A thermodynamic model for evaluation of mass action concentrations of Ce$_2$O$_3$-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$_2$O$_3$-Al$_2$O$_3$, CaO-Al$_2$O$_3$-Ce$_2$O$_3$ and CaO-Al$_2$O$_3$-SiO$_2$-Ce$_2$O$_3$ slag systems has been formulated. The results show that when the mole fraction of Ce$_2$O$_3$ is at 0.49 in the binary slag, the mass action concentration of Ce$_2$O$_3$$\cdot$Al$_2$O$_3$ achieves its maximum value 0.90. In a composition area of CaO/Al$_2$O$_3$ (mass fraction ratio) from 0.7 to 1.5 and Ce$_2$O$_3$ content (mass fraction) from 0 to 45% of the ternary slag at 1773K, the results show that trends of calculated $N_{\text{Al}_2\text{O}_3}$ are in good agreement with reported measured trends of $a_{\text{Al}_2\text{O}_3}$. The iso-curves of $N_{\text{Ce}_2\text{O}_3}$ and $N_{\text{CaO}}$ are also drawn from the calculated results. The thermodynamic model application to the equilibrium between 55.83%CaO-23%Al$_2$O$_3$-11.17%SiO$_2$-10%Ce$_2$O$_3$ 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$_2$O$_3$ to replace Al$_2$O$_3$ can effectively reduce $N_{\text{Al}_2\text{O}_3}$, certain content of Ce can dissolve in steel.

Keywords: CaO-Al$_2$O$_3$-Ce$_2$O$_3$, CaO-Al$_2$O$_3$-SiO$_2$-Ce$_2$O$_3$, coexistence theory, mass action concentration, thermodynamic model

1. Introduction

In Al-killed steel, Al$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ and improve the fluidity properties of refining slag can effectively promote the refining slag absorption ability for Al$_2$O$_3$ inclusions [2, 3]. Shigeru UEDA et al. [4] have found that the activity coefficient of Al$_2$O$_3$ decreases with the increasing concentration of Ce$_2$O$_3$ to the CaO-Al$_2$O$_3$-Ce$_2$O$_3$ system. In addition, the equilibrium of refining slag containing Ce$_2$O$_3$ 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$_2$O$_3$ inclusions and micro-alloying in steel. Long Hu et al. [6] investigated on the melting and fluidity properties of refining slag containing Ce$_2$O$_3$. They have found that the high basicity refining slag with appropriate content of Ce$_2$O$_3$ has good melting and
fluidity properties. The above investigations show that the activity of Al\textsubscript{2}O\textsubscript{3} in the slag is reduced with the addition of Ce\textsubscript{2}O\textsubscript{3} to traditional refining slag used for absorption Al\textsubscript{2}O\textsubscript{3} inclusions, as a result of formation of xCe\textsubscript{2}O\textsubscript{3}\cdot yAl\textsubscript{2}O\textsubscript{3} compounds. Meanwhile the equilibrium between refining slag containing Ce\textsubscript{2}O\textsubscript{3} and molten steel containing Al would have certain Ce dissolved in steel.

Therefore, it is of great significance that the research on Al\textsubscript{2}O\textsubscript{3}-Ce\textsubscript{2}O\textsubscript{3}, CaO-Al\textsubscript{2}O\textsubscript{3}-Ce\textsubscript{2}O\textsubscript{3} and CaO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2}-Ce\textsubscript{2}O\textsubscript{3} slags which attained from the addition of Ce\textsubscript{2}O\textsubscript{3} to traditional refining slags (CaO-Al\textsubscript{2}O\textsubscript{3}, CaO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2}). At present, only Shigeru UEDA et al. \cite{4} have measured the activity of Al\textsubscript{2}O\textsubscript{3} in CaO-Al\textsubscript{2}O\textsubscript{3}-Ce\textsubscript{2}O\textsubscript{3} ternary system at 1773 K. Enough detailed data, systematic research and the thermodynamic calculation model of the Ce\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{3}-Al\textsubscript{2}O\textsubscript{3}, CaO-Al\textsubscript{2}O\textsubscript{3}-Ce\textsubscript{2}O\textsubscript{3} and CaO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2}-Ce\textsubscript{2}O\textsubscript{3} are formulated. Mass action concentrations of each structure units were gained with Matlab software. And the mass action concentration of Al\textsubscript{2}O\textsubscript{3} was compared with reported experimental activity of Al\textsubscript{2}O\textsubscript{3} in CaO-Al\textsubscript{2}O\textsubscript{3}-Ce\textsubscript{2}O\textsubscript{3} slag system. Influencing factors of mass action concentration for Al\textsubscript{2}O\textsubscript{3}, Ce\textsubscript{2}O\textsubscript{3} and CaO were investigated. On this basis, the equilibrium between CaO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2}-Ce\textsubscript{2}O\textsubscript{3} and steel was also calculated from the view point of thermodynamics to study the probability of reduction of Ce\textsubscript{2}O\textsubscript{3} to metals by aluminum and the probability of modification of Al\textsubscript{2}O\textsubscript{3} inclusions by the cerium reduced from Ce\textsubscript{2}O\textsubscript{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 \cite{7}, the main assumptions in the developed thermodynamic model for calculating the mass action concentrations of structural units or ion-pair inclusions in Ce\textsubscript{2}O\textsubscript{3}-Al\textsubscript{2}O\textsubscript{3}, CaO-Al\textsubscript{2}O\textsubscript{3}-Ce\textsubscript{2}O\textsubscript{3} and CaO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2}-Ce\textsubscript{2}O\textsubscript{3} slags can be simply summarized as follows:

