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

*Chengchuan WU, Guoguang CHENG, Hu LONG and Xiaohong YANG*

*School of Metallurgical and Ecological Engineering, University of Science and technology Beijing,*

*Beijing 100083, China*

**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]:

$$(Ca^{2+}+O^{2-})_{(s)}+Al_2O_{3(s)}=CaO \cdot Al_2O_{3(s)} \quad \Delta G^{\theta} = -18120 - 19.62T \quad N_5 = K_1 \cdot N_1 \cdot N_2 \tag{1}$$

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

$$(Ca^{2+}+O^{2-})_{(s)}+6Al_2O_{3(s)}=CaO \cdot 6Al_2O_{3(s)} \quad \Delta G^{\theta} = -17430 - 37.2T \quad N_7 = K_3 \cdot N_1 \cdot N_2^6 \tag{3}$$

$$3(Ca^{2+}+O^{2-})_{(s)}+Al_2O_{3(s)}=3CaO \cdot Al_2O_{3(s)} \quad \Delta G^{\theta} = -17000 - 32.0T \quad N_8 = K_4 \cdot N_1^3 \cdot N_2 \tag{4}$$

$$12(Ca^{2+}+O^{2-})_{(s)}+7Al_2O_{3(s)}=12CaO \cdot 7Al_2O_{3(s)} \quad \Delta G^{\theta} = -86100 - 205.1T \quad N_9 = K_5 \cdot N_1^{12} \cdot N_2^7 \tag{5}$$

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

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

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

$$\left(2Ce^{3+} + 3O^{2-}\right)_{(s)} + Al_2O_{3(s)} = Ce_2O_3 \cdot Al_2O_{3(s)} \quad \Delta G^{\theta} = -58555.5 - 15.04T \quad N_{13} = K_9 \cdot N_2 \cdot N_4 \tag{9}$$

$$\left(2Ce^{3+} + 3O^{2-}\right)_{(s)} + 11Al_2O_{3(s)} = Ce_2O_3 \cdot 11Al_2O_{3(s)} \quad \Delta G^{\theta} = 49323 - 80.56T \quad N_{14} = K_{10} \cdot N_2 \cdot N_4^{11} \tag{10}$$

$$(Ca^{2+}+O^{2-})_{(s)}+Al_2O_{3(s)}+2SiO_{2(s)}=CaO \cdot Al_2O_3 \cdot 2SiO_{2(s)} \quad \Delta G^{\theta} = -13816.4 - 55.23T \quad N_{15} = K_{11} \cdot N_1 \cdot N_2 \cdot N_3^2 \tag{11}$$

$$2(Ca^{2+}+O^{2-})_{(s)}+Al_2O_{3(s)}+SiO_{2(s)}=2CaO \cdot Al_2O_3 \cdot SiO_{2(s)} \quad \Delta G^{\theta} = -61964.6 - 60.29T \quad N_{16} = K_{12} \cdot N_1^2 \cdot N_2 \cdot N_3 \tag{12}$$

$$3Al_2O_{3(s)}+2SiO_{2(s)}=3Al_2O_3 \cdot 2SiO_{2(s)} \quad \Delta G^{\theta} = -4351 - 10.46T\ J/mol \quad N_{17} = K_{13} \cdot N_2^3 \cdot N_3^2 \tag{13}$$

The equilibrium constant $K_i^{\theta}$ 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:

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

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

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

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:

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

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

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

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

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:

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

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

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

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

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

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 $Ce_2O_3 \cdot Al_2O_3$ 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 $Ce_2O_3 \cdot Al_2O_3$. 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.

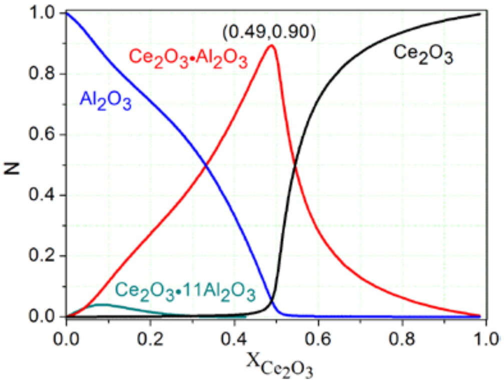

Fig.1 The relationship between $N_i$ in $Ce_2O_3$-$Al_2O_3$ slag and the mole fraction of $Ce_2O_3$ at 1873 K

### 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**.

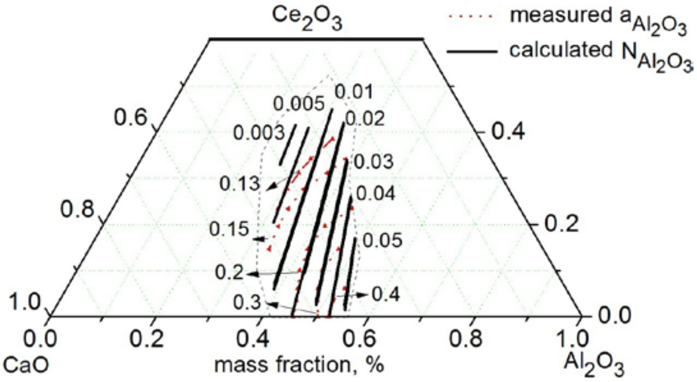

**Fig.2** The calculated iso-mass action concentration curves of $Al_2O_3$ and measured iso-activity curves of $Al_2O_3$ in CaO-$Al_2O_3$-$Ce_2O_3$ ternary slag system at 1773 K

