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Calulation of phase diagrams for the CaO-CaF_2 and CaO-BaO binary systems by using molecular dynamics

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The thermodynamic properties for the CaO-CaF_2 and CaO-BaO systems were calculated by molecular dynamics(MD) simulation using Born-Mayer-Huggins type pair potential. The parameters of interatomic potential were obtained by fitting the thermodynamics properties of CaO, CaF_2 and BaO with the experimental data. The phase diagrams for the CaO-CaF_2 and CaO-BaO systems were calculated by the thermodynamic properties obtained by MD simulation. The eutectic composition and temperature of the CaO-CaF_2 system calculated by MD simulation were about 28 mole per cent CaO and 1575K, respectively. The calculated eutectic point agrees very well with experimental data, which are about 22 mole per cent CaO and 1633K, respectively.

Keywords: molecular dynamics simulation, thermodynamics, phase diagram, calcium oxide, calcium fluoride, barium oxide.

Introduction

Recently, the thermodynamic properties and phase diagrams of multiphase molten oxides are generally obtained by thermodynamic calculation such as FactSage, Thermo-Calc and ChemSage software. However, the application of these calculation methods is very limited because the experimentally obtained thermodynamic data are required for the calculation of thermodynamic properties of multiphase molten oxides. Molecular dynamics (MD) simulation can be used to calculate the thermodynamic properties based on the dynamic quantities of individual particles of solids and fluids without the thermodynamic database. Therefore, the thermodynamic properties of various systems can be calculated for the system, where experiments are difficult.

The CaO-based slag system such as the CaO-CaF_2 and CaO-BaO-CaF_2 systems are generally used in steelmaking process. There have been many investigations about the physical and chemical properties. Barium oxide-based slags have been attractive with the possibility of application in hot metal pretreatment making use of their high basicity and low melting temperature. However, in spite of importance of these slag systems, thermodynamic properties and phase diagram of barium-based systems have remained obscure because of the difficulties associated with experimental measurements.

The purpose of the present research is to calculate the thermodynamic properties and phase diagram of the CaO-CaF_2 and CaO-BaO binary systems using MD simulation with optimum parameters obtained by fitting the thermodynamic properties of CaO, CaF_2 and BaO.

Molecular dynamics calculation

Interatomic potential

The potential energy was calculated by the sum of pairwise interactions between atoms in the Born-Mayer-Huggins type pair potential according to Equation [1].

$$\phi_{ij} = Z_i \cdot Z_j e^2 / r_{ij} + f_0\left(b_i + b_j\right) \exp\left\{\left(\sigma_i + \sigma_j - r_{ij}\right)/\left(b_i + b_j\right)\right\} \quad [1]$$

where r_{ij} is the interatomic distance between ions i and j, Z_i is the valence of the ion i, e is the electron charge, f is a standard force of 4.184kJÅ^{-1} mol^{-1},σ_i and b_i are repulsive radius and softness parameters of the ion i. The interatomic pair potential terms represent Coulombic and repulsion interactions without the dispersion terms.

Belashchenko *et al.*[1–2] and Hirao *et al.*[3] calculated the interatomic potential parameters for the CaF_2, CaO and BaO systems. These interatomic potential parameters show good agreement with the structural properties obtained by the experimental methods. However, these parameters have a limitation for the calculation of thermodynamics properties such as melting point and fusion data of the CaF_2, CaO and BaO system.

In the present study, interatomic potential parameters for Ca and O were taken from Matsumiya *et al.*[4] which reproduces the various properties such as thermodynamic, structural and transport property of CaO solid and CaO-SiO_2 melt very well. The optimum parameters for Ba and F were calculated by fixing the interaction parameters of Ca and O. The interatomic potential parameters used in this study are listed in Table I.

Methods for calculation

The MD simulation was carried out using the isobaric and isothermal ensemble. Temperature is controlled by velocity scaling method. Pressure is controlled by Parrinello and Rahmann method at atmospheric pressure.

