Thermodynamic Properties of the CaO–AlO$_{1.5}$–CeO$_{1.5}$ System

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1. Introduction
To control the dissolved oxygen content in molten steel, deoxidizing agents are added during secondary refining processes, and these remove oxygen from molten steel as oxides that have lower densities than that of molten iron. Aluminum is frequently used as a deoxidizing agent because it is cost efficient, has a strong affinity for oxygen, and can be removed as an oxide. However, some Al$_2$O$_3$ remains in the melt and forms clusters during the casting process; these clusters can cause inner and surface defects. Therefore, calcium is often added to the melt to control the inclusions, converting Al$_2$O$_3$ to CaO–Al$_2$O$_3$.1,2) This mixed oxide is a liquid under process conditions, which allows for easier removal; however, the vapor pressure of Ca under these conditions is so high that the yield is limited.

Rare earth metals (REMs) have a strong affinity for oxygen; consequently, they are expected to be effective deoxidizing agents. In addition, they form complex oxides with Al and can improve the properties of inclusion compounds.3) During secondary refining, fluxes containing CaO are added to the ladle for desulfurization. When both Al and REMs are added, the inclusions consist of a CaO–AlO$_{1.5}$–REOX system due to exchange redox reactions of the reductants with the fluxes in molten steel. Hence, knowledge of the thermodynamic properties of the CaO–AlO$_{1.5}$–REOX system is indispensable for the accurate control of inclusions in the Al-RE complex deoxidizing processes. In practice, mischmetal, an alloy of rare earth elements, is often used. Ueda et al. reported4) the phase equilibria and activity of AlO$_{1.5}$ for the CaO–AlO$_{1.5}$–CeO$_{1.5}$ system at 1 773 K. For accurate control of the inclusion compositions, thermodynamic properties at the temperature of the secondary refining process are necessary. In this study, we focused on Cerium, a representative component of mischmetal, and the phase equilibria for CaO–AlO$_{1.5}$–CeO$_{1.5}$ at 1 823 K and 1 873 K and activities of the components at 1 873 K have been investigated.

2. Experimental
In this study, a MoSi$_2$ resistance furnace, mullite reaction tube (60 × 52 × 1 000 mm), and graphite crucible were used for all the experiments. The temperature of the hot zone was measured using a Pt–6%Rh/Pt–30%Rh thermocouple and was maintained at the experimental temperature ±1 K with a proportional-integral-derivative (PID) controller. A DIGAMIX® gas mixing pump was used for mixing Ar and CO. CaO was prepared by calcination of CaCO$_3$ in air at 1 273 K for 24 h, while reagent grade CeO$_2$ was used for CeO$_{1.5}$ without pretreatment, assuming that reduction occurred during the experiment.

2.1. Valence of Ce in the Molten Oxides
Either trivalent (Ce$^{3+}$) or tetravalent (Ce$^{4+}$) cerium species are present in the molten oxides, depending on the ambient oxygen potential. While CeO$_2$ is the major component at room temperature, CeO$_{1.5}$ is the major component under the conditions of steel deoxidation. The oxygen partial pressure, which allows coexistence of CeO$_{1.5}$ and CeO$_2$, is determined by Eq. (1), and its Gibbs energy of reaction,
\( \Delta G'_1 \), is expressed by Eq. (2).\(^5\)
\[
\text{CeO}_{1.5}(s) + 1/4 O_2(g) \rightarrow \text{CeO}_2(s) \tag{1}
\]
\[
\Delta G'_1 = -177 \, 000 + 63.4 \, T \, (J/mol) \tag{2}
\]
The equilibrium oxygen partial pressures were found to be 9.17 \( \times \) \( 10^{-3} \) Pa and 3.19 \( \times \) \( 10^{-2} \) Pa at 1 823 K and 1 873 K, respectively. The valence of Ce in the various melts and under different CO partial pressures was investigated with X-ray absorption fine structure (XAFS) analyses at NW-10A of the Photon Factory in the High Energy Accelerator Research Organization (KEK-PF, Tsukuba, Japan). CeO\(_2\) and CeAlO\(_3\), which were prepared by sintering a mixture of AlO\(_{1.5}\) and CeO\(_2\), were used as standard samples of tetravalent and trivalent Ce.

