm{C}e^{3+}+3\mathrm{O}^{2-})_{(s)}+\mathrm{A}l_2O_{3(s)}=\mathrm{Ce_2O_3}\cdot\mathrm{A}l_2\mathrm{O}_{3(s)} \quad \Delta G^{\theta}=-58555.5-15.04T \quad N_{13}=K_9\cdot N_2\cdot N_4 \tag{9}$$

$$(2\mathrm{C}e^{3+}+3\mathrm{O}^{2-})_{(s)}+11\mathrm{A}l_2O_{3(s)}=\mathrm{Ce_2O_3}\cdot 11\mathrm{A}l_2\mathrm{O}_{3(s)} \quad \Delta G^{\theta}=49323-80.56T \quad N_{14}=K_{10}\cdot N_2\cdot N_4^{11} \tag{10}$$

$$(\mathrm{Ca}^{2+}+\mathrm{O}^{2-})_{(s)}+\mathrm{Al_2O}_{3(s)}+2\mathrm{SiO}_{2(s)}=\mathrm{CaO}\cdot\mathrm{Al_2O_3}\cdot 2\mathrm{SiO}_{2(s)} \quad \Delta G^{\theta}=-13816.4-55.23T \quad N_{15}=K_{11}\cdot N_1\cdot N_2\cdot N_3^2 \tag{11}$$

$$2(\mathrm{Ca}^{2+}+\mathrm{O}^{2-})_{(s)}+\mathrm{Al_2O}_{3(s)}+\mathrm{SiO}_{2(s)}=2\mathrm{CaO}\cdot\mathrm{Al_2O_3}\cdot\mathrm{SiO}_{2(s)} \quad \Delta G^{\theta}=-61964.6-60.29T \quad N_{16}=K_{12}\cdot N_1^2\cdot N_2\cdot N_3 \tag{12}$$

$$3\mathrm{Al_2O}_{3(s)}+2\mathrm{SiO}_{2(s)}=3\mathrm{Al_2O_3}\cdot 2\mathrm{SiO}_{2(s)} \quad \Delta G^{\theta}=-4351-10.46T\ J/mol \quad N_{17}=K_{13}\cdot N_2^3\cdot N_3^2 \tag{13}$$

The equilibrium constant K_i^{θ} of the all reactions can be calculated by $K_i^{\theta} = \exp\left(-\Delta_r G_{m,i}^{\theta}/RT\right)$.

2.3.1 Ce_2O_3-Al_2O_3 slag system

The total equilibrium mole number of all structural units in Ce_2O_3-Al_2O_3 slags can be expressed as $\sum n_i = 5n_2 + n_4 + n_{13} + n_{14}$ (mol).

The mass action concentration of the structural unit is defined as a ratio of the equilibrium mole number of structural unit *i* to the total equilibrium mole numbers of all structural units according to IMCT, and all structural units in the form of simple ions, simple molecules, and complex molecules can be calculated by $N_i = \frac{n_i}{\sum n_i}$. The $N_{Me_2O_3}$ such as ion-pair ($2Me^{3+}+3O^{2-}$), should be calculated by $N_{MeO} = N_{Me^{2+},MeO} + N_{O^{2-},MeO} = \frac{2n_{Me^{3+},MeO} + 3n_{O^{2-},MeO}}{\sum n_i} = \frac{5n_{MeO}}{\sum n_i}$.

Mass equilibrium formulas were listed below:

$$b_2 = \sum n \cdot (0.2N_2 + N_{13} + N_{14}) \tag{14}$$

$$a_2 = \sum n \cdot (N_4 + N_{13} + 11N_{14}) \tag{15}$$

$$N_2 + N_4 + N_{13} + N_{14} = 1 \tag{16}$$

Therefore, the equation(9), (10) and (14)-(16) are the governing equations of the developed thermodynamic model for calculating mass action concentrations N_i of structural units or ion couples in the Ce_2O_3-Al_2O_3 slag.

2.3.2 CaO-Al_2O_3-Ce_2O_3 slag system

The total equilibrium mole number of all structural units in CaO-Al_2O_3-Ce_2O_3 slag can be expressed as $\sum n_i = 2n_1 + 5n_2 + n_4 + n_5 + n_6 + n_7 + n_8 + n_9 + n_{13} + n_{14}$ (mol).