The CaO and BaO crystals have a cubic rocksalt structure. The CaF_2 crystal has a CaF^2 structure. The MD basic cell for CaO, BaO and CaF_2 solid phase is composed with 5×5×5 unit cell of CaO, BaO and CaF_2 crystals in the cubic cell. The total number of atoms in CaO, CaF_2 and BaO were 1000, 1500 and 1000. In the case of the liquid phase of CaO, CaF_2 and BaO, the initial atomic

configurations were set to be random in the cubic cell. The total number of atoms in CaO, CaF_2 and BaO were 1000, 1500 and 1000. The initial atomic configurations for the CaO-CaF_2 and CaO-BaO binary systems were set to be random in the cubic cell. The total number of atoms was taken to be from 1000 to 1500 with changing composition of the binary systems. The densities of basic cells for the CaO-CaF_2 and CaO-BaO systems of 3.18–3.34 g/cm^3 and 3.34–5.72 g/cm^3 were used. The periodic boundary condition was employed for each simulation. The long range Coulomb interactions have been summated by Ewald method. The equations of motion were integrated with fifth-order Gear's predictor-corrector algorithms with a time step of 1fs. Each MD run durations involved 10 000 steps. The thermodynamic properties were calculated by statistical analyses of velocities and position data after reaching equilibrium for the system at the various temperatures. The MD simulation was carried out using WinMASPHYC program.

Table I
Parameters of interatomic potential used for the simulation

	Z_i	σ_i ()	b_i ()
Ca	2	1.9995	0.2101
Ba	2	2.55	0.2685
O	-2	1.84	0.13
F	-1	1.4848	0.116

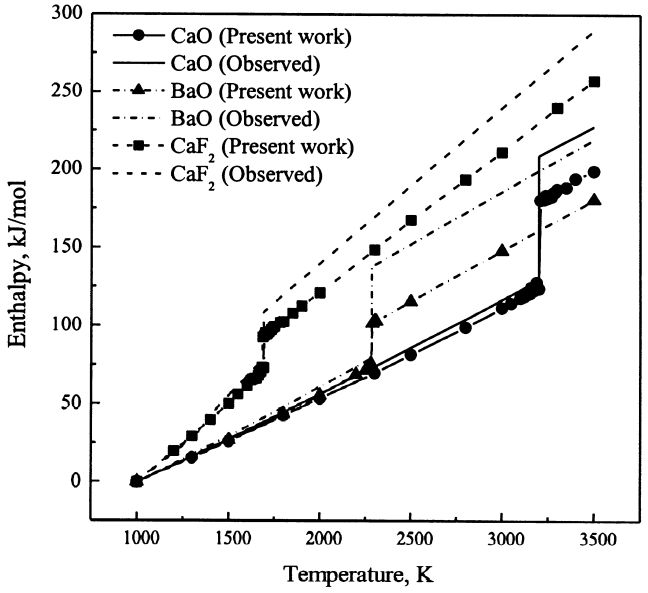

Figure 1. Variation of calculated and observed enthalpy of CaO, CaF2 and BaO at atmospheric pressure as a function of temperature. (Reference state: 1000K)

Results and discussion

CaO, CaF_2 and BaO system

The enthalpies of solid and liquid phase for CaO, CaF_2 and BaO were calculated as a function of temperature at the atmospheric pressure. Figure 1 shows the calculated and observed[5] enthalpy for CaO, CaF_2 and BaO as a function of temperature. The values of the enthalpy are calculated for a reference temperature of 1000K by neglecting quantum corrections in this study. Table II shows the melting point, enthalpy and entropy of fusion of CaO, CaF_2 and BaO calculated by MD simulation compared with the observed data[5]. The thermodynamics properties of CaO, CaF_2 and BaO calculated by the MD simulation are, on the whole, in good agreement with experimentally observed data. The potential equation and parameters used in the present study are reasonable for the calculation of thermodynamic properties of the CaO, CaF_2 and BaO system.

The CaO, CaF_2 and CaO-BaO binary systems

Calculation of Gibbs energy of mixing

The enthalpy of mixing of CaO-CaF_2 and CaO-BaO binary systems directly calculated by MD simulation at various temperatures and compositions. The enthalpy of mixing is expressed by Equation [2].

$$\Delta H^M = \left(X_A \overline{H}_A + X_B \overline{H}_B\right) - \left(X_A H_A^o + X_B H_B^o\right) \quad [2]$$

where $\overline{H}_i$ and H_i^o are the partial molar enthalpy of component i in the solution and the standard molar enthalpy of component i, respectively. Figure 2 shows the enthalpy of mixing curves of the CaO-CaF_2 binary system calculated by MD simulation at various temperatures. The enthalpy of mixing curve of the CaO-CaF_2 system shows the negative values in a composition and it does not show temperature dependence.