(a) Structural units in the studied slags are composed of Ca\textsuperscript{2+}, Ce\textsuperscript{3+} and O\textsuperscript{2-} as simple ions, SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{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\textsuperscript{2+}+O\textsuperscript{2-}) or (2Ce\textsuperscript{3+}+3O\textsuperscript{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\textsuperscript{3+}+3O\textsuperscript{2-}) and Al\textsubscript{2}O\textsubscript{3} to form Ce\textsubscript{2}O\textsubscript{3}\cdot Al\textsubscript{2}O\textsubscript{3} as an example as (2Ce\textsuperscript{3+}+3O\textsuperscript{2-}) +Al\textsubscript{2}O\textsubscript{3} = (Ce\textsubscript{2}O\textsubscript{3}\cdot Al\textsubscript{2}O\textsubscript{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$_2$O$_3$-Al$_2$O$_3$, CaO-Al$_2$O$_3$-Ce$_2$O$_3$ and CaO-Al$_2$O$_3$-SiO$_2$-Ce$_2$O$_3$ slags at metallurgical temperature based on the ion and molecule coexistence theory.

<table>
<thead>
<tr>
<th>Slag system</th>
<th>Structural units</th>
<th>No</th>
<th>Mole number of structural units</th>
<th>Mass action concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$_2$O$_3$-Al$_2$O$_3$</td>
<td>2Ce$^{3+}$+3O$^{2-}$</td>
<td>2</td>
<td>$n_2 = n_{Ce_2O_3}$</td>
<td>$N_2 = 5n_1\sum n_i$</td>
</tr>
<tr>
<td></td>
<td>Al$_2$O$_3$</td>
<td>4</td>
<td>$n_4 = n_{Al_2O_3}$</td>
<td>$N_4 = n_1\sum n_i$</td>
</tr>
<tr>
<td></td>
<td>Ce$_2$O$_3$·Al$_2$O$_3$</td>
<td>13</td>
<td>$n_{13} = n_{Ce_2O_3} \cdot Al_2O_3$</td>
<td>$N_{13} = n_1\sum n_i$</td>
</tr>
<tr>
<td>CaO-Al$_2$O$_3$</td>
<td>Ce$_2$O$_3$·11Al$_2$O$_3$</td>
<td>14</td>
<td>$n_{14} = n_{Ce_2O_3} \cdot 11Al_2O_3$</td>
<td>$N_{14} = n_1\sum n_i$</td>
</tr>
<tr>
<td>CaO-Al$_2$O$_3$</td>
<td>Ca$^{2+}$+O$^{2-}$</td>
<td>1</td>
<td>$n_1 = n_{CaO}$</td>
<td>$N_1 = 2n_1\sum n_i$</td>
</tr>
<tr>
<td>CaO-Al$_2$O$_3$</td>
<td>CaO·Al$_2$O$_3$</td>
<td>5</td>
<td>$n_5 = n_{CaO \cdot Al_2O_3}$</td>
<td>$N_5 = n_1\sum n_i$</td>
</tr>
<tr>
<td>CaO-Al$_2$O$_3$</td>
<td>CaO·2Al$_2$O$_3$</td>
<td>6</td>
<td>$n_6 = n_{CaO \cdot 2Al_2O_3}$</td>
<td>$N_6 = n_1\sum n_i$</td>
</tr>
<tr>
<td>CaO-Al$_2$O$_3$</td>
<td>CaO·6Al$_2$O$_3$</td>
<td>7</td>
<td>$n_7 = n_{CaO \cdot 6Al_2O_3}$</td>
<td>$N_7 = n_1\sum n_i$</td>
</tr>
<tr>
<td>CaO-Al$_2$O$_3$</td>
<td>3CaO·Al$_2$O$_3$</td>
<td>8</td>
<td>$n_8 = n_{3CaO \cdot Al_2O_3}$</td>
<td>$N_8 = n_1\sum n_i$</td>
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<tr>
<td>CaO-Al$_2$O$_3$</td>
<td>12CaO·7Al$_2$O$_3$</td>
<td>9</td>
<td>$n_9 = n_{12CaO \cdot 7Al_2O_3}$</td>
<td>$N_9 = n_1\sum n_i$</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>SiO$_2$</td>
<td>3</td>
<td>$n_3 = n_{SiO_2}$</td>
<td>$N_3 = n_1\sum n_i$</td>
</tr>
<tr>
<td>CaO·SiO$_2$</td>
<td>10</td>
<td>$n_{10} = n_{CaO \cdot SiO_2}$</td>
<td>$N_{10} = n_1\sum n_i$</td>
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</tr>
<tr>
<td>2CaO·SiO$_2$</td>
<td>11</td>
<td>$n_{11} = n_{2CaO \cdot SiO_2}$</td>
<td>$N_{11} = n_1\sum n_i$</td>
<td></td>
</tr>
<tr>
<td>3CaO·SiO$_2$</td>
<td>12</td>
<td>$n_{12} = n_{3CaO \cdot SiO_2}$</td>
<td>$N_{12} = n_1\sum n_i$</td>
<td></td>
</tr>
<tr>
<td>2CaO·Al$_2$O$_3$·SiO$_2$</td>
<td>15</td>
<td>$n_{15} = n_{2CaO \cdot Al_2O_3 \cdot SiO_2}$</td>
<td>$N_{15} = n_1\sum n_i$</td>
<td></td>
</tr>
<tr>
<td>CaO·Al$_2$O$_3$·2SiO$_2$</td>
<td>16</td>
<td>$n_{16} = n_{CaO \cdot Al_2O_3 \cdot 2SiO_2}$</td>
<td>$N_{16} = n_1\sum n_i$</td>
<td></td>
</tr>
<tr>
<td>3Al$_2$O$_3$·2SiO$_2$</td>
<td>17</td>
<td>$n_{17} = n_{3Al_2O_3 \cdot 2SiO_2}$</td>
<td>$N_{17} = n_1\sum n_i$</td>
<td></td>
</tr>
</tbody>
</table>

### 2.2 Structural units in Ce$_2$O$_3$-Al$_2$O$_3$, CaO-Al$_2$O$_3$-Ce$_2$O$_3$ and CaO-Al$_2$O$_3$-SiO$_2$-Ce$_2$O$_3$ slags