Mass equilibrium formulas were listed below:

$$b_1 = \sum n \cdot (0.5N_1 + N_5 + N_6 + N_7 + 3N_8 + 12N_9) \tag{17}$$

$$b_2 = \sum n \cdot (0.2N_2 + N_{13} + N_{14}) \tag{18}$$

$$a_2 = \sum n \cdot (N_4 + N_5 + 2N_6 + 6N_7 + N_8 + 7N_9 + N_{13} + 11N_{14}) \tag{19}$$

$$N_1 + N_2 + N_4 + N_5 + N_6 + N_7 + N_8 + N_9 + N_{13} + N_{14} = 1 \tag{20}$$

Therefore, the equation (1)-(5), (9), (10) and (17)-(20) are the governing equations of the developed thermodynamic model for calculating mass action concentrations N_i of structural units or ion couples in the CaO-Al_2O_3-Ce_2O_3 slag.

2.3.3 CaO-Al_2O_3-SiO_2-Ce_2O_3 slag system

The total equilibrium mole number of all structural units in CaO-Al_2O_3-SiO_2-Ce_2O_3 slag can be expressed as $\sum n_i = 2n_1 + 5n_2 + n_3 + n_4 + n_5 + n_6 + n_7 + n_8 + n_9 + n_{10} + n_{11} + n_{12} + n_{13} + n_{14} + n_{15} + n_{16} + n_{17}$ (mol).

Mass equilibrium formulas were listed below:

$$b_1 = \sum n \cdot (0.5N_1 + N_5 + N_6 + N_7 + 3N_8 + 12N_9 + N_{10} + 2N_{11} + 3N_{12} + 2N_{15} + N_{16}) \tag{21}$$

$$b_2 = \sum n \cdot (0.2N_2 + N_{13} + N_{14}) \tag{22}$$

$$a_1 = \sum n \cdot (N_3 + N_{10} + N_{11} + N_{12} + N_{15} + 2N_{16} + 2N_{17}) \tag{23}$$

$$a_2 = \sum n \cdot (N_4 + N_5 + 2N_6 + 6N_7 + N_8 + 7N_9 + N_{13} + 11N_{14} + N_{15} + N_{16} + N_{16} + 3N_{17}) \tag{24}$$

$$N_1 + N_2 + N_3 + \cdots + N_{16} + N_{17} = 1 \tag{25}$$

Therefore, the equation (1)-(13) and (21)-(25) are the governing equations of the developed thermodynamic model for calculating mass action concentrations N_i of structural units or ion couples in the CaO-Al_2O_3-SiO_2-Ce_2O_3 slag.

3. Results and discussion

In a certain temperature, the calculation could carry out with certain slag components using the governing equations under the conditions of equilibrium state and the standard state. After linearization, Newton iterative method was used in Matlab software to gain all the mass action concentrations of each structural units or ion couples.

3.1 Ce_2O_3-Al_2O_3 slag system

The relationship between mass action concentrations of each structural unit in binary slag system of Ce_2O_3-Al_2O_3 gained from the established thermodynamic model at 1873 K and the mole fraction of Ce_2O_3 is presented respectively in **Fig.1**. These results can be confirmed from **Fig.1** that when mole fraction of Ce_2O_3 equals 0.49, the mass action concentration of Ce_2O_3•Al_2O_3 achieves its maximum value 0.90 and both the mass action concentrations of Ce_2O_3 and Al_2O_3 maintain at very low levels owing to the strong combination ability of Ce_2O_3 and Al_2O_3, which combine to form Ce_2O_3•Al_2O_3. However, if the mole fraction of Ce_2O_3 is greater than 0.49, the mass action concentration of Ce_2O_3 would increases sharply. Oppositely, when the mole fraction of Ce_2O_3 is smaller than 0.49, the mass action concentration of Al_2O_3 would increases rapidly.