The internal energy and enthalpy of the systems can be calculated by the MD simulation as a function of particle positions and velocities. However, the entropy cannot directly be calculated by the MD simulation. Therefore, in this study, assuming that CaO-CaF_2 and CaO-BaO binary melts are complete ionic solutions and all the ions of CaO-CaF_2 and CaO-BaO binary melts have a random configuration, the entropy was calculated. The entropy of mixing can be calculated from ion fractions of solution by Equation [3].

$$\Delta S^M = -R\left(X_i \ln X_i + X_j \ln X_j + X_k \ln X_k\right) \quad [3]$$

where the X_i, X_j and X_k are fractions of ions in the solution. Figure 3 shows the entropy of mixing of CaO-CaF_2 and CaO-BaO binary systems.

The Gibbs energy of mixing of Equation [4] is calculated

Table II
Comparison of observed and calculated thermodynamics properties of CaO, CaF_2 and BaO

	CaO		CaF_2		BaO	
	Observed	Present work	Observed	Present work	Observed	Present work
Melting point (K)	3200±50	3210±10	1691±5	1695±5	2285±15	2285±5
$\Delta_{fus}H^o$ (kJ mol^{-1})	79.5	55.1	29.7	22.25	58.6	28.3
$\Delta_{fus}S^o$ (J K^{-1} mol^{-1})	24.8	17.2	17.6	13.1	25.6	12.4

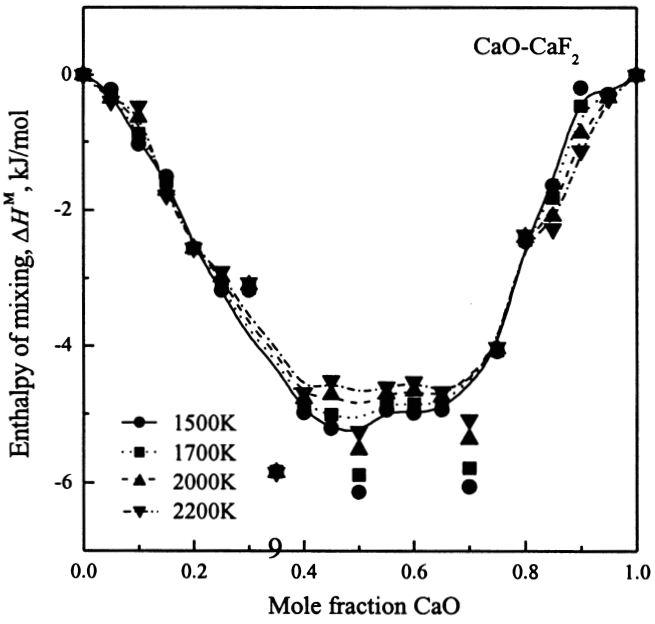

Figure 2. Enthalpy of mixing curves calculated at various temperatures for the CaO-CaF_2 binary system as a function of composition

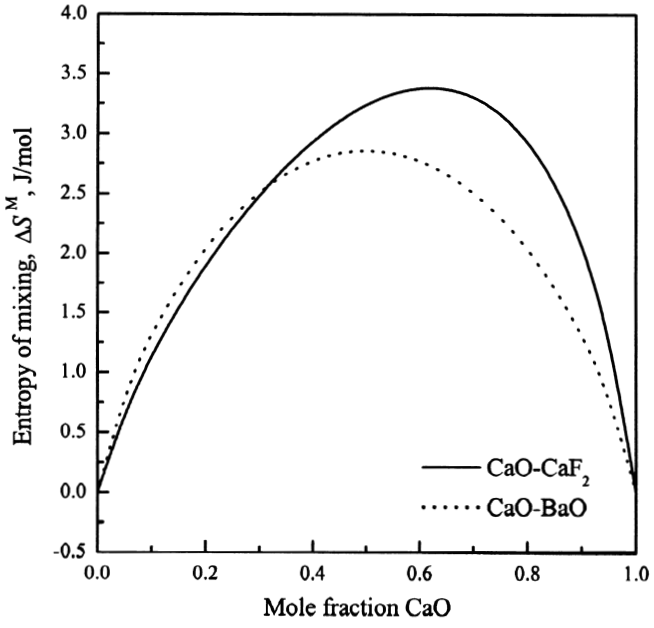

Figure 3. Calculated entropy of mixing curves of CaO-CaF_2 and CaO-BaO binary systems as a function of composition

by the values of enthalpy of mixing obtained by the MD simulation and the entropy of mixing calculated by Equation [3].

$$\Delta G^M = \Delta \mathrm{H}^{\mathrm{M}} - T\Delta S^M \quad [4]$$

Figure 4 shows the Gibbs energy of mixing of the CaO-CaF_2 system as a function of composition at various temperatures.

