Determination of Gibbs Energy of Formation of Cuspidine (3CaO·2SiO2·CaF2) by Transpiration Method

Hiroyuki FUKUYAMA, Hideki TABATA, Tadayuki OSHIMA and Kazuhiro NAGATA

Formerly at Department of Chemistry and Materials Science, Tokyo Institute of Technology, Tokyo 152-8552 Japan. Now at Institute of Multidisciplinary Research for Advanced Materials (IMR-AM), Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577 Japan. 1) Department of Chemistry and Materials Science, Tokyo Institute of Technology, Tokyo 152-8552 Japan.

(Received on March 8, 2004; accepted in final form on May 28, 2004)

1. Introduction

Cuspidine (3CaO·2SiO2·CaF2) is one of the most important compounds crystallized in mold flux films during casting in continuous casting process of steel, because cuspidine affects the heat transfer through the films to mold. In order to discuss the crystallization behavior of cuspidine, the present authors have experimentally determined the CaO–SiO2–CaF2 ternary phase diagram around cuspidine. Moreover, the Gibbs energy of formation of cuspidine has been experimentally determined from the electromotive force method (EMF method) using CaF2 as solid electrolyte to discuss the stability field of cuspidine in multicomponent systems of mold flux. However, the EMF measurements were limited in the narrow temperature range from 1 313 to 1 329 K due to the experimental requirements such as satisfying the ternary solid phase equilibrium of cuspidine (3CaO·2SiO2·CaF2)–2CaO·SiO2–CaF2 and using a gold lead wire (melting point = 1 337 K).

Thus, the present study aims for experimentally determining the Gibbs energy of formation of cuspidine from a transpiration method in a wide range of temperature. A chemical potential diagram and constituent activities for the CaO–SiO2–CaF2 system have been evaluated based on the obtained thermodynamic data.

The constituent activities of the CaO–SiO2–CaF2 system and fluorine emission from the system at elevated temperatures have been evaluated based on the obtained thermodynamic data.

KEY WORDS: Gibbs energy of formation; cuspidine; 3CaO·2SiO2·CaF2; CaO–SiO2–CaF2 system; transpiration method; mold powder.

2. Experimental

2.1. Principle

Cuspidine (3CaO·2SiO2·CaF2) reacts with water vapor to form 2CaO·SiO2 and HF at elevated temperatures as represented by,

\[ 3\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{CaF}_2(s) + \text{H}_2\text{O}(g) = 2(2\text{CaO} \cdot \text{SiO}_2)(s) + 2\text{HF}(g) \]

The standard Gibbs energy change for the above reaction is experimentally determined by using a transpiration method. The equilibrium constant of the above reaction, \( K_1 \), is expressed by

\[ K_1 = \frac{a_i^2}{a_{3\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{CaF}_2} \cdot P_{\text{H}_2\text{O}}^2} \]

where \( a_i \) and \( P_i \) are activities of component \( i \) with reference to pure substance and 1 bar (10^5 Pa), respectively. When the activities of cuspidine and 2CaO·SiO2 are unity, the standard Gibbs energy change of reaction (1), \( \Delta_r G^\circ \), is simply expressed by

\[ \Delta_r G^\circ = -RT \ln \frac{P_{\text{HF}}^2}{P_{\text{H}_2\text{O}}} \]

where \( R \) is the gas constant (8.314 J K^{-1} mol^{-1}) and \( T \) is the absolute temperature. The reaction (1) must occur in an ap-
propriate ternary equilibrium on the basis of the phase rule for the CaO–SiO\textsubscript{2}–CaF\textsubscript{2} ternary system. Thus, the ternary solid-phase equilibrium of cuspidine, 3CaO·2SiO\textsubscript{2} and 2CaO·SiO\textsubscript{2}, which exists below 1 508 K\textsuperscript{°} was chosen in the present study. The mixed powder, which consists of cuspidine, 3CaO·2SiO\textsubscript{2} and 2CaO·SiO\textsubscript{2} is allowed to react with an Ar–H\textsubscript{2}O carrier gas. HF gas is immediately generated by reaction (1) and carried out in the Ar–H\textsubscript{2}O gas. The HF gas is quantitatively analyzed, which determines the partial pressure of HF. A flow rate of carrier gas is varied to meet the condition of HF gas saturation in the carrier gas. Consequently, substituting partial pressures of H\textsubscript{2}O and HF into Eq. (3) gives the standard Gibbs energy change of the reaction (1).