According to the reported binary phase diagram of Ce$_2$O$_3$-Al$_2$O$_3$ slag \[8\], it can be reasonably obtained that there are two simple ions Ce$^{3+}$ and O$^{2-}$, one simple molecule Al$_2$O$_3$ and two kinds of complex molecules Ce$_2$O$_3$·Al$_2$O$_3$ and Ce$_2$O$_3$·11Al$_2$O$_3$, in the Ce$_2$O$_3$-Al$_2$O$_3$ slag, as listed in Table 1, at metallurgical temperature based on IMCT. Additionally, according to the ternary phase diagram of CaO-Al$_2$O$_3$-Ce$_2$O$_3$ slag \[4\], as compared with Ce$_2$O$_3$-Al$_2$O$_3$ slag, there were added one simple ion Ca$^{2+}$ and five kinds of complex molecules, such as: CaO·Al$_2$O$_3$, CaO·2Al$_2$O$_3$, CaO·6Al$_2$O$_3$, 3CaO·Al$_2$O$_3$ and 12CaO·7Al$_2$O$_3$ in the CaO-Al$_2$O$_3$-Ce$_2$O$_3$ 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$_2$O$_3$ in CaO-Al$_2$O$_3$-SiO$_2$-Ce$_2$O$_3$ slag at metallurgical temperature with respect to the ion and molecule coexistence theory. According to the reported binary phase diagram of Ce$_2$O$_3$-Al$_2$O$_3$ and Ce$_2$O$_3$-SiO$_2$ \[9,10\] slags, ternary phase diagrams of CaO-Al$_2$O$_3$-Ce$_2$O$_3$ and CaO–Al$_2$O$_3$–SiO$_2$ slags \[11\], in a refining temperature range from 1873 K to 1973 K, 16 kinds of complex molecules such as: CaO·Al$_2$O$_3$, CaO·2Al$_2$O$_3$, CaO·6Al$_2$O$_3$, 3CaO·Al$_2$O$_3$, 12CaO·7Al$_2$O$_3$, CaO·SiO$_2$, 2CaO·SiO$_2$, 3CaO·SiO$_2$, Ce$_2$O$_3$·Al$_2$O$_3$,
Ce2O3, 11Al2O3, Ce2Si2O7, Ce4.47(SiO4)3O, CeSi2O5, 2CaO·Al2O3·SiO2, CaO·Al2O3·2SiO2 and 3Al2O3·2SiO2, can be formed in CaO-Al2O3-SiO2-Ce2O3 slag. However, the Gibbs free energy of three complex molecules among them such as: Ce2Si2O7, Ce4.47(SiO4)3O and CeSi2O5 are unknown. Therefore, this model mainly takes into account 13 kinds of complex molecules, as listed in Table 1.

Finally, as listed in Table 1, the structural units of Ce2O3-Al2O3, CaO-Al2O3-Ce2O3 and CaO-Al2O3-SiO2-Ce2O3 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: 
\[ \begin{align*}
    & h = \sum n_{CaO} + \sum n_{CeO_2} + \sum n_{SiO_2}, \\
    & a_1 = n_{AlO}, \\
    & a_2 = n_{SiO_2}. 
\end{align*} \]

The symbols of the mass action concentrations for all structure units were listed as following:

The chemical equations in the temperature range of 1600-1700 \( ^\circ C \) can be defined as follows [12, 13]:

\[
\begin{align*}