Calculation of the phase diagram for the CaO-CaF_2 system

The phase diagrams for the CaO-CaF2 system is calculated by double tangent method of Gibbs energy of mixing. Figure 5 shows the phase diagram of CaO-CaF_2 system calculated by MD simulation compared with the observed results[6]. The calculated eutectic composition and temperature for the CaO-CaF_2 system are 28 mole per cent CaO and 1573K, respectively. The eutectic point calculated by MD simulation was in good agreement with observed result of 22 mole per cent CaO at 1633K.

Conclusions

The optimum interatomic potential parameters of Ca, Ba, O and F were calculated for the MD simulation of the CaO-CaF_2 and CaO-BaO systems. The thermodynamics properties, such as melting point and enthalpy for solid and

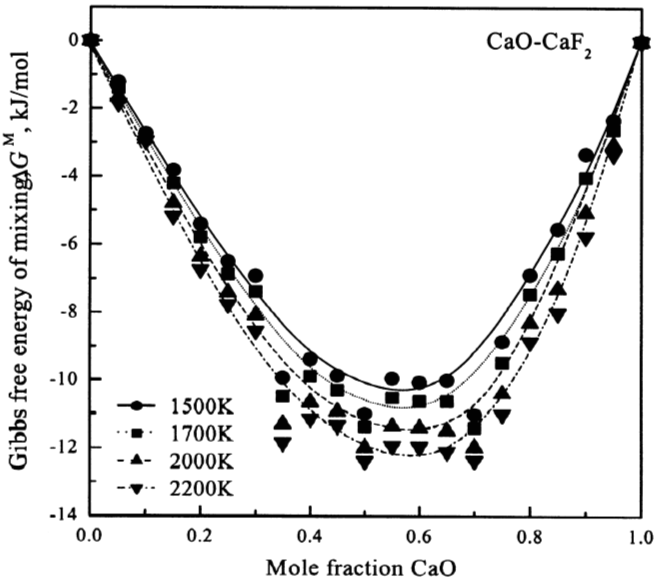

Figure 4. The calculated Gibbs energy of mixing at various temperatures for the CaO-CaF_2 binary system as a function of composition

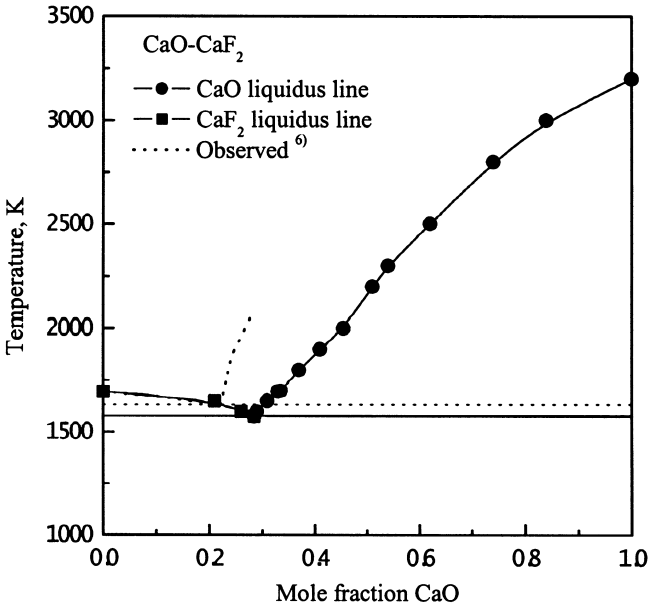

Figure 5. Calculated phase diagram of CaO-CaF_2 binary system with observed result

liquid phases of the CaO, CaF_2 and BaO, calculated by using potential parameters were in good agreement with observed values. The phase diagrams for the CaO-CaF_2 system were calculated by double tangent method of Gibbs energy of mixing. The eutectic composition and temperature for the CaO-CaF_2 system were calculated by MD simulation to be 28 mole per cent CaO and 1573K, respectively. The calculated eutectic point was in good agreement with observed result. It is concluded that the MD method can be used for the calculation of thermodynamic data for molten oxide systems and the estimation of phase diagrams of oxides at high temperature.

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