2.2. Sample Preparation

Reagent grade powders of CaCO\textsubscript{3} (99.95 mass%), SiO\textsubscript{2} (Quartz 99.9 mass%) and CaF\textsubscript{2} (99.5 mass%) were used. CaO powder was obtained by firing CaCO\textsubscript{3} powder at 1 273 K for 72 ks in air. First, mixed powders of 3CaO·2SiO\textsubscript{2} and 2CaO·SiO\textsubscript{2} were prepared by firing appropriate amounts of CaO and SiO\textsubscript{2} in a dried argon atmosphere at 1 673 K for 72 ks. CaF\textsubscript{2} powder was added to the obtained mixture of 3CaO·2SiO\textsubscript{2} and 2CaO·SiO\textsubscript{2}, and the mixed powder was subsequently fired at 1 473 K for 72 ks in a dried argon atmosphere to obtain the ternary mixture of cuspidine (3CaO·2SiO\textsubscript{2}·CaF\textsubscript{2}), 3CaO·2SiO\textsubscript{2} and 2CaO·SiO\textsubscript{2} at the mass ratio of cuspidine:3CaO·2SiO\textsubscript{2}:2CaO·SiO\textsubscript{2}=3:1:1. The formation of compounds was confirmed by X-ray diffraction analysis (XRD).

2.3. Procedure of Transpiration Experiment

The experimental apparatus consists of a reaction tube and a HF gas-corrector as shown in Fig. 1. The reaction tube was made of larger SiO\textsubscript{2} tube (44 mm outside diameter, 40 mm inside diameter) joined with smaller SiO\textsubscript{2} tube (6 mm outside diameter, 4 mm inside diameter). A doughnut-shaped SiO\textsubscript{2} tube (38 mm outside diameter) was inserted into the reaction tube to eliminate the free space inside the reaction tube. Ar gas was saturated with water vapor by passing the Ar gas through a water bath kept at 313 K or the reaction tube. Ar gas was saturated with water vapor by passing the Ar gas through a water bath kept at 313 K or the reaction tube. Ar gas was saturated with water vapor by passing the Ar gas through a water bath kept at 313 K or the reaction tube. Ar gas was saturated with water vapor by passing the Ar gas through a water bath kept at 313 K or the reaction tube. Ar gas was saturated with water vapor by passing the Ar gas through a water bath kept at 313 K or the reaction tube. Ar gas was saturated with water vapor by passing the Ar gas through a water bath kept at 313 K or the reaction tube.

A flow rate of the Ar gas was controlled by a mass flow controller within a relative uncertainty of ±1%. Saturation with water vapor was confirmed in the range of Ar gas flow rate from 92 to 458 cm\textsuperscript{3}·min\textsuperscript{−1} s.t.p. Partial pressures of H\textsubscript{2}O were (7.33±0.22)×10\textsuperscript{−3} MPa at 313 K and (3.48±0.10)×10\textsuperscript{−3} MPa at 300 K, which agree with the literature data cited in NIST-JANAF Thermochemical Tables\textsuperscript{10} within reasonable experimental uncertainties.

The mixed powder containing cuspidine, 3CaO·2SiO\textsubscript{2} and 2CaO·SiO\textsubscript{2} was stuffed in a platinum container made of a platinum gauze (55 mesh). The platinum container with the sample was placed at the bottom of a SiO\textsubscript{2} reaction chamber. A Pt–Pt·13%Rh thermocouple was inserted in the middle of the sample powder. The sample was heated by using a vertically mounted image furnace of infrared radiation. The temperature variation in the sample was within ±2.5 K in the temperature range from 1 373 to 1 473 K. The mixed powders containing cuspidine, 3CaO·2SiO\textsubscript{2} and 2CaO·SiO\textsubscript{2} were allowed to react with the Ar–H\textsubscript{2}O gas mixture for 900 s in the temperature range from 1 221 to 1 469 K. Generated HF gas was carried out with the Ar–H\textsubscript{2}O gas and collected in a mixed solution of distilled water (100 cm\textsuperscript{3}) and TISAB solution (10 cm\textsuperscript{3}, total ionic strength adjustment buffer solution, TISAB-01, TOA Electronics Ltd., Tokyo, Japan). To ensure complete HF gas collection, three traps containing the TISAB solution were used as shown in the figure. 99% of the total HF gas was absorbed in the first trap. The second trap contained rest of the HF gas, and fluoride content in the third trap was less than analytical limit (<1×10\textsuperscript{−6} mol/cm\textsuperscript{3}). After the experiment, the sample was examined by XRD and it was confirmed that the initial constituents remained throughout the experiment.