(\text{Ca}^{2+} + \text{O}^2-) + \text{Al}_2\text{O}_3 & = \text{CaO} \cdot \text{Al}_2\text{O}_3 \quad \Delta G^\theta = -18120 - 19.62T \quad N_5 = K_1 \cdot N_1 \cdot N_2^2 \quad (1) \\
(\text{Ca}^{2+} + \text{O}^2-) + \text{SiO}_2 & = \text{CaO} \cdot \text{SiO}_2 \quad \Delta G^\theta = -16400 - 26.8T \quad N_6 = K_2 \cdot N_1 \cdot N_2^2 \quad (2) \\
3(\text{Ca}^{2+} + \text{O}^2-) + \text{SiO}_2 & = 3\text{CaO} \cdot \text{SiO}_2 \quad \Delta G^\theta = -17430 - 37.2T \quad N_7 = K_3 \cdot N_1 \cdot N_2^6 \quad (3) \\
12(\text{Ca}^{2+} + \text{O}^2-) + 7\text{Al}_2\text{O}_3 & = 12\text{CaO} + 7\text{Al}_2\text{O}_3 \quad \Delta G^\theta = -86100 - 205.1T \quad N_8 = K_4 \cdot N_1 \cdot N_2^4 \quad (4) \\
(\text{Ca}^{2+} + \text{O}^2-) + \text{SiO}_2 & = \text{CaO} \cdot \text{SiO}_2 \quad \Delta G^\theta = -81416 - 10.498T \quad N_9 = K_5 \cdot N_1^2 \cdot N_2^3 \quad (5) \\
2(\text{Ca}^{2+} + \text{O}^2-) + \text{SiO}_2 & = 2\text{CaO} \cdot \text{SiO}_2 \quad \Delta G^\theta = -160431 + 4.016T \quad N_10 = K_6 \cdot N_1 \cdot N_2^3 \quad (6) \\
3(\text{Ca}^{2+} + \text{O}^2-) + \text{SiO}_2 & = 3\text{CaO} \cdot \text{SiO}_2 \quad \Delta G^\theta = -93366 - 23.03T \quad N_11 = K_7 \cdot N_1 \cdot N_2^3 \quad (7) \\
2\text{Ca}^{2+} + 3\text{O}^2- & = \text{Ca}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3 \quad \Delta G^\theta = -58555.5 - 15.04T \quad N_12 = K_8 \cdot N_1^2 \cdot N_3 \quad (8) \\
2\text{Ca}^{2+} + 3\text{O}^2- & = \text{Ca}_2\text{O}_3 \cdot 11\text{Al}_2\text{O}_3 \quad \Delta G^\theta = 49323 - 80.56T \quad N_14 = K_{10} \cdot N_1 \cdot N_2 \cdot N_4^{11} \quad (9) \\
(\text{Ca}^{2+} + \text{O}^2-) + \text{Al}_2\text{O}_3 + 2\text{SiO}_2 & = \text{CaO} \cdot \text{Al}_2\text{O}_3 + 2\text{SiO}_2 \quad \Delta G^\theta = -13816.4 - 55.23T \quad N_{15} = K_{11} \cdot N_1 \cdot N_2 \cdot N_2^2 \quad (10) \\
2(\text{Ca}^{2+} + \text{O}^2-) + \text{Al}_2\text{O}_3 + \text{SiO}_2 & = 2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \quad \Delta G^\theta = -61964.6 - 60.29T \quad N_{16} = K_{12} \cdot N_1^2 \cdot N_2 \cdot N_3 \quad (11) \\
3\text{Al}_2\text{O}_3 + 2\text{SiO}_2 & = 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \quad \Delta G^\theta = -4351 - 10.46T / \text{mol} \quad N_{17} = K_{13} \cdot N_1^3 \cdot N_3 \quad (13)
\end{align*}
\]

