Molecular Dynamics Study of CaO–Al$_2$O$_3$ Melts

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Abstract—Molecular dynamics simulations with Born–Mayer pair potentials taking into account the effective dipole–dipole interaction were used to study CaO–Al$_2$O$_3$ oxides at 1873 K. In each simulation, the system included about 500 ions in a cubic central box with periodic boundary conditions. The thermodynamic, structural, and topological properties of the system were calculated. The inclusion of the dipole–dipole interaction allowed reasonable agreement with the experimental heats of formation to be achieved. According to the simulation results, all of the oxides have a loose structure. At Al$_2$O$_3$ contents of up to 50 mol %, the Al ions are predominantly in tetrahedral coordination. In the melts containing ≥25 mol % Al$_2$O$_3$, the Al$^{3+}$ subsystem is fully polymerized. The electrical conductivity of the melts exceeds the error of determination only for CaO-rich compositions. The self-diffusion coefficients of the ions are very low.

INTRODUCTION

The CaO–Al$_2$O$_3$ system is of considerable technological interest, since materials of this system are widely used in the production of aluminous cements and various ceramics and also to remove sulfur and nonmetal impurities from molten steel. Therefore, computer simulation studies of this system are of practical importance. The CaO–Al$_2$O$_3$ system is known to contain compounds with CaO : Al$_2$O$_3$ molar ratios of 3 : 1, 12 : 7, 1 : 1, 1 : 2, and 1 : 6. At 1873 K, the single-phase liquid region extends from 25 to 56 mol % Al$_2$O$_3$ [1]. The thermodynamic properties of CaO–Al$_2$O$_3$ oxides were studied in [2–4]. The heats of mixing of CaO–Al$_2$O$_3$ melts were reported to change from positive to negative with increasing Al$_2$O$_3$ content (15–23 kJ/mol for the 3 : 1 and 1 : 1 compounds, –6 kJ/mol for 1 : 2, and –3 kJ/mol for 1 : 6). Melt densities in the composition range 0–70 mol % Al$_2$O$_3$ were measured by Elyutin et al. [5].

Computer simulations of noncrystalline CaO and Al$_2$O$_3$ were carried out earlier [6] in a purely ionic bonding model with Born–Mayer pair potentials; Coulomb interactions were evaluated by the Ewald–Ansen method.

PAIR POTENTIALS

We used an ionic model of the CaO–Al$_2$O$_3$ system with Born–Mayer pair potentials:

$$u_{ij}(r) = Z_i Z_j e^2 r + B_{ij} \exp(-r/R_{ij}) + C_{ij}/r^6. \quad (1)$$

Here, $r$ is the center-to-center interionic distance, $Z_i$ is the charge of ion $i$ in elementary charges, and $B_{ij}$ and $R_{ij}$ are the repulsion parameters of ionic shells for ions $i$ and $j$. The $C_{ij}/r^6$ term represents the effective dipole–dipole interaction. Usually, only the first two terms in (1) are considered [6]. It was however shown [7] that, although the contribution of $C_{ij}$ to the total energy is small compared to those from the Coulomb interaction and repulsion of ionic shells, the inclusion of the effective dipole–dipole interaction improves the description of thermodynamic properties in binary oxide systems.

In this work, the thermodynamic properties of CaO–Al$_2$O$_3$ oxides were simulated with allowance for the dipole–dipole interaction and without. All of the $R_{ij}$ values were taken to be 29 pm [6]. With notation 1 for Ca, 2 for Al, and 3 for O, the ionic charges are $Z_1 = 2$, $Z_2 = 3$, and $Z_3 = -2$. Further, for the fairly widely separated pairs 1, 12, and 22, we set $B_{11} = B_{12} = B_{22} = 0$. Earlier computations for pure CaO and Al$_2$O$_3$ yielded $B_{12} = 3283.0$ eV, $B_{23} = 1479.86$ eV, and $B_{33} = 1500$ eV [6]. In a later study [8], $B_{33}$ for pure Al$_2$O$_3$ and systems containing Al$_2$O$_3$ was taken to be 1231.86 eV. Of all $C_{ij}$, only $C_{12}$ differs from zero and will be determined below.

MODELS AND SIMULATION PROCEDURE

Molecular dynamics (MD) simulations were first carried out for (CaO)$_x$(Al$_2$O$_3$)$_{1-x}$ oxides with $x = 0.75, 0.5, 0.333, 0.143$, and 0 at 1873 K for $C_{12} = 0$. The numbers of ions in each simulation are specified in Table 1. Coulomb interactions between ions were evaluated by the Ewald–Ansen method [6–8]. In simulations, we used Verlet’s algorithm. The system was relaxed over 10000 time steps (1 time step = 1.22 fs) to reach thermodynamic equilibrium. During relaxation, an almost zero pressure in the system was maintained.
by varying the length of the simulation box. During the subsequent 10000 time steps, the structural and thermodynamic properties of the system were computed. Next, an electric field was applied to the system [8]. In each run, we computed the charge flow for each ionic species and the current as the sum of these flows. The system was relaxed over 1000 time steps, and then averaging was carried out over the subsequent 10000 steps. The average current was used to determine melt conductivity.