Fluoride ions trapped in the TISAB-solution were quantitatively analyzed based on Japanese Industrial Standards (JIS K 0102). Fluoride ion concentration in the solution was electrochemically measured by using a fluoride ion selective electrode as an indicator and a Ag–AgCl electrode as a reference. During the measurements, the solution was stirred by a magnetic stirrer. Calibration was conducted using standard solution of fluoride ion ranging from 1 ppm to 100 ppm. A good linearity between electromotive force and logarithmic of fluoride ion concentration was obtained in the concentration range. A flow rate of the carrier gas was varied from 100 to 500 cm\textsuperscript{3}·min\textsuperscript{−1} s.t.p. to confirm the saturation of HF gas in the carrier gas.

3. Results

3.1. XRD Analysis

Figure 2 shows XRD profile of the sample before and after the transpiration experiment. Peaks of cuspidine became smaller and on the contrary peaks of 2CaO·SiO\textsubscript{2} be-
came larger through the experiment, indicating that cuspidine reacted with water vapor forming $2\text{CaO} \cdot \text{SiO}_2$ by reaction (1). Thus, the ternary phase relation of cuspidine, $3\text{CaO} \cdot 2\text{SiO}_2$ and $2\text{CaO} \cdot \text{SiO}_2$ was confirmed throughout the experiment.

### 3.2. Dependence of Flow Rate of Carrier Gas

Figure 3 shows dependence of partial pressure of HF on flow rate of carrier gas with $P_{\text{H}_2\text{O}/\text{MPa}}=(7.33 \pm 0.22) \times 10^{-3}$ at 1319 K. The experiments were repeated three or four times at each gas flow rate. The average values associated with error bar are plotted in the figure. The figure can be divided into three regions:

- **Region (i):** HF gas generation is controlled by gas supply,
- **Region (ii):** the carrier gas is saturated with HF gas, and
- **Region (iii):** the carrier gas is not saturated with HF gas.

Thus, the equilibrium partial pressure of HF was obtained from the value in the region (ii). The same procedure was taken to obtain equilibrium values for different experimental conditions and all data are listed in Table 1.

#### 3.3. Gibbs Energy of Formation of Cuspidine

Figure 4 shows the standard Gibbs energy change of reaction (1) as a function of temperature. Solid circles and open triangle are data obtained under $P_{\text{H}_2\text{O}/\text{MPa}}=7.33 \times 10^{-3}$ and $3.48 \times 10^{-3}$, respectively. All data points were subjected to a least-squares fitting, which gives

$$3\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{CaF}_2(s) + \text{H}_2\text{O}(g) = 2(2\text{CaO} \cdot \text{SiO}_2)(s) + 2\text{HF}(g)$$