The equilibrium constant \( K_i^\theta \) of the all reactions can be calculated by \( K_i^\theta = \exp(-\Delta G_m^\theta / RT) \).

2.3.1 Ce2O3-Al2O3 slag system
The total equilibrium mole number of all structural units in Ce₂O₃-Al₂O₃ slags can be expressed as
\[ \sum n_i = 5n_2 + n_4 + n_{13} + n_{14} \text{ (mol)}. \]

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 \( N_i = \frac{n_i}{\sum n_j} \). The \( N_{MeO} \) such as ion-pair (2Me³⁺+3O²⁻), should be calculated by \( N_{MeO} = N_{Me³⁺,MeO} + N_{O^{2⁻},MeO} = \frac{2n_{Me³⁺,MeO} + 3n_{O^{2⁻},MeO}}{\sum n_i} = \frac{5n_{MeO}}{\sum n_i} \).

Mass equilibrium formulas were listed below:

\[ b_2 = \sum n \cdot (0.2N_2 + N_{13} + N_{14}) \quad (14) \]

\[ a_2 = \sum n \cdot (N_4 + N_{13} + 11N_{14}) \quad (15) \]

\[ N_2 + N_4 + N_{13} + N_{14} = 1 \quad (16) \]

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 Ce₂O₃-Al₂O₃ slag.

### 2.3.2 CaO-Al₂O₃-Ce₂O₃ slag system

The total equilibrium mole number of all structural units in CaO-Al₂O₃-Ce₂O₃ slag can be expressed as
\[ \sum n_i = 2n_1 + 5n_2 + n_4 + n_5 + n_6 + n_7 + n_8 + n_9 + n_{13} + n_{14} \text{ (mol)}. \]

The mass equilibrium formulas were listed below:

\[ b_1 = \sum n \cdot (0.5N_1 + N_5 + N_6 + N_7 + 3N_8 + 12N_9) \quad (17) \]

\[ b_2 = \sum n \cdot (0.2N_2 + N_{13} + N_{14}) \quad (18) \]

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

\[ N_1 + N_2 + N_4 + N_5 + N_6 + N_7 + N_8 + N_9 + N_{13} + N_{14} = 1 \quad (20) \]

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-Al₂O₃-Ce₂O₃ slag.