2.2. Evaluation of Ternary Intermediate Compounds
Unknown ternary intermediate compounds were investigated by comparing the X-ray diffraction (XRD) data with those of similar compounds in the CaO–AlO\(_{1.5}\)–LaO\(_{1.5}\) system reported in respect to composition and crystal structure. Regarding the CaO–AlO\(_{1.5}\)–LaO\(_{1.5}\) system, two ternary compounds, CaO·AlO\(_{1.5}\)·LaO\(_{1.5}\) and CaO·3AlO\(_{1.5}\)·LaO\(_{1.5}\), are known to be present.\(^7\),\(^8\) Samples (0.5 g) consisting of CaO·AlO\(_{1.5}\)·CeO\(_{1.5}\) in 1:1:1 and 1:3:1 ratios were prepared by mixing each component. Then, the prepared samples were kept at 1 873 K in a graphite crucible in an Ar atmosphere. After 20 h, the samples were quenched and subjected to XRD analysis for comparison with those of the CaO–AlO\(_{1.5}\)–LaO\(_{1.5}\) system.

2.3. Phase Equilibria for the CaO–AlO\(_{1.5}\)–CeO\(_{1.5}\) System
Phase equilibria experiments were carried under Ar at a flow rate of 150 to 200 mL/min and graphite crucibles were used. Samples of initial molten oxide compositions (0.5 g) were prepared by weighing and mixing each chemical to designed molten compositions, followed by equilibration with saturated oxide compounds (0.5 g) at either 1 823 or 1 873 K for 16 h. Saturated compounds were prepared by sintering at either 1 823 K or 1 873 K for 20 h after compression at 200 MPa for 3 min. When molten oxides were saturated with two compounds, both compounds were ground to powder and mixed for compression and sintering. In case of CaO saturation, a chunk of a commercially available fused material was used, because sintered CaO was found to be unstable during the experiment.

2.4. Activity Coefficients of the Solutes
Activity coefficients of the highly dilute solutes in the reference metals were investigated by equilibrating a reference metal with the oxide whose activity is unity or another fixed value. The CaO–AlO\(_{1.5}\) melt, which is saturated with CaO, or CeO\(_2\), which is reduced to CeO\(_{1.5}\) during the experiment, was used as the oxides, while Cu or Ag were used as the reference metals. Ar and CO gases were mixed at a fixed ratio, and they were blown onto the sample with a gas lance that was positioned 10 cm from the sample.

2.5. Activities of the Oxides in the Molten Oxides
For the experiments using Cu as the reference metal, the molten oxide (1.0 g) and Cu (1.5 g) were equilibrated in the furnace under Ar and CO mixed gas (Ar:CO = 1:9). After equilibration in the furnace, Cu was removed and cleaned with HCl for 4 h to remove the oxide, and then, analyzed using inductively coupled plasma (ICP) emission spectroscopy. The Al concentration did not change between 25 and 40 h, so 25 h was considered to be sufficient time for equilibration.

For the experiments using Ag as the reference metal, the molten oxide (1.0 g), 1.0 g of Ag, and mixed gas (Ar:CO = 1:1) were used. The solute concentrations did not show difference between 16 and 36 h, so 16 h was considered sufficient time for equilibration.

3. Results and Discussion
3.1. Valence of Ce in the Molten Oxides
The composition of the molten oxides and the atmosphere are listed in Table 1. Figure 2 shows the X-ray absorption near-edge structure (XANES) spectra of Ce by XAFS analysis and the first derivative XANES spectra. Ce was confirmed to be trivalent in this study, based on a comparison of the spectra of the samples with those of standards.

3.2. Evaluation of Ternary Intermediate Compounds
The crystal structures of both CaO·AlO\(_{1.5}\)·LaO\(_{1.5}\) (CAL) and CaO·3AlO\(_{1.5}\)·LaO\(_{1.5}\) (CA\(_3\)L) are tetragonal, and their

