PHASE DIAGRAM $CaO\text{-}SiO_2\text{-}CaF_2$ AROUND CUSPIDINE
- KEY TO DESIRABLE MOLD FLUXES -

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Abstract

Equilibrium phase diagram for the ternary system $CaO\text{-}SiO_2\text{-}CaF_2$ around cuspidine ($3CaO{\cdot}2SiO_2{\cdot}CaF_2$) has been experimentally studied to optimize mold flux composition for the continuous casting of steel. Hermetically closed platinum capsules were used in the quenching method and differential thermal analysis (DTA) to prevent fluorine loss in the form of HF and SiF_4 by reaction of the CaF_2 with water vapor or SiO_2.

INTRODUCTION

Further development in mold flux for the continuous casting of steel is indispensable to improve the casting rate and quality of products. One of the primary troubles is a longitudinal crack on the cast surface. Frequency of the crack-occurrence is effectively reduced with a lower and uniform heat flux in a mold at an early stage of solidification of steel near meniscus. To decrease the heat flux in the mold, mold powders with high crystallization temperature have been ordinarily used [1-6]. Cuspidine ($3CaO \cdot 2SiO_2 \cdot CaF_2$) is the most popular compound which crystallizes in mold flux films during the casting [4, 5], and the crystallization may decrease the radiative heat transfer through the films [2]. The present authors have emphasized that cuspidine should be fully utilized to decrease heat flux due to its crystallization layer formed in the flux films. For the most effective utilization of cuspidine, the phase diagram of the CaO-SiO_2-CaF_2 system around cuspidine must be established. From this point of view, the authors have focused on the ternary system [6, 7]. However, the ternary phase diagram has not been clearly understood yet, because of the experimental difficulties in studying a system containing CaF_2. Thus, the aim of this study is to experimentally determine the phase diagram of the CaO-SiO_2-CaF_2 ternary system around cuspidine by employing the quenching method and differential thermal analysis (DTA). To prevent fluorine loss in the form of HF and SiF_4 by reaction of the CaF_2 with water vapor or SiO_2, samples were hermetically sealed in platinum containers, resulting reproducible data.

EXPERIMENTAL

Equilibrium Experiments by Quenching Method

Reagent grade powders of $CaCO_3$ (99.5 mass%), SiO_2 (99.9 mass%) and CaF_2 (99.95 mass%) were mixed at various ratios, and then were hermetically sealed in platinum pipes (ϕ4 mm x ϕ3.8 mm x 25 mm). Furthermore, dried argon gas was passed through a reaction tube during the experimental runs. The samples in the platinum container were hung at a uniform temperature region in a SiC resistance furnace. In order to promote reactions, the samples were first melted at 1723 K for 7.2 ks (2 h), and subsequently the temperature was gradually decreased down to the experimental temperatures at a rate of 0.25 K/min and the samples were held for 43.2 ks (12 h) to 259.2 ks (72 h) to attain equilibrium, followed by water quenching. The quenched samples were identified by X-ray diffractometry (XRD) and electron probe microanalysis (EPMA). Even employing water quenching, some extent of crystallization of liquid phase occurred in case of CaF_2-rich samples. In such cases, a large analytical area was taken to obtain liquidus compositions in quantitative analysis by EPMA. Amorphous SiO_2, single crystalline CaF_2, synthetic dense cuspidine and various CaO-SiO_2-CaF_2 glasses were used as standard samples in the quantitative analysis. The difficulty in quantitative analysis of fluorine by EPMA was coped with the help of differential thermal analysis (DTA). Platinum containers were sometimes chemically attacked in case of long-time and high-temperature experiments using CaF_2-rich samples. Only fine samples were used in this study.

Differential Thermal Analysis (DTA)

Figure 1 (a) shows the experimental setup for DTA. DTA was performed using a vertically mounted image furnace of infrared radiation. An alumina cap coated with a platinum foil was covered on samples to obtain a large uniform temperature region. Temperature was controlled within ± 0.2 K using a PID controller. A sample holder has been developed to prevent the

reaction of CaF_2 with water vapor. A sample was held in a platinum holder, which was made of a platinum pipe (ϕ4 mm x ϕ3.8 mm x 15 mm), as shown in Fig.1 (b). Both ends of the platinum pipe were hermetically welded with a thermocouple inserted from the bottom. The same hermetic platinum holder was used for a reference holder to satisfy the identical condition with the sample holder. α-alumina was used as reference material. Argon gas (99.9999 vol.%) was passed through a reaction chamber at a flow rate of 50 ml/min during DTA. A thermocouple was calibrated using the melting points of MgF_2 and CaF_2. Single crystalline MgF_2 (99.99 mass%) and CaF_2 (99.994 mass%) were used, and these melting points are reported as 1521 K[12] and 1695 K[13], respectively. Weighed powders of CaO, CaF_2 and SiO_2 were mixed to give various initial compositions of samples. Prior to the measurements, each sample was first melted at 1723 K at a rate of 5 K/min, and subsequently cooled down to the room temperature at 50 K/min to standardize initial conditions. DTA results obtained on heating were taken as data, because of occurrence of supercooling. Change in mass of samples during the course of DTA was negligible, taking into account mass loss of platinum capsules by evaporation. This means that the initial compositions of samples did not alter during DTA.