$$\Delta_{\text{r1}}G^\circ/\text{kJ} = 265 - 0.116T \pm (16)$$

$$(1221 < T/K < 1469)$$

### Table 1. Experimental results of transpiration method.

<table>
<thead>
<tr>
<th>$T/K$</th>
<th>$P_{\text{H}_2\text{O}}/\text{MPa}$</th>
<th>$P_{\text{H}_2\text{O}}/\text{MPa}$</th>
<th>$P_{\text{HF}}/\text{MPa}$</th>
<th>$K$</th>
<th>$\Delta_{\text{r1}}G^\circ/\text{kJ}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1221</td>
<td>$7.33 \times 10^{-3}$</td>
<td>$7.30 \times 10^{-3}$</td>
<td>$5.97 \times 10^{-5}$</td>
<td>4.83 $\times 10^{-6}$</td>
<td>124.3</td>
</tr>
<tr>
<td>1268</td>
<td>$7.33 \times 10^{-3}$</td>
<td>$7.26 \times 10^{-3}$</td>
<td>$1.29 \times 10^{-4}$</td>
<td>2.28 $\times 10^{-5}$</td>
<td>112.7</td>
</tr>
<tr>
<td>1319</td>
<td>$7.33 \times 10^{-3}$</td>
<td>$7.24 \times 10^{-3}$</td>
<td>$1.74 \times 10^{-5}$</td>
<td>4.13 $\times 10^{-5}$</td>
<td>110.7</td>
</tr>
<tr>
<td>1383</td>
<td>$7.33 \times 10^{-3}$</td>
<td>$7.93 \times 10^{-3}$</td>
<td>$2.81 \times 10^{-4}$</td>
<td>9.85 $\times 10^{-5}$</td>
<td>106.1</td>
</tr>
<tr>
<td>1469</td>
<td>$7.33 \times 10^{-3}$</td>
<td>$7.02 \times 10^{-3}$</td>
<td>$5.82 \times 10^{-4}$</td>
<td>4.77 $\times 10^{-4}$</td>
<td>93.4</td>
</tr>
<tr>
<td>1268</td>
<td>$3.48 \times 10^{-3}$</td>
<td>$3.44 \times 10^{-3}$</td>
<td>$6.31 \times 10^{-5}$</td>
<td>1.15 $\times 10^{-5}$</td>
<td>120.0</td>
</tr>
</tbody>
</table>

$P_{\text{H}_2\text{O}}$: Initial partial pressure of H$_2$O gas
where the uncertainty expresses the standard deviation.

The standard Gibbs energy of formation of cuspidine from elements, $\Delta_f G^\circ$ (cuspidine), is expressed by the following equation and evaluated as,

$$
\Delta_f G^\circ (\text{cuspidine})/\text{kJ mol}^{-1} = \frac{D_f G^\circ (\text{CaO})}{\text{kJ mol}^{-1}} - \frac{2D_f G^\circ (\text{SiO}_2)}{\text{kJ mol}^{-1}} - \frac{D_f G^\circ (\text{H}_2\text{O})}{\text{kJ mol}^{-1}} + E\text{r(1)}\text{G}^\circ /\text{kJ mol}^{-1}/H^{11002} \ 1/11002
$$

The standard Gibbs energy of formation of cuspidine from CaO, SiO$_2$ and CaF$_2$, $\Delta_{\text{r(6)}} G^\circ$, is given by the following equation:

$$
3\text{CaO}(s) + 2\text{SiO}_2(s) + \text{CaF}_2(s) = 3\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{CaF}_2(s) \ ..............................................................................(6)
$$

$$
\Delta_{\text{r(6)}} G^\circ /\text{kJ mol}^{-1} = \frac{D_f G^\circ (\text{CaO})}{\text{kJ mol}^{-1}} - \frac{2D_f G^\circ (\text{SiO}_2)}{\text{kJ mol}^{-1}} - \frac{D_f G^\circ (\text{CaF}_2)}{\text{kJ mol}^{-1}} + E\text{r(1)}\text{G}^\circ /\text{kJ mol}^{-1}/H^{11002} \ 1/11005 \ 5.178
$$

The values of the standard Gibbs energy of formation of cuspidine obtained by the transpiration method are compared with the values obtained by the EMF method as shown in Fig. 5. These values show an excellent agreement with the difference being less than 4 kJ, which is within a reasonable experimental error.