### 2.3.3 CaO-Al₂O₃-SiO₂-Ce₂O₃ slag system

The total equilibrium mole number of all structural units in CaO-Al₂O₃-SiO₂-Ce₂O₃ slag can be expressed as
\[ \sum n_i = 2n_1 + 5n_2 + n_3 + n_4 + n_5 + n_6 + n_7 + n_8 + n_9 + n_{10} + n_{11} + n_{12} + n_{13} + n_{14} + n_{15} + n_{16} + n_{17} \text{ (mol)}. \]

The mass equilibrium formulas were listed below:

\[ b_1 = \sum n \cdot (0.5N_1 + N_5 + N_6 + N_7 + 3N_8 + 12N_9 + N_{10} + 2N_{11} + 3N_{12} + 2N_{15} + N_{16}) \quad (21) \]
\[ b_2 = \sum n \cdot (0.2N_2 + N_{13} + N_{14}) \] (22)
\[ a_1 = \sum n \cdot (N_3 + N_{10} + N_{11} + N_{12} + N_{15} + 2N_{16} + 2N_{17}) \] (23)
\[ a_2 = \sum n \cdot (N_4 + N_5 + 2N_6 + 6N_7 + N_8 + 7N_9 + N_{13} + 11N_{14} + N_{15} + N_{16} + N_{17} + 3N_{17}) \] (24)
\[ N_1 + N_2 + N_3 + \cdots + N_{16} + N_{17} = 1 \] (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-Al₂O₃-SiO₂-Ce₂O₃ 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 Ce₂O₃-Al₂O₃ slag system

The relationship between mass action concentrations of each structural unit in binary slag system of Ce₂O₃-Al₂O₃ gained from the established thermodynamic model at 1873 K and the mole fraction of Ce₂O₃ is presented respectively in Fig.1. These results can be confirmed from Fig.1 that when mole fraction of Ce₂O₃ equals 0.49, the mass action concentration of Ce₂O₃ \( \cdot \) Al₂O₃ achieves its maximum value 0.90 and both the mass action concentrations of Ce₂O₃ and Al₂O₃ maintain at very low levels owing to the strong combination ability of Ce₂O₃ and Al₂O₃, which combine to form Ce₂O₃ \( \cdot \) Al₂O₃. However, if the mole fraction of Ce₂O₃ is greater than 0.49, the mass action concentration of Ce₂O₃ would increases sharply. Oppositely, when the mole fraction of Ce₂O₃ is smaller than 0.49, the mass action concentration of Al₂O₃ would increases rapidly.

Fig.1 The relationship between \( N_i \) in Ce₂O₃-Al₂O₃ slag and the mole fraction of Ce₂O₃ at 1873 K

3.2 CaO-Al₂O₃-Ce₂O₃ slag system

According to the established thermodynamic model, the mass action concentrations of each structural unit in CaO-Al₂O₃-Ce₂O₃ ternary system were calculated at 1773 K, while CaO/Al₂O₃ (mass fraction) is in the range of 0.7~1.5 and the mass fraction of Ce₂O₃ is in the range of 0~45%.
3.2.1 Mass action concentrations of Al$_2$O$_3$

According to the calculation results, the iso-mass action concentrations curves of Al$_2$O$_3$ were drawn and compared with the iso-activity curves of Al$_2$O$_3$ measured by Shigeru \(^4\), as shown in Fig.2.

![Diagram of iso-mass action concentrations and measured iso-activity curves of Al$_2$O$_3$ in CaO-Al$_2$O$_3$-Ce$_2$O$_3$ ternary slag system at 1773 K.]

Fig.2 The calculated iso-mass action concentration curves of Al$_2$O$_3$ and measured iso-activity curves of Al$_2$O$_3$ in CaO-Al$_2$O$_3$-Ce$_2$O$_3$ 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$_2$O$_3$- Ce$_2$O$_3$ flux under a controlled oxygen partial pressure, the trends of $N_{Al_2O_3}$ decreasing with the increasing of CaO/Al$_2$O$_3$ or Ce$_2$O$_3$/Al$_2$O$_3$ are in good agreement with the reported measured trends of $a_{Al_2O_3}$ in CaO-Al$_2$O$_3$-Ce$_2$O$_3$ slag system. This is closely related with the strong combination ability of Ce$_2$O$_3$ and CaO with Al$_2$O$_3$, which can combine to form various compounds. However, the calculated mass action concentrations of Al$_2$O$_3$ are 0.1 times that of the measured activity of Al$_2$O$_3$. 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$_2$O$_3$ decreases with the increasing of CaO/Al$_2$O$_3$ at a certain content of Ce$_2$O$_3$ and with the increasing of Ce$_2$O$_3$ content at a certain value of CaO/Al$_2$O$_3$, as shown in Fig.3. It can be observed from Fig.3 that the mass action concentration of Al$_2$O$_3$ has a small value when the value of CaO/Al$_2$O$_3$ is big and the content of Ce$_2$O$_3$ is high.
3.2.2 Mass action concentrations of Ce$_2$O$_3$ and CaO