| Sample | \( X_{\text{CaO}} \) | \( X_{\text{Al}} \) | \( X_{\text{CeO}_2} \) | \( P_{\text{CO}} \) |
|--------|----------------|----------------|----------------|--------------|
| Atmosphere 1 | 0.480 | 0.396 | 0.123 | 0 |
| Atmosphere 2 | 0.480 | 0.396 | 0.123 | 0.2 |
| Atmosphere 3 | 0.480 | 0.396 | 0.123 | 0.4 |
| Composition 1 | 0.480 | 0.396 | 0.123 | 0 |
| Composition 2 | 0.418 | 0.460 | 0.122 | 0 |
| Composition 3 | 0.356 | 0.522 | 0.122 | 0 |
| Composition 4 | 0.295 | 0.584 | 0.121 | 0 |
lattice constants and atomic coordinates are listed in Table 2. Figure 3 shows their crystal structures, and Fig. 4 shows the X-ray diffraction patterns of sintered samples together with calculated diffraction patterns. Comparing Figs. 4(a) and 4(c) with Figs. 4(b) and 4(d), the XRD patterns of the sintered samples of CaO:AlO$_{1.5}$:CeO$_{1.5}$ at ratios of 1:1:1 and 1:3:1 were found to be quite similar to those of CaO:AlO$_{1.5}$:LaO$_{1.5}$ and CaO:3AlO$_{1.5}$:LaO$_{1.5}$. From this result, the presence of CaO:AlO$_{1.5}$:CeO$_{1.5}$ (CA$_{1}$Ce) and CaO:3AlO$_{1.5}$:CeO$_{1.5}$ (CA$_{3}$Ce) was confirmed, and these compounds are considered to have the same crystal structure as those of CAL and CA$_{3}$L. In the spectrum shown in Fig. 4(c), some peaks do not correspond to those observed in Fig. 4(d). These peaks correspond to those of AlO$_{1.5}$:CeO$_{1.5}$ (ACe), whose diffraction pattern is shown in Fig. 4(e). Small amounts of ACe form during sintering due to a slight deviation from the 1:3:1 ratio of CaO:AlO$_{1.5}$:CeO$_{1.5}$. The ionic radius of Ce is smaller than that of La due to the lanthanide contraction; therefore, diffraction peaks arising

![Image](image_url)

**Fig. 2.** The results of X-ray absorption spectroscopy. (a) XANES spectra of samples. (b) First derivation of XANES spectra.

**Fig. 3.** Crystal structures of the ternary intermediate compounds for the CaO–AlO$_{1.5}$–LaO$_{1.5}$ system. (a) CaO:AlO$_{1.5}$:LaO$_{1.5}$ and (b) CaO:3AlO$_{1.5}$:LaO$_{1.5}$.

**Table 2.** Lattice constants and atomic coordinates of (a) CaO:AlO$_{1.5}$:LaO$_{1.5}$ and (b) CaO:3AlO$_{1.5}$:LaO$_{1.5}$.

(a)

| Lattice constant | Site | Element | Wyckoff Symbol | Symmetry  | X   | Y   | Z   |
|------------------|------|---------|----------------|-----------|-----|-----|-----|
| a=0.3716 b=0.3716 c=1.233 | O1 O | 4e | 4 mm | 0 | 0 | 0.15531 |
| M1 0.500Ca+0.500La | 4e | 4 mm | 0 | 0 | 0.35377 |
| O2 O | 4c | mmm. | 0 | 0.5 | 0 |
| Al1 Al | 2a | 4/mmm | 0 | 0 | 0 |

(b)

| Lattice constant | Site | Element | Wyckoff Symbol | Symmetry  | X   | Y   | Z   |
|------------------|------|---------|----------------|-----------|-----|-----|-----|
| a=0.78075 b=0.78075 c=0.51564 | O1 O | 8f | 1 | 0.0808 | 0.16 | 0.2373 |
| M1 0.500Ca+0.500La | 4e | ..m | 0.1522 | 0.6522 | 0.5047 |
| O2 O | 4e | ..m | 0.6417 | 0.1417 | 0.3106 |
| Al1 Al | 4e | ..m | 0.6474 | 0.1474 | 0.9563 |
| O3 O | 2c | 2.mm | 0 | 0.5 | 0.2081 |
| Al2 Al | 2a | ..-4.. | 0 | 0 | 0 |
from CA3Ce are shifted to lower angle than those calculated peaks for CA3L. Consequently, the lattice parameters of CA3Ce are larger than those of CA3L.

### 3.3. Phase Equilibria for the CaO–AlO1.5–CeO1.5 System

Tables 3 and 4 show the experimental results of the phase equilibria at 1823 and 1873 K. Figure 5 shows the liquidus composition and liquidus curves for the CaO–AlO1.5–CeO1.5 system. Figure 5(a) is shown by mass percent, while Figs. 5(b) and 5(c) are by mole fraction. Composition of samples 423, 424, 426 and 427 listed in Table 6 was investigated by SEM-EDX and only ACe, CA3Ce, and CA2 were found to exist. Hence it is considered that no ternary compounds exist other than CACe and CA3Ce in the present system. The shape of the liquid region is similar to that at 1773 K, and the area of the liquid region was found to increase with temperature. At 1873 K, CaO·2AlO1.5, which was one of the solids in equilibrium with the liquid phase at 1823 K, disappeared; while CaO·4AlO1.5 was present as a saturating solid. Although the temperature dependence of the CaO saturated composition was found to be small, those of other compounds, such as CACe, ACe, CA3Ce, and CaO·2AlO1.5 (CaO·4AlO1.5), were found to be large.