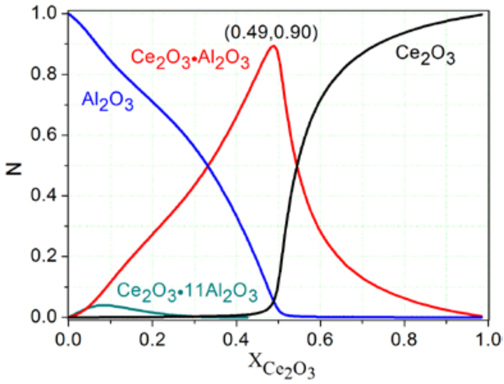

Fig.1 The relationship between N_i in Ce_2O_3-Al_2O_3 slag and the mole fraction of Ce_2O_3 at 1873 K

3.2 CaO-Al_2O_3-Ce_2O_3 slag system

According to the established thermodynamic model, the mass action concentrations of each structural unit in CaO-Al_2O_3-Ce_2O_3 ternary system were calculated at 1773 K, while CaO/Al_2O_3 (mass fraction) is in the range of 0.7~1.5 and the mass fraction of Ce_2O_3 is in the range of 0~45%.

3.2.1 Mass action concentrations of Al_2O_3

According to the calculation results, the iso-mass action concentrations curves of Al_2O_3 were drawn and compared with the iso-activity curves of Al_2O_3 measured by Shigeru [4] , as shown in **Fig.2**.

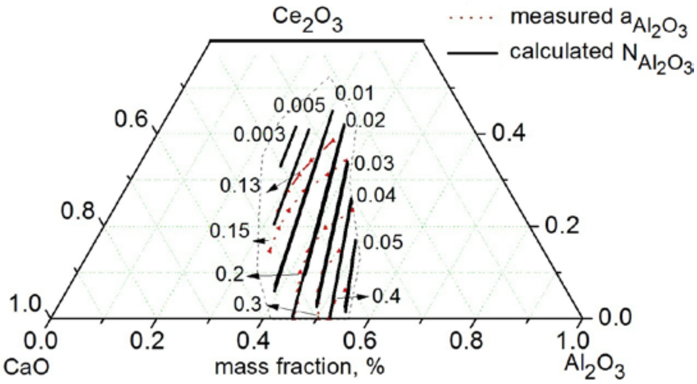

Fig.2 The calculated iso-mass action concentration curves of Al_2O_3 and measured iso-activity curves of Al_2O_3 in CaO-Al_2O_3-Ce_2O_3 ternary slag system at 1773 K

Fig.2 shows that compared with the $a_{Al_2O_3}$, measured by equilibrating molten Cu and the CaO-Al_2O_3- Ce_2O_3 flux under a controlled oxygen partial pressure, the trends of $N_{Al_2O_3}$ decreasing with the increasing of CaO/Al_2O_3 or Ce_2O_3/Al_2O_3 are in good agreement with the reported measured trends of $a_{Al_2O_3}$ in CaO-Al_2O_3-Ce_2O_3 slag system. This is closely related with the strong combination ability of Ce_2O_3 and CaO with Al_2O_3, which can combine to form various compounds. However, the calculated mass action concentrations of Al_2O_3 are 0.1 times that of the measured activity of Al_2O_3. The possible reason of the great difference between calculated $N_{Al_2O_3}$ and measured $a_{Al_2O_3}$ is that the activity and mass action concentration are having different standard states. In addition, the thermodynamic data is not accurate and the structural unit of slag has uncertainty at high temperature, which still need be further perfected.

Further studies reveal that the mass action concentration of Al_2O_3 decreases with the increasing of CaO/Al_2O_3 at a certain content of Ce_2O_3 and with the increasing of Ce_2O_3 content at a certain value of CaO/Al_2O_3, as shown in **Fig.3**. It can be observed from **Fig.3** that the mass action concentration of Al_2O_3 has a small value when the value of CaO/Al_2O_3 is big and the content of Ce_2O_3 is high.