To assess stability of the first coordination shells [8], the nearest neighbors of each ion were recorded at the initial instant of time, and then the number of ions remaining in the same coordination shell was followed over 10000 time steps. From these data, we computed the half-lifes of the first coordination shells for different ion pairs.

RESULTS AND DISCUSSION

Thermodynamic Properties of \((\text{CaO})_x(\text{Al}_2\text{O}_3)_{1-x}\)

The thermodynamic properties of oxides derived from MD simulations at \(C_{12} = 0\) are summarized in Table 1, where \(l\) is the length of the cubic simulation box, \(N\) is the number of ions, \(V/N\) is the volume per gram-ion, \(E_t\) is the total energy of the system in reference to the energy of free ions being at rest in infinity, \(\Delta E_f\) is the energy change upon the formation of 1 mol molten oxide from \(x\) mol liquid CaO and \(1 - x\) mol liquid Al\(_2\)O\(_3\), and \(\Delta V_f\) is the volume change upon the formation of 1 mol mixed melt.

The computed molar volumes of the mixed oxides agree well with experimental data, except at \(x = 0.143\). Good agreement is also observed for pure Al\(_2\)O\(_3\). The formation of mixed oxides from constituent oxides is accompanied by a significant increase in molar volume relative to the additivity rule—up to 16% at \(x = 0.143\).

At \(C_{12} = 0\), the energy of formation of mixed oxides is negative and amounts to \(-62.5\) kJ/mol at \(x = 0.5\). The simulation results differ drastically from experimental data [3] (figure, curves 1, 2), suggesting that, in potential (1), the dipole–dipole interaction between Ca and Al should be taken into account. To increase \(E_t\) and \(\Delta E_f\), \(C_{12}\) must be positive.

For \(x = 0.75, 0.5,\) and \(0.333\), we carried out simulations with \(C_{12} = 0, 75, 200,\) and \(250\) eV \(\text{Å}^6\) and determined \(\Delta E_f\) as a function of \(C_{12}\). For example, at \(x = 0.5\), fitting with a quadratic polynomial yields

\[
\Delta E_f = -62.946 + 0.235635 C_{12} + 5.20265 \times 10^{-5} C_{12}^2. \tag{2}
\]

Substituting the experimental values of \(\Delta E_f\), we find \(C_{12}^\circ\) for each \(x\) (Table 2). Since these values differ insignificantly, in what follows, we use the average \(C_{12} = 204.7\) eV \(\text{Å}^6\).

The thermodynamic characteristics given in Table 2 were computed with this \(C_{12}\). The increase in the length

Table 1. Thermodynamic characteristics of \((\text{CaO})_x(\text{Al}_2\text{O}_3)_{1-x}\) oxides at 1873 K and \(C_{12} = 0\)

<table>
<thead>
<tr>
<th>(x)</th>
<th>(N)</th>
<th>(l, \text{nm})</th>
<th>(p_{av}, \text{MPa})</th>
<th>(V/N, \text{cm}^3/\text{g-ion})</th>
<th>(-E_t, \text{kJ/g-ion})</th>
<th>(-\Delta E_f, \text{kJ/mol})</th>
<th>(\Delta V_f, \text{cm}^3/\text{mol})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>492</td>
<td>2.0341</td>
<td>-15</td>
<td>10.30</td>
<td>1689.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.75</td>
<td>495</td>
<td>1.9802</td>
<td>37</td>
<td>9.44</td>
<td>2334.5</td>
<td>50.3</td>
<td>4.3</td>
</tr>
<tr>
<td>0.5</td>
<td>497</td>
<td>1.9428</td>
<td>-19</td>
<td>8.88</td>
<td>2692.2</td>
<td>62.5</td>
<td>9.6</td>
</tr>
<tr>
<td>0.333</td>
<td>492</td>
<td>1.8917</td>
<td>60</td>
<td>8.28</td>
<td>2848.7</td>
<td>40.8</td>
<td>5.6</td>
</tr>
<tr>
<td>0.143</td>
<td>480</td>
<td>1.8598</td>
<td>-50</td>
<td>8.07</td>
<td>2985.0</td>
<td>13.1</td>
<td>-</td>
</tr>
<tr>
<td>0</td>
<td>500</td>
<td>1.7616</td>
<td>-25</td>
<td>6.58</td>
<td>3068.3</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

RESUL TS AND DISCUSSION

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