### 3.4. Activity Coefficients of the Solutes in the Reference Metals

The activity coefficient of Al in Cu ($\gamma_{\text{Al in Cu}}$) in a highly

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**Table 3.** Experimental results of phase relations for the CaO–AlO1.5–CeO1.5 system at 1823 K.

| Sample | $X_{\text{CaO}}$ | $X_{\text{AlO1.5}}$ | $X_{\text{CeO1.5}}$ | Saturation Phase |
|--------|----------------|---------------------|---------------------|-----------------|
| 1823-1 | 0.557          | 0.443               | 0.000               | C               |
| 1823-2 | 0.544          | 0.404               | 0.052               | C               |
| 1823-3 | 0.527          | 0.382               | 0.090               | C               |
| 1823-4 | 0.486          | 0.329               | 0.184               | C               |
| 1823-5 | 0.416          | 0.353               | 0.231               | C, CACe         |
| 1823-6 | 0.406          | 0.366               | 0.228               | CACe            |
| 1823-7 | 0.356          | 0.422               | 0.222               | CACe            |
| 1823-8 | 0.369          | 0.411               | 0.220               | CACe            |
| 1823-9 | 0.307          | 0.449               | 0.244               | CACe, ACe       |
| 1823-10| 0.293          | 0.475               | 0.232               | ACe             |
| 1823-11| 0.298          | 0.490               | 0.213               | ACe             |
| 1823-12| 0.284          | 0.493               | 0.223               | ACe, CA3Ce      |
| 1823-13| 0.284          | 0.524               | 0.192               | CA3Ce           |
| 1823-14| 0.306          | 0.569               | 0.124               | CA3Ce           |
| 1823-15| 0.296          | 0.598               | 0.106               | CA3Ce, CA2      |
| 1823-16| 0.296          | 0.633               | 0.071               | CA2             |
| 1823-17| 0.335          | 0.626               | 0.039               | CA2             |
| 1823-18| 0.372          | 0.600               | 0.027               | CA2             |
| 1823-19| 0.357          | 0.643               | 0.000               | CA2             |

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**Table 4.** Experimental results for phase relationships for the CaO–AlO1.5–CeO1.5 system at 1873 K.

| Sample No. | $X_{\text{CaO}}$ | $X_{\text{AlO1.5}}$ | $X_{\text{CeO1.5}}$ | Saturation Phase |
|------------|----------------|---------------------|---------------------|-----------------|
| 1873-1     | 0.587          | 0.413               | 0.000               | C               |
| 1873-2     | 0.517          | 0.351               | 0.132               | C               |
| 1873-3     | 0.485          | 0.299               | 0.216               | C               |
| 1873-4     | 0.423          | 0.326               | 0.251               | C, CACe         |
| 1873-5     | 0.426          | 0.329               | 0.246               | CACe            |
| 1873-6     | 0.358          | 0.374               | 0.269               | CACe            |
| 1873-7     | 0.345          | 0.383               | 0.272               | CACe            |
| 1873-8     | 0.367          | 0.388               | 0.244               | CACe            |
| 1873-9     | 0.307          | 0.421               | 0.271               | CACe            |
| 1873-10    | 0.284          | 0.426               | 0.290               | CACe, ACe       |
| 1873-11    | 0.280          | 0.464               | 0.256               | ACe             |
| 1873-12    | 0.255          | 0.484               | 0.261               | ACe, CA3Ce      |
| 1873-13    | 0.261          | 0.502               | 0.237               | CA3Ce           |
| 1873-14    | 0.250          | 0.566               | 0.184               | CA3Ce           |
| 1873-15    | 0.241          | 0.594               | 0.164               | CA3Ce           |
| 1873-16    | 0.215          | 0.621               | 0.163               | CA3Ce, CA4      |
| 1873-17    | 0.289          | 0.711               | 0.000               | CA4             |
| 1873-18    | 0.305          | 0.672               | 0.022               | CA4             |
| 1873-19    | 0.267          | 0.696               | 0.037               | CA4             |
| 1873-20    | 0.224          | 0.680               | 0.096               | CA4             |
| 1873-21    | 0.232          | 0.629               | 0.139               | CA4             |
fig found to be $2.02 \times 10^{-3}$. Based on this value, the value of $\gamma_{Al_{\text{in Ag}}}$ was calculated to be $0.014$ by using Eqs. (4)–(5). Values of $\gamma_{Al_{\text{in Ag}}}$ have been reported as $0.0055^{(11)}$, $0.002^{(12)}$ or $0.0020^{(13)}$ at $1737$ K. The values reported by Hultgren et al.\cite{24} and Oyamada et al.\cite{25} are in good agreement. In addition, Oyamada et al. reported values of $0.0032$ and $0.0045$ at $1473$ K and $1573$ K, respectively. Assuming that the Cu–Al binary alloy in the highly dilute region to be a regular solution ($T_0 \log \gamma_{Al} = T_1 \log \gamma_{Al}$), we calculated a value of $0.011$ by extrapolation to $1873$ K. The value from present work was slightly larger than that calculated from Oyamada’s results.