RESULTS AND DISCUSSION

Phase Diagram of the Cuspidine-CaF_2 System

Figure 2 shows the phase diagram of the cuspidine-CaF_2 system constructed based on the all results measured by both the quenching method and the DTA. Half-filled and filled circles denote the initial compositions of the samples annealed in the two-phase regions of (cuspidine plus liquid), (CaF_2 plus liquid) and (cuspidine plus CaF_2), respectively, obtained by the quenching experiments. Open circles with error bars express the corresponding liquidus compositions measured by EPMA. Open squares express the initial composition of the samples, which are in a homogeneous liquid region. On the other hand, two kinds of filled triangles express the liquidus and eutectic temperatures obtained by DTA. The eutectic temperature and composition are determined as 1515 ± 3 K and 46 mass% $3CaO*2SiO_2$ - 54 mass% CaF_2, respectively. The liquidus lines are drawn by more preferentially relying on the DTA results, because the quantitative analysis of fluorine by EPMA contains a relatively large experimental uncertainty.

Phase Equilibria of the CaO-SiO_2-CaF_2 System

Figure 3 shows the isothermal section of the CaO-SiO_2-CaF_2 system at 1473 K. The closed triangles are liquidus compositions in the system $3CaO{\cdot}2SiO_2$-SiO_2-CaF_2, which have been experimentally determined. On the other hand, phase equilibria in the system $2CaO{\cdot}SiO_2$-CaO-CaF_2 have been evaluated based on the results obtained by Mukerji [8] and Gutt and Osborne [9]. Thus, cuspidine can be in equilibrium with $CaO{\cdot}SiO_2$, $3CaO{\cdot}2SiO_2$, $2CaO{\cdot}SiO_2$, CaF_2 and two liquid phases at 1473 K.

CONCLUSION

Phase diagram in the system cuspidine($3CaO{\cdot}2SiO_2{\cdot}CaF_2$)-$CaF_2$ and isothermal phase equilibria around cuspidine in the system CaO-SiO_2-CaF_2 at 1473 K have been experimentally determined by the quenching method and differential thermal analysis (DTA). The cuspidine-CaF_2 system presents a simple eutectic type of phase diagram. The eutectic composition and temperature are 46 mass% $3CaO\square 2SiO_2$ - 54 mass% CaF_2 and 1515 ± 3 K,

respectively.

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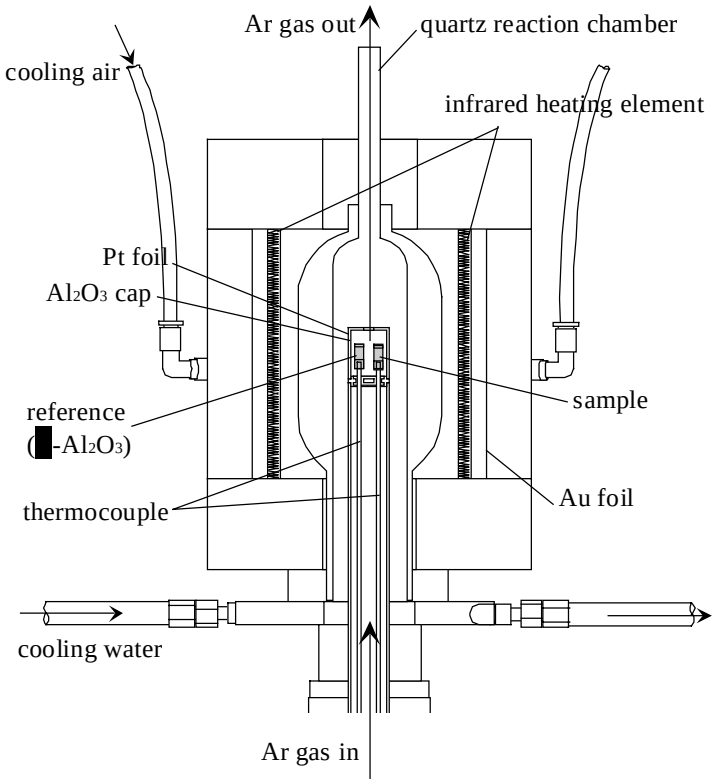
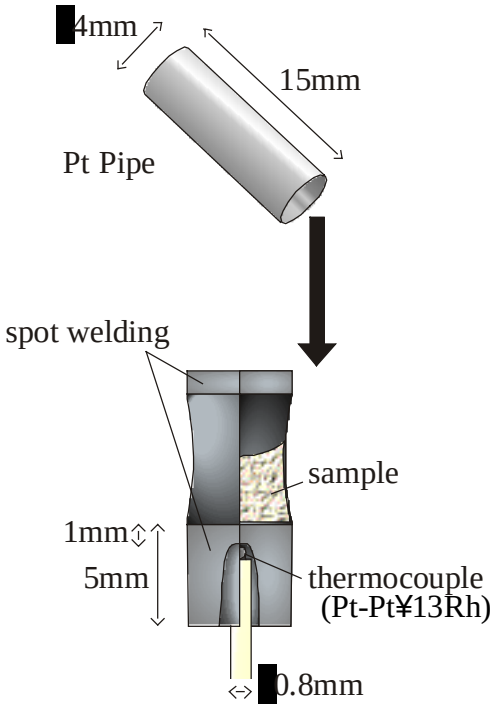