4. Discussion

4.1. Second Law Analysis

Due to the lack of reliable data of heat capacity lower than 1 100 K$^{13}$, the third-law analysis cannot be applied for the evaluation of the standard enthalpy of formation of cuspidine, $\Delta_f H^\circ$ (cuspidine). Therefore, the value of $\Delta_f H^\circ$ (cuspidine) has been estimated from the present study assuming the second-law analysis. The $\Delta_f H^\circ$ (cuspidine) has been obtained from the slope of the linear relation between $\Delta_f G^\circ$ (cuspidine)/$T$ and $1/T$ presented in Fig. 6.

$$
\Delta_f H^\circ (\text{cuspidine})/\text{kJ mol}^{-1} = -5178 \pm 19 \ (\text{estimated from 1 221 to 1 469 K}) \ ..........(8)
$$

The values of $\Delta_f G^\circ$ (cuspidine)/$T$ determined from the EMF study$^9$ are also plotted in the figure, which are represented by triangle. The value of $\Delta_f H^\circ$ (cuspidine) has been determined to be $-5198 \pm 20 / \text{kJ mol}^{-1}$ by the EMF method. These values are in good agreement with each other within a reasonable uncertainty. Taking into account that the value from the EMF study has been determined in the narrow range of temperature, the value from the present study is more reliable. While, Jacques$^{14}$ determined the value of $\Delta_f H^\circ_{298.15}$ (cuspidine) to be $-5104.1 \pm 18.8$ by measuring the heat of solution of cuspidine in aqueous hydrofluoric acid at 298 K.
Because of the large difference in experimental temperature, direct comparison is not very meaningful, however, these values are relatively close each other, indicating that the present results are reasonable.

4.2. Chemical Potential Diagram

It is interesting to discuss the stability of cuspidine in terms of chemical potential of the constituent, because practical mold fluxes consist of multicomponent system. Figure 7 shows the three-dimensional chemical potential diagram developed as a function of the activities of CaO, SiO2 and CaF2 at 1323 K. The thermodynamic data used for constructing the diagram are tabulated in Table 2.

4.3. Activities in the CaO–SiO2–CaF2 System

Figure 8(a) represents the ternary equilibrium in the CaO–SiO2–CaF2 system in the temperature range from 1313 to 1376 K. The constituent activities for the system have been determined in the temperature range from 1320 to 1380 K as shown in Figs. 8(b)–8(d), where the numbers in the figures represent the corresponding ternary equilibrium.

Fig. 7. Three-dimensional chemical potential diagram for the CaO–SiO2–CaF2 system at 1323 K.

Fig. 8. Phase relations and constituent activities in the CaO–SiO2–CaF2 system. (a) Phase relations, (b) CaO activity, (c) SiO2 activity, (d) CaF2 activity, (e) partial pressure of SiF4 and (f) partial pressure of HF under $P_{H_2O}/MPa=0.00423$. 

© 2004 ISIJ 1492
um in the system.

4.4. Fluorine Emission as SiF_4 and HF

From the environmental point of view, it is very important to evaluate fluorine emission as SiF_4 and HF gases from mold powder. Based on the activities for the condensed phase as shown in Figs. 8(b)–8(d), equilibrium partial pressure of SiF_4 can be evaluated from the following equilibrium relation and shown in Fig. 8(e), where the Gibbs energy of formation of SiF_4 is given in Table 2.

\[ \text{SiO}_2(s) + 2\text{CaF}_2(s) = 2\text{CaO}(s) + \text{SiF}_4(g) \] ........(9)

On the other hand, assuming \( P_{\text{H}_2\text{O}} = 0.00423 \text{ MPa} \), which corresponds to typical Japanese summer (temperature 30°C and relative humidity 80%), equilibrium partial pressure of HF can be evaluated from the following equilibrium relation and shown in Fig. 8(f).

\[ \text{CaF}_2(s) + \text{H}_2\text{O}(g) = \text{CaO}(s) + 2\text{HF}(g) \] ........(10)

The both partial pressures of SiF_4 and HF considerably increase with increasing \( \text{SiO}_2 \) activity in the ternary.

5. Conclusions

The standard Gibbs energy of formation of cuspidine has been determined to discuss the thermodynamic stability by the transpiration method as

\[ \Delta_f G^\circ (\text{cuspidine}) / \text{kJ mol}^{-1} = -5178 + 0.813T \quad (\pm 19) \]

\[ (1221 < T / K < 1469) \]

The constituent activities of the CaO–SiO_2–CaF_2 system and fluorine emission from the system at elevated temperatures have been evaluated based on the obtained thermodynamic data.

Acknowledgements

This research was supported by the Iron and Steel Institute of Japan (ISIJ Research Promotion Grant).

REFERENCES