The activity coefficients of Ca and Al in Ag ($\gamma_{Ca_{\text{in Ag}}}$ and $\gamma_{Al_{\text{in Ag}}}$) in the highly dilute region of Ca and Al were obtained by equilibrating a CaO–AlO$_{1.5}$ melt saturated with CaO ($a_{CaO} = 1$) and Ag under Ar and CO mixed gas (Ar:CO = 1:9, $P_{CO} = 3.54 \times 10^{-11}$ Pa) at $1873$ K.

$$\gamma_{Ca_{\text{in Ag}}} + \gamma_{Al_{\text{in Ag}}} = 1$$

$$\Delta G_6 = 524000 \times 193 \ T \ [J / mol]$$

$$K_6 = \gamma_{Ca_{\text{in Ag}}} \cdot X_{Ca} \cdot P_{CO} / a_{CaO} \cdot a_{C}$$

The Ca mole fraction in Ag ($X_{Ca}$) was found to be $5.94 \times 10^{-4}$. With this value, $\gamma_{Ca_{\text{in Ag}}}$ and $\gamma_{Al_{\text{in Ag}}}$ were calculated to be $5.5 \times 10^{-3}$ and $1.4 \times 10^{-1}$ with Eqs. (4)–(5), (7)–(8). $\gamma_{Ca_{\text{in Ag}}}$ has been reported by Tago et al.\cite{14} between $1573$ K and $1773$ K, and $\gamma_{Al_{\text{in Ag}}}$ has been reported by Wilder et al.\cite{25} between $973$ K and $1223$ K. The values of $\gamma_{Ca_{\text{in Ag}}}$ and $\gamma_{Al_{\text{in Ag}}}$ were calculated to be $4.3 \times 10^{-3}$ and $1.1 \times 10^{-1}$ by extrapolation to $1873$ K. The values of $\gamma_{Ca_{\text{in Ag}}}$ and $\gamma_{Al_{\text{in Ag}}}$ were slightly larger than those calculated from the results of Tago and Wilder. When Tago’s results were extrapolated to $1873$ K, $\gamma_{Ca_{\text{in Ag}}}$ at $1773$ K was removed from the extrapolation because the mole fraction of Ca was $2.33 \times 10^{-2}$ and the behavior may be different from that of dilute samples. The Ca mole fractions of other samples were lower than $7.67 \times 10^{-3}$.

The activity coefficient of Ce in Ag at infinite dilute solution ($\gamma_{Ce_{\text{in Ag}}}$) was obtained by equilibrating CeO$_2$ (which is reduced to CeO$_{1.5}$, $a_{CeO_{1.5}} = 1$) and Ag in a graphite crucible with Ar and CO gas mixture (Ar:CO = 1:9, $P_{CO} = 3.54 \times 10^{-11}$ Pa) at $1873$ K.

$$\Delta G_5 = 745000 \times 284 \ T \ [J / mol]$$

$$K_7 = \gamma_{Ce_{\text{in Ag}}} \cdot X_{Ce} \cdot P_{CO} / a_{CeO_{1.5}}$$

The concentration of Ce in Ag was $8.45 \times 10^{-6}$. Using this value, $\gamma_{Ce_{\text{in Ag}}}$ was calculated to be $9.4 \times 10^{-3}$ with Eqs. (10)–(11). In this study, to calculate the value of $\gamma_{Ce_{\text{in Ag}}}$ at $1873$ K, a Ag–Ce binary alloy in the highly dilute region was assumed to be a regular solution. Therefore, the value of $\gamma_{Ce_{\text{in Ag}}}$ at $1873$ K was calculated to be $3.54 \times 10^{-4}$ by using the value of our result at $1773$ K.
3.5. Activities of the Oxides in the Molten Oxides

The composition of the molten oxides after the experiments, the concentration of the solutes in the reference metal, and the activities of each oxide in the melts at 1 873 K are listed in Tables 5 and 6. Activity coefficients of the solutes in the reference metal in the highly dilute region, which were obtained in Section 3.4, were used to calculate the activities of the oxides. The concentration of the solutes in the reference metal was considered to be sufficiently dilute for Henry’s law to be used. Figure 6 shows the iso-activity curves of each oxide drawn from the present work. When the iso-activity curves of CaO and AlO1.5 were drawn, we referred to the values reported by Rein et al. From iso-activity curves of CaO and AlO1.5, iso-activity curves of CeO1.5 were derived using Gibbs-Duhem equation and shown by dotted curves in high XAlO1.5 and low XCeO1.5 regions.