**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.

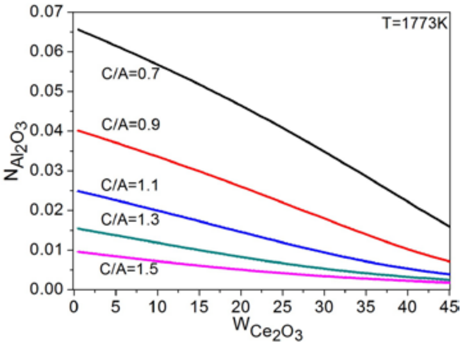

**Fig.3.** The influence of $CaO/Al_2O_3$ and $Ce_2O_3$ content on mass action concentration of $Al_2O_3$ at 1773 K

### 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).

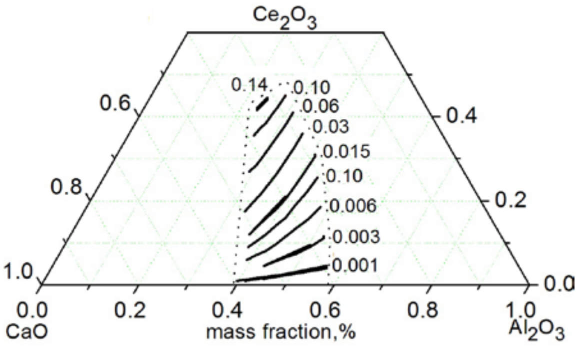

Fig.4 The iso-mass action concentration curves of $Ce_2O_3$ in $CaO-Al_2O_3-Ce_2O_3$ ternary slag system at 1773 K

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.

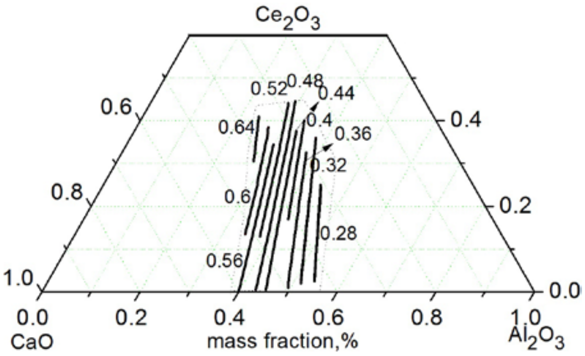

**Fig.5** The iso-mass action concentration curves of CaO in $CaO-Al_2O_3-Ce_2O_3$ ternary slag system at 1773 K

### 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.

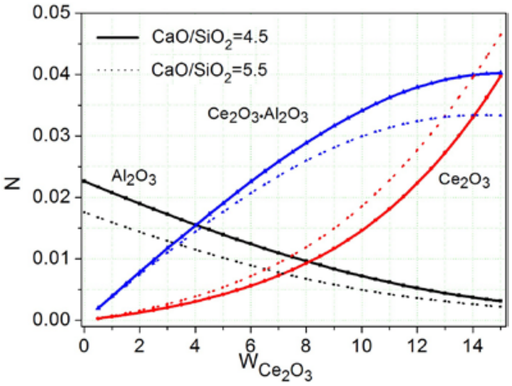

**Fig.6** The influence of the content of $Ce_2O_3$ and basicity on the mass action concentrations of $Ce_2O_3$, $Al_2O_3$ and $Ce_2O_3 \cdot Al_2O_3$ at 1773 K

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 $Ce_2O_3 \cdot Al_2O_3$ 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 $Ce_2O_3 \cdot Al_2O_3$ 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 $Ce_2O_3 \cdot Al_2O_3$ 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].

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

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

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

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

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

$$2.30[\%Al] + \lg[\%Al] - 0.047[\%Ce] - \lg[\%Ce] = 4.72 \quad (30)$$

$$2.30[\%Al] + \lg[\%Al] - 0.047[\%Ce] - \lg[\%Ce] = 2.76 \quad (31)$$

T=1973K

$$2.30[\%Al] + \lg[\%Al] - 0.047[\%Ce] - \lg[\%Ce] = 4.53 \quad (32)$$

$$2.30[\%Al] + \lg[\%Al] - 0.047[\%Ce] - \lg[\%Ce] = 2.60 \quad (33)$$

**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 $Al_2O_3$.

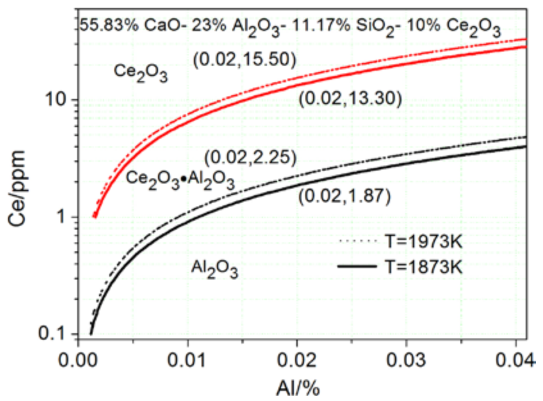

**Fig.7 $Ce_2O_3$, $Ce_2O_3$•$Al_2O_3$ and $Al_2O_3$ formation conditions of [Ce] and [Al] at 1873K and 1973K**

## 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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