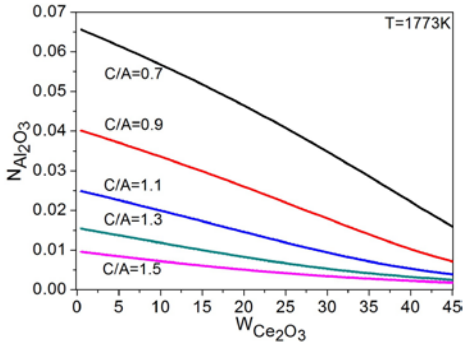

Fig.3. The influence of CaO/Al_2O_3 and Ce_2O_3 content on mass action concentration of Al_2O_3 at 1773 K

3.2.2 Mass action concentrations of Ce_2O_3 and CaO

The iso-mass action concentration curves of Ce_2O_3 in CaO-Al_2O_3-Ce_2O_3 slag system at 1773K were shown in **Fig.4**. It can be seen from **Fig.4** that when CaO/Al_2O_3 (mass ratio) is constant, the mass action concentrations of Ce_2O_3 increase with the increasing of the content of Ce_2O_3. In addition, when the content of Ce_2O_3 is constant, the mass action concentrations of Ce_2O_3 increase with the increasing of CaO/Al_2O_3 (mass ratio).

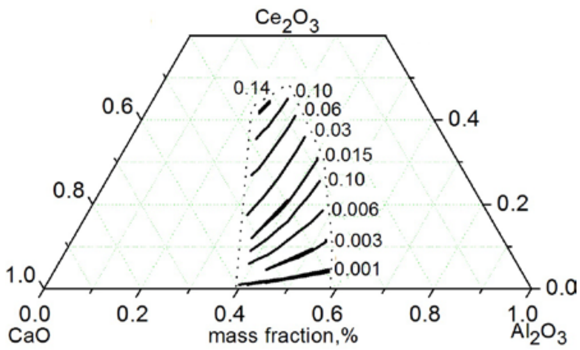

Fig.4 The iso-mass action concentration curves of Ce_2O_3 in CaO-Al_2O_3-Ce_2O_3 ternary slag system at 1773 K

The iso-mass action concentration curves of CaO in CaO-Al_2O_3-Ce_2O_3 slag system at 1773K were shown in **Fig.5**. It can be seen from **Fig.5** that when CaO/Al_2O_3 (mass ratio) is constant, increasing of the content of Al_2O_3 can result in decreasing the mass action concentrations of CaO; in addition, when the content of CaO is constant, increasing of CaO/Al_2O_3 (mass ratio) can lead to decreasing the mass action concentrations of CaO.

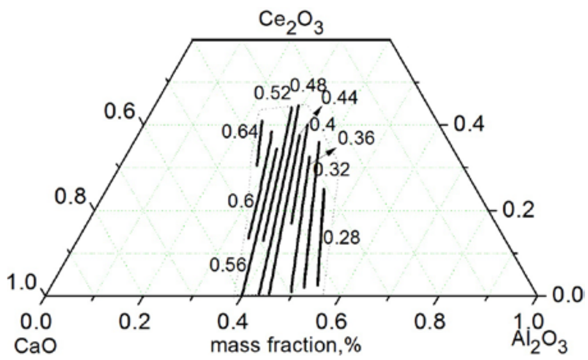

Fig.5 The iso-mass action concentration curves of CaO in CaO-Al_2O_3-Ce_2O_3 ternary slag system at 1773 K

3.3 CaO-Al_2O_3-SiO_2-Ce_2O_3 slag system

According to the established thermodynamic model, the mass action concentrations of each structural unit in CaO-Al_2O_3-SiO_2-Ce_2O_3 quaternary slag system were calculated at the condition of that Al_2O_3+Ce_2O_3=33%, the CaO/Al_2O_3 equals to 4.5 and 5.5 and Ce_2O_3 content is in the range of 0~15% at 1773K.