The activity of CeO1.5 for melts saturated with AlO1.5·CeO1.5 was calculated from Eq. (13) based on the reaction shown in Eq. (12). From Eq. (13) and by using an aAlO1.5 value of 0.10, aCeO1.5 was calculated to be 0.22 ± 0.07. The value of aCeO1.5 calculated here is in good agreement with the calculated value.

\[ \text{AlO}_{1.5} + \text{CeO}_{1.5} \rightarrow \text{AlO}_{1.5} \cdot \text{CeO}_{1.5} \]  
\[ \Delta G^{'}_{298} = -40000 - 10T(\pm 5200) \text{ (J/mol)} \]  

Figure 7 shows activity coefficients of the components in the melts. The activity coefficient of AlO1.5 decreases with increasing XCeO1.5/XCaO, while those of CaO and CeO1.5 decreases with increasing the value of XAlO1.5/XCeO1.5 and XAlO1.5/XCaO, respectively. Pauling electronegativities of the cations (γ), basicity moderating parameters (β), and optical basicity of the oxides (λ) are listed in Table 7. Basicity moderating parameters of CaO and AlO1.5 were obtained from the literature, while that of CeO1.5 was calculated from Duffy's empirical law. The optical basicities of CaO and CeO1.5 are comparatively larger than that of AlO1.5, so that CaO and CeO1.5 are considered to behave as basic oxides while AlO1.5 behaves as an acidic oxide in the CaO–AlO1.5–CeO1.5 melts. Based on this, the activity coefficients of CaO and CeO1.5 are considered to decrease when the AlO1.5 concentration in the melts increase. In addition, the tendency of the activity coefficient of AlO1.5 suggests that interaction between AlO1.5 and CeO1.5 is larger than that of AlO1.5 and CaO.

### Table 5. Slag compositions, concentrations of Al in Cu, and activities of AlO1.5 in the CaO–AlO1.5–CeO1.5 melts at 1 873 K.

| Sample | XCa | XAl | XCe | XAl in Cu (×10^-3) | aAlO1.5 |
|--------|-----|-----|-----|---------------------|---------|
| 221    | 0.383 | 0.587 | 0.030 | 8.65 | 0.324 |
| 222    | 0.301 | 0.668 | 0.031 | 9.71 | 0.364 |
| 223    | 0.363 | 0.583 | 0.054 | 7.34 | 0.275 |
| 224    | 0.382 | 0.506 | 0.113 | 2.42 | 0.091 |
| 225    | 0.297 | 0.593 | 0.110 | 10.03 | 0.376 |
| 226    | 0.243 | 0.510 | 0.246 | 2.91 | 0.109 |
| 227    | 0.234 | 0.550 | 0.216 | 2.43 | 0.091 |
| 228    | 0.237 | 0.585 | 0.037 | 7.39 | 0.277 |
| 229    | 0.331 | 0.634 | 0.035 | 10.22 | 0.383 |
| 230    | 0.278 | 0.694 | 0.028 | 9.05 | 0.339 |
| 231    | 0.364 | 0.541 | 0.094 | 4.88 | 0.183 |
| 232    | 0.347 | 0.585 | 0.068 | 8.05 | 0.302 |
| 233    | 0.273 | 0.660 | 0.067 | 8.98 | 0.337 |
| 234    | 0.280 | 0.629 | 0.091 | 10.06 | 0.377 |
| 235    | 0.340 | 0.555 | 0.105 | 6.25 | 0.234 |
| 236    | 0.273 | 0.586 | 0.141 | 8.57 | 0.321 |
| 237    | 0.291 | 0.480 | 0.229 | 3.21 | 0.120 |
| 238    | 0.351 | 0.425 | 0.224 | 2.61 | 0.098 |
| 239    | 0.312 | 0.433 | 0.256 | 2.91 | 0.109 |
| 240    | 0.397 | 0.437 | 0.166 | 3.30 | 0.124 |

### Table 6. Slag compositions, concentrations of solutes in Ag, and activities of the components in the CaO–AlO1.5–CeO1.5 melts at 1 873 K.