The iso-mass action concentration curves of Ce$_2$O$_3$ in CaO-Al$_2$O$_3$-Ce$_2$O$_3$ slag system at 1773K were shown in Fig.4. It can be seen from Fig.4 that when CaO/Al$_2$O$_3$ (mass ratio) is constant, the mass action concentrations of Ce$_2$O$_3$ increase with the increasing of the content of Ce$_2$O$_3$. In addition, when the content of Ce$_2$O$_3$ is constant, the mass action concentrations of Ce$_2$O$_3$ increase with the increasing of CaO/Al$_2$O$_3$ (mass ratio).

Fig.4 The iso-mass action concentration curves of Ce$_2$O$_3$ in CaO-Al$_2$O$_3$-Ce$_2$O$_3$ ternary slag system at 1773 K

The iso-mass action concentration curves of CaO in CaO-Al$_2$O$_3$-Ce$_2$O$_3$ slag system at 1773K were shown in Fig.5. It can be seen from Fig.5 that when CaO/Al$_2$O$_3$ (mass ratio) is constant, increasing of the content of Al$_2$O$_3$ can result in decreasing the mass action concentrations of CaO; in addition, when the content of CaO is constant, increasing of CaO/Al$_2$O$_3$ (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$_2$O$_3$-Ce$_2$O$_3$ ternary slag system at 1773 K
3.3 CaO-Al₂O₃-SiO₂-Ce₂O₃ slag system

According to the established thermodynamic model, the mass action concentrations of each structural unit in CaO-Al₂O₃-SiO₂-Ce₂O₃ quaternary slag system were calculated at the condition of that Al₂O₃+Ce₂O₃=33%, the CaO/Al₂O₃ equals to 4.5 and 5.5 and Ce₂O₃ content is in the range of 0~15% at 1773K.

![Fig.6](image)

The influence of the content of Ce₂O₃ and basicity on the mass action concentrations of Ce₂O₃, Al₂O₃ and Ce₂O₃•Al₂O₃ at 1773 K

When the value of CaO/SiO₂ equals to 4.5 and 5.5 respectively, the influence of the mass fraction of Ce₂O₃ on the mass action concentrations of Ce₂O₃, Al₂O₃ and Ce₂O₃•Al₂O₃ at 1773 K were shown in Fig.6. It can be seen from Fig.6 that with the increasing of the mass fraction of Ce₂O₃, the mass action concentrations of Ce₂O₃ and Ce₂O₃•Al₂O₃ increase and the mass action concentration of Al₂O₃ decreases respectively. Fig.6 also reveals that with the value of CaO/SiO₂ increasing from 4.5 to 5.5, the mass action concentrations of Al₂O₃ and Ce₂O₃•Al₂O₃ decreases and the mass action concentration of Ce₂O₃ increases respectively.

On the basis of previous work, the thermodynamic model application to the equilibrium between CaO-Al₂O₃-SiO₂-Ce₂O₃ refining slag and molten steel containing aluminum has been further discussed. The composition of the slag is represented as 55.83%CaO-23%Al₂O₃-11.17%SiO₂-10%Ce₂O₃. 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

\[2[Ce] + 2(Al₂O₃) = (Ce₂O₃ \cdot Al₂O₃) + 2[Al] \Delta G^\circ = -285315.5 - 41.96T \text{ J/mol} \]  \hspace{0.5cm} (26)

\[2[Ce] + (Ce₂O₃ \cdot Al₂O₃) = 2(Ce₂O₃) + 2[Al] \Delta G^\circ = -168204.5 - 11.88T \text{ J/mol} \]  \hspace{0.5cm} (27)

\[a_{Al} = f_{Al}^v[\%Al] \quad \lg f_{Al} = \sum_{j=1}^{n} e_{Alj}[^{\%}j] \]  \hspace{0.5cm} (28)

\[a_{Ce} = f_{Ce}^v[\%Ce] \quad \lg f_{Ce} = \sum_{j=1}^{n} e_{Cej}[^{\%}j] \]  \hspace{0.5cm} (29)
The relevant solute interaction coefficients of Ce and Al are listed in Table 2\textsuperscript{[15]}. And the mass action concentrations of Ce\textsubscript{2}O\textsubscript{3}, Al\textsubscript{2}O\textsubscript{3} and Ce\textsubscript{2}O\textsubscript{3}•Al\textsubscript{2}O\textsubscript{3} are listed in Table 3.