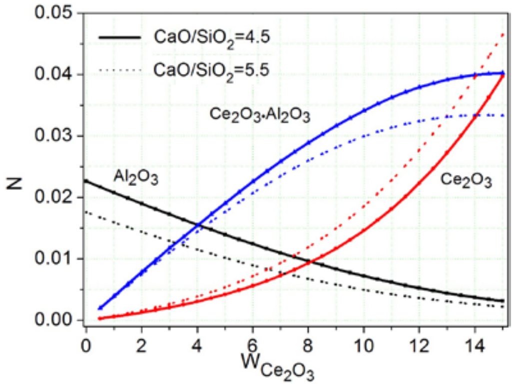

Fig.6 The influence of the content of Ce_2O_3 and basicity on the mass action concentrations of Ce_2O_3, Al_2O_3 and Ce_2O_3·Al_2O_3 at 1773 K

When the value of CaO/SiO_2 equals to 4.5 and 5.5 respectively, the influence of the mass fraction of Ce_2O_3 on the mass action concentrations of Ce_2O_3, Al_2O_3 and Ce_2O_3·Al_2O_3 at 1773 K were shown in **Fig.6**. It can be seen from **Fig.6** that with the increasing of the mass fraction of Ce_2O_3, the mass action concentrations of Ce_2O_3 and Ce_2O_3·Al_2O_3 increase and the mass action concentration of Al_2O_3 decreases respectively. **Fig.6** also reveals that with the value of CaO/SiO_2 increasing from 4.5 to 5.5, the mass action concentrations of Al_2O_3 and Ce_2O_3·Al_2O_3 decrease and the mass action concentration of Ce_2O_3 increases respectively.

On the basis of previous work, the thermodynamic model application to the equilibrium between CaO-Al_2O_3-SiO_2-Ce_2O_3 refining slag and molten steel containing aluminum has been further discussed. The composition of the slag is represented as 55.83%CaO-23%Al_2O_3-11.17%SiO_2-10%Ce_2O_3. The mass action concentrations of structural units in this slag were gained by previous formulated thermodynamic model basis on IMCT.

Reaction (26), (27) and their standard Gibbs free energy can be deduced from reaction (9), Al and Ce deoxidization reaction [14].

$$2[Ce]+2(Al_2O_3)=(Ce_2O_3\cdot Al_2O_3)+2[Al]\ \Delta G^{\theta}=-285315.5-41.96T\text{ ,J/mol} \quad (26)$$

$$2[Ce]+(Ce_2O_3\cdot Al_2O_3)=2(Ce_2O_3)+2[Al]\ \Delta G^{\theta}=-168204.5-11.88T\text{ , J/mol} \quad (27)$$

$$a_{Al}=f_{Al}[\%Al]\quad \lg f_{Al}=\sum_{j=1}^{n}e_{Al}^{j}[\%j] \quad (28)$$

$$a_{Ce}=f_{Ce}[\%Ce]\quad \lg f_{Ce}=\sum_{j=1}^{n}e_{Ce}^{j}[\%j] \quad (29)$$

The relevant solute interaction coefficients of Ce and Al are listed in **Table 2**[15]. And the mass action concentrations of Ce_2O_3, Al_2O_3 and $Ce_2O_3 \cdot Al_2O_3$ are listed in **Table 3**.

The relation between cerium and aluminum in molten steel equilibrated with 55.83% CaO-23% Al_2O_3-11.17% SiO_2-10% Ce_2O_3 quaternary slag were found out using equations (26)-(29) and data from **Table 2** and **Table 3** at 1873K and 1973K, which is expressed as equations (30)-(33).

Table 2 The interaction coefficient e_i^j of the various elements in liquid steel in 1600-1700℃

i, j	Al, Al	Al, Ce	Ce, Ce	Ce, Al
e_i^j	0.043	-0.043	0.0039	-2.25

Table 3 The mass action concentration of Ce_2O_3, Al_2O_3 and $Ce_2O_3 \cdot Al_2O_3$ in 55.83% CaO-23% Al_2O_3-11.17% SiO_2-10% Ce_2O_3 quaternary slag

N	Al_2O_3	Ce_2O_3	$Ce_2O_3 \cdot Al_2O_3$
T=1873K	0.006171	0.01929	0.03122
T=1973K	0.006398	0.02200	0.03050