| Sample | XCa | XAl | XCe | XCa in Ag (×10^-3) | XAl in Ag (×10^-3) | aCaO | aAlO1.5 | aCeO1.5 |
|--------|-----|-----|-----|---------------------|---------------------|-------|---------|---------|
| 423    | 0.348 | 0.485 | 0.167 | 8.18 | 1.98 | 5.33 | 0.768 | 0.245 |
| 424    | 0.285 | 0.551 | 0.164 | 6.50 | 1.28 | 4.20 | 0.610 | 0.159 |
| 425    | 0.360 | 0.413 | 0.227 | 9.20 | 0.76 | 6.98 | 0.863 | 0.094 |
| 426    | 0.328 | 0.477 | 0.195 | 7.96 | 1.05 | 6.29 | 0.747 | 0.129 |
| 427    | 0.359 | 0.581 | 0.060 | 4.01 | 3.23 | 1.49 | 0.451 | 0.472 |
| 428    | 0.373 | 0.518 | 0.109 | 4.78 | 1.39 | 4.21 | 0.538 | 0.204 |
| 429    | 0.362 | 0.495 | 0.143 | 4.64 | 0.76 | 3.76 | 0.522 | 0.111 |
| 430    | 0.477 | 0.468 | 0.055 | 8.23 | 0.96 | 6.26 | 0.772 | 0.140 |
| 431    | 0.419 | 0.530 | 0.051 | 6.21 | 1.52 | 4.12 | 0.583 | 0.222 |
| 432    | 0.442 | 0.456 | 0.102 | 7.98 | 1.36 | 7.69 | 0.749 | 0.198 |
| 433    | 0.385 | 0.530 | 0.085 | 5.77 | 1.60 | 5.76 | 0.542 | 0.233 |
| 434    | 0.429 | 0.415 | 0.157 | 5.67 | 0.79 | 5.63 | 0.532 | 0.115 |
| 435    | 0.429 | 0.415 | 0.157 | 5.67 | 0.79 | 5.63 | 0.532 | 0.115 |
3.6. Thermodynamic Relationships among Iso-activity Curves

Because both the pressure and temperature used in this study were constant, the Gibbs-Duhem equation for the system can be written as Eq. (14)

\[ \sum X_i \frac{\partial \ln X_i}{\partial T} \cdot \Delta T + \sum \Delta \ln X_i \cdot \Delta \ln X_i = 0 \] .......................... (14)

This relationship can be expressed as a simple algebraic relationship between the tangent intercept values for the three iso-activity curves. In Fig. 8(a), the point X represents the intersection of iso-activity curves of \( a_{\text{CaO}} = 0.5 \) and \( a_{\text{AlO}1.5} = 0.3 \). The tangent of the iso-activity curves of CaO at point X meet with the AlO1.5–CeO1.5 binary system at point Y. That of AlO1.5 meets with the CaO–CeO1.5 binary system at point Z in the same way. The line YZ meet with CaO–AlO1.5 binary system at point W. The line WX represents the inclination of the iso-activity curve of CeO1.5 at point X. Figure 8(b) shows the iso-activity curves of CeO1.5 and the line WX. From the tendency of the iso-activity curves, the inclination of line WX corresponds to the tangent of the iso-activity curve of CeO1.5 at the point X. These geometric relationships among the iso-activity curves have been checked at representative compositions.

3.7. Equilibria between Molten Iron and the Inclusions

The composition of molten iron and the inclusions that consists of CaO–AlO1.5–CeO1.5 system can be calculated with the value of the activities of the oxide in the inclusion and the equilibrium constants described by Eqs. (16) and (18). The reactions among the deoxidizing agents, O in the molten iron, and the inclusion can be described by Eqs. (15) and (17) when Al and Ce are used as the deoxidizing agents.

\[
\text{AlO}_1.5(s) = \text{Al} + 3/2 \text{O} \quad \text{(15)}
\]

\[
\text{CeO}_1.5(s) = \text{Ce} + 3/2 \text{O} \quad \text{(17)}
\]

Equilibrium constants \( K_{(15)} \) and \( K_{(17)} \) can be described by \( f_{\text{Al}}, f_{\text{Ce}}, \) and \( f_{\text{O}} \), the activity coefficients of Al, Ce, and O, respectively, in the molten iron.

\[
K_{(15)} = f_{\text{Al}}^{\% \text{Al}^{1.5} / X_{\text{AlO}1.5}} / f_{\text{O}}^{\% \text{O}^{1.5} / X_{\text{CAO}}} \quad \text{(19)}
\]

\[
K_{(17)} = f_{\text{Ce}}^{\% \text{Ce}^{1.5} / X_{\text{AlO}1.5}} / f_{\text{O}}^{\% \text{O}^{1.5} / X_{\text{CAO}}} \quad \text{(20)}
\]