The relation between cerium and aluminum in molten steel equilibrated with 55.83% CaO-23% Al\textsubscript{2}O\textsubscript{3}-11.17% SiO\textsubscript{2}-10% Ce\textsubscript{2}O\textsubscript{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 $e_{ij}^j$ of the various elements in liquid steel in 1600-1700°C

<table>
<thead>
<tr>
<th>$i,j$</th>
<th>Al, Al</th>
<th>Al, Ce</th>
<th>Ce, Ce</th>
<th>Ce, Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_{ij}^j$</td>
<td>0.043</td>
<td>-0.043</td>
<td>0.0039</td>
<td>-2.25</td>
</tr>
</tbody>
</table>

Table 3 The mass action concentration of Ce\textsubscript{2}O\textsubscript{3}, Al\textsubscript{2}O\textsubscript{3} and Ce\textsubscript{2}O\textsubscript{3}•Al\textsubscript{2}O\textsubscript{3} in 55.83% CaO-23% Al\textsubscript{2}O\textsubscript{3}-11.17% SiO\textsubscript{2}-10% Ce\textsubscript{2}O\textsubscript{3} quaternary slag

<table>
<thead>
<tr>
<th>$N$</th>
<th>Al\textsubscript{2}O\textsubscript{3}</th>
<th>Ce\textsubscript{2}O\textsubscript{3}</th>
<th>Ce\textsubscript{2}O\textsubscript{3}•Al\textsubscript{2}O\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>T=1873K</td>
<td>0.006171</td>
<td>0.01929</td>
<td>0.03122</td>
</tr>
<tr>
<td>T=1973K</td>
<td>0.006398</td>
<td>0.02200</td>
<td>0.03050</td>
</tr>
</tbody>
</table>

T=1873K

2.30[\%Al] + lg[\%Al] - 0.047[\%Ce]- lg[\%Ce] =4.72 \hspace{2cm} (30)

2.30[\%Al] + lg[\%Al] - 0.047[\%Ce] - lg[\%Ce] =2.76 \hspace{2cm} (31)

T=1973K

2.30[\%Al] + lg[\%Al] - 0.047[\%Ce] - lg[\%Ce] =4.53 \hspace{2cm} (32)

2.30[\%Al] + lg[\%Al] - 0.047[\%Ce] - lg[\%Ce] =2.60 \hspace{2cm} (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\textsubscript{2}O\textsubscript{3}•Al\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{3}. 
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 Ce₂O₃-Al₂O₃, CaO-Al₂O₃-Ce₂O₃ and CaO-Al₂O₃-SiO₂-Ce₂O₃ slag systems are established. The mass action concentrations of each structural unit were gained in the three slag systems.

(2) In Ce₂O₃-Al₂O₃ slag system, results show that when mole fraction of Ce₂O₃ is 0.49, the mass action concentration of Ce₂O₃·Al₂O₃ achieves its maximum value 0.90 and both the mass action concentrations of Ce₂O₃ and Al₂O₃ maintain at very low values. However, if mole fraction of Ce₂O₃ is greater than 0.49 the mass action concentration of Ce₂O₃ would increases sharply. Oppositely, when mole fraction of Ce₂O₃ is smaller than 0.49 the mass action concentration of Al₂O₃ would increases rapidly.

(3) In CaO-Al₂O₃-Ce₂O₃ slag system, the trends of calculated mass action concentration of Al₂O₃ are in good agreement with the reported measured trends of activity of Al₂O₃, namely, the mass action concentration of Al₂O₃ decreases with the increasing of CaO/Al₂O₃ at a certain content of Ce₂O₃ and with the increasing of Ce₂O₃ content at a certain value of CaO/Al₂O₃. The iso-mass action concentration curves of Ce₂O₃ and CaO are drawn from the calculated results.

(4) On the basis of previous work, the thermodynamic model application to the equilibrium between CaO-Al₂O₃-SiO₂-Ce₂O₃ 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%Al₂O₃-11.17%SiO₂-10%Ce₂O₃ 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.

References