T=1873K

$$2.30[\%Al] + \lg[\%Al] - 0.047[\%Ce] - \lg[\%Ce] = 4.72 \tag{30}$$

$$2.30[\%Al] + \lg[\%Al] - 0.047[\%Ce] - \lg[\%Ce] = 2.76 \tag{31}$$

T=1973K

$$2.30[\%Al] + \lg[\%Al] - 0.047[\%Ce] - \lg[\%Ce] = 4.53 \tag{32}$$

$$2.30[\%Al] + \lg[\%Al] - 0.047[\%Ce] - \lg[\%Ce] = 2.60 \tag{33}$$

Fig.7 shows the thermodynamics conditions for different type of inclusions formation which is expressed as equations (31), (32) at 1873K and equations (33), (34) at 1973K. **Fig.7** reveals that the content of cerium dissolved in steel increases with the increasing of temperature and the content of aluminum. It can be seen from **Fig.7** that the $Ce_2O_3 \cdot Al_2O_3$ type inclusions would be formed when the content of aluminum was 0.02% with the cerium content in the range of 1.87ppm to 13.30ppm at 1873K and with the cerium content in the range of 2.25ppm to 15.50ppm at 1973K. Consequently, Ce_2O_3 inclusions would form when cerium content higher than this range. On the other hand, when cerium content is lower than this range, the stable inclusions are mainly Al_2O_3.

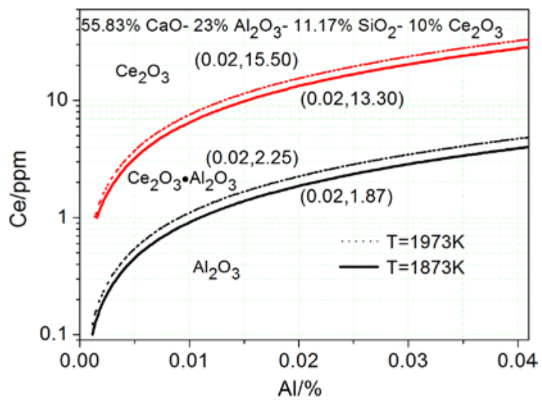

Fig.7 Ce_2O_3, Ce_2O_3•Al_2O_3 and Al_2O_3 formation conditions of [Ce] and [Al] at 1873K and 1973K

4. Conclusions

(1)Based on ion and molecule coexistence theory, the thermodynamic model formulations for calculating the mass action concentrations of structural units or ion-pair in Ce_2O_3-Al_2O_3, CaO-Al_2O_3-Ce_2O_3 and CaO-Al_2O_3-SiO_2-Ce_2O_3 slag systems are established. The mass action concentrations of each structural unit were gained in the three slag systems.

(2) In Ce_2O_3-Al_2O_3 slag system, results show that when mole fraction of Ce_2O_3 is 0.49, the mass action concentration of Ce_2O_3•Al_2O_3 achieves its maximum value 0.90 and both the mass action concentrations of Ce_2O_3 and Al_2O_3 maintain at very low values. However, if mole fraction of Ce_2O_3 is greater than 0.49 the mass action concentration of Ce_2O_3 would increases sharply. Oppositely, when mole fraction of Ce_2O_3 is smaller than 0.49 the mass action concentration of Al_2O_3 would increases rapidly.

(3) In CaO-Al_2O_3-Ce_2O_3 slag system, the trends of calculated mass action concentration of Al_2O_3 are in good agreement with the reported measured trends of activity of Al_2O_3, namely, the mass action concentration of Al_2O_3 decreases with the increasing of CaO/Al_2O_3 at a certain content of Ce_2O_3 and with the increasing of Ce_2O_3 content at a certain value of CaO/Al_2O_3.The iso-mass action concentration curves of Ce_2O_3 and CaO are drawn from the calculated results.

(4) On the basis of previous work, the thermodynamic model application to the equilibrium between CaO-Al_2O_3-SiO_2-Ce_2O_3 slag and molten steel containing aluminum has been discussed. Results show that certain content of cerium would be dissolved in molten steel equilibrated with 55.83%CaO-23%Al_2O_3-11.17%SiO_2-10%Ce_2O_3 slag, which increases with the increasing of temperature and aluminum content, and the corresponding cerium content is in the range of 1.87~13.30ppm when the aluminum content is 0.02% at 1873K.

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