As shown in Eqs. (21)–(23), \( f_{\text{Al}}, f_{\text{Ce}}, \) and \( f_{\text{O}} \) can be described by interaction parameters, \( e_i^l \). The values of \( e_i^l \) used for these calculations are listed in Table 8.

\[
\log f_{\text{Al}} = e_{\text{Al}}^{\% \text{Al}^{1.5} / X_{\text{AlO}1.5}} + e_{\text{Ce}}^{\% \text{Ce}} + e_{\text{O}}^{\% \text{O}} \quad \text{(21)}
\]

\[
\log f_{\text{Ce}} = e_{\text{Al}}^{\% \text{Al}^{1.5} / X_{\text{AlO}1.5}} + e_{\text{Ce}}^{\% \text{Ce}} + e_{\text{O}}^{\% \text{O}} \quad \text{(22)}
\]

\[
\log f_{\text{O}} = e_{\text{Al}}^{\% \text{Al}^{1.5} / X_{\text{AlO}1.5}} + e_{\text{Ce}}^{\% \text{Ce}} + e_{\text{O}}^{\% \text{O}} \quad \text{(23)}
\]

The composition of molten iron being equilibrated with the inclusions, which consist of the CaO–AlO1.5–CeO1.5 system, has been calculated with an O concentration in molten iron of 10 ppm. Figure 9 shows the relationship between the concentration of CeO1.5 in the inclusions and Al and Ce in the molten iron. Because the activity coefficient of CeO1.5 in the oxide melts decreases with increasing \( X_{\text{AlO}1.5} / X_{\text{CAO}} \), inclusions with higher \( X_{\text{AlO}1.5} \) will equilibrate with molten iron that has a lower Ce concentration when the CeO1.5 concentration in the inclusion is the same. In other words, some
Table 8. Interaction parameters between Al, Ce and O in the molten iron at 1873 K. 20–22)

| i→j       | Al   | Ce   | O    |
|-----------|------|------|------|
| Al        | 0.043 | −0.440 | −0.39 |
| Ce        | −2.67  | 0.0039 | −560 |
| O         | −0.23  | −64   | −0.17 |

Fig. 7. Activity coefficients of the components in the CaO–AlO$_{1.5}$–CeO$_{1.5}$ melt at 1873 K.

Fig. 8. Geometric relationships in iso-activity curves.

Fig. 9. Relationships between composition of the CaO–AlO$_{1.5}$–CeO$_{1.5}$ inclusion and contents of Al and Ce in the steel at 1873 K.

Table 7. Electronegativities, basicity moderating parameters, and optical basicities for each component.

| Oxide | $\chi$ | $\gamma$ | $\Lambda$ |
|-------|--------|---------|---------|
| CaO   | 1.0    | 1.00    | 1.00    |
| AlO$_{1.5}$ | 1.5   | 1.65    | 0.61    |
| CeO$_{1.5}$ | 1.1   | 1.1     | 0.88    |
AlO$_{1.5}$ in the inclusion reduces the amount of Ce required.

4. Conclusion

In this study, thermodynamic properties of the CaO–AlO$_{1.5}$–CeO$_{1.5}$ system were investigated. Ternary intermediate compounds in the system, which had not previously been fully studied, have been finally clarified in terms of chemical composition and crystal structure. In addition, phase equilibria and activities of the components for the system at 1 823 and 1 873 K have been investigated by a chemical equilibration technique. The following conclusions about CaO–AlO$_{1.5}$–CeO$_{1.5}$ system may be drawn from our findings.

- The existence of CaO·AlO$_{1.5}$·CeO$_{1.5}$ and CaO·3AlO$_{1.5}$·CeO$_{1.5}$ phases were confirmed, and their crystal structures are considered to be the same as those of CaO·AlO$_{1.5}$·LaO$_{1.5}$ and CaO·3AlO$_{1.5}$·LaO$_{1.5}$.
- The liquid area of the system at 1 823 K is around $X_{CaO}/X_{AlO_{1.5}} \approx 0.8$ and $X_{CeO_{1.5}} < 0.25$. At 1 873 K, CA$_4$ emerges as the new saturated phase instead of CA$_2$, and the liquid area is $X_{CeO_{1.5}} < 0.29$.
- In the CaO–AlO$_{1.5}$–CeO$_{1.5}$ melt, AlO$_{1.5}$ is considered to behave as an acidic oxide while CaO and CeO$_{1.5}$ are considered to behave as basic oxides.
- As the activity coefficient of CeO$_{1.5}$ in the oxide melts decreases with increasing $X_{AlO_{1.5}}/X_{CaO}$, a certain level of AlO$_{1.5}$ concentration reduces the quantity of Ce required.

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