(a)



(b)

Fig.1 Schematic diagram of (a) apparatus for differential thermal analysis (DTA) and (b) platinum-sealed sample holder.

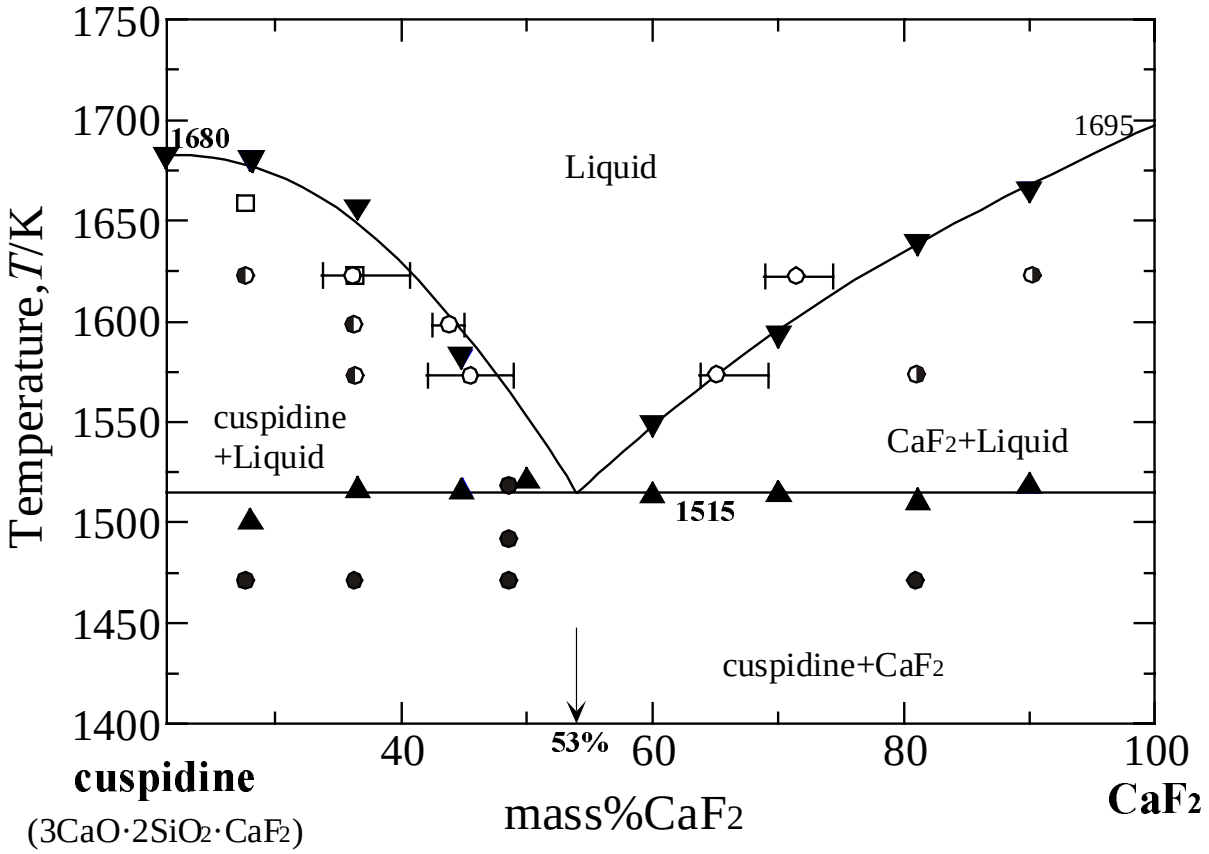


Fig.2 Phase diagram of the system cuspidine($3CaO \cdot 2SiO_2 \cdot CaF_2$)-$CaF_2$.
Data from DTA are designated by triangles, and circles and squares express the results of the quenching method.

Quenching method

Phases	Initial composition	Liquidus composition
cuspidine + CaF_2	●	
cuspidine + liquid	◐	⊢○⊣
CaF_2 + liquid	◑	
Liquid	□	

DTA

Eutectic temperature	Liquidus temperature
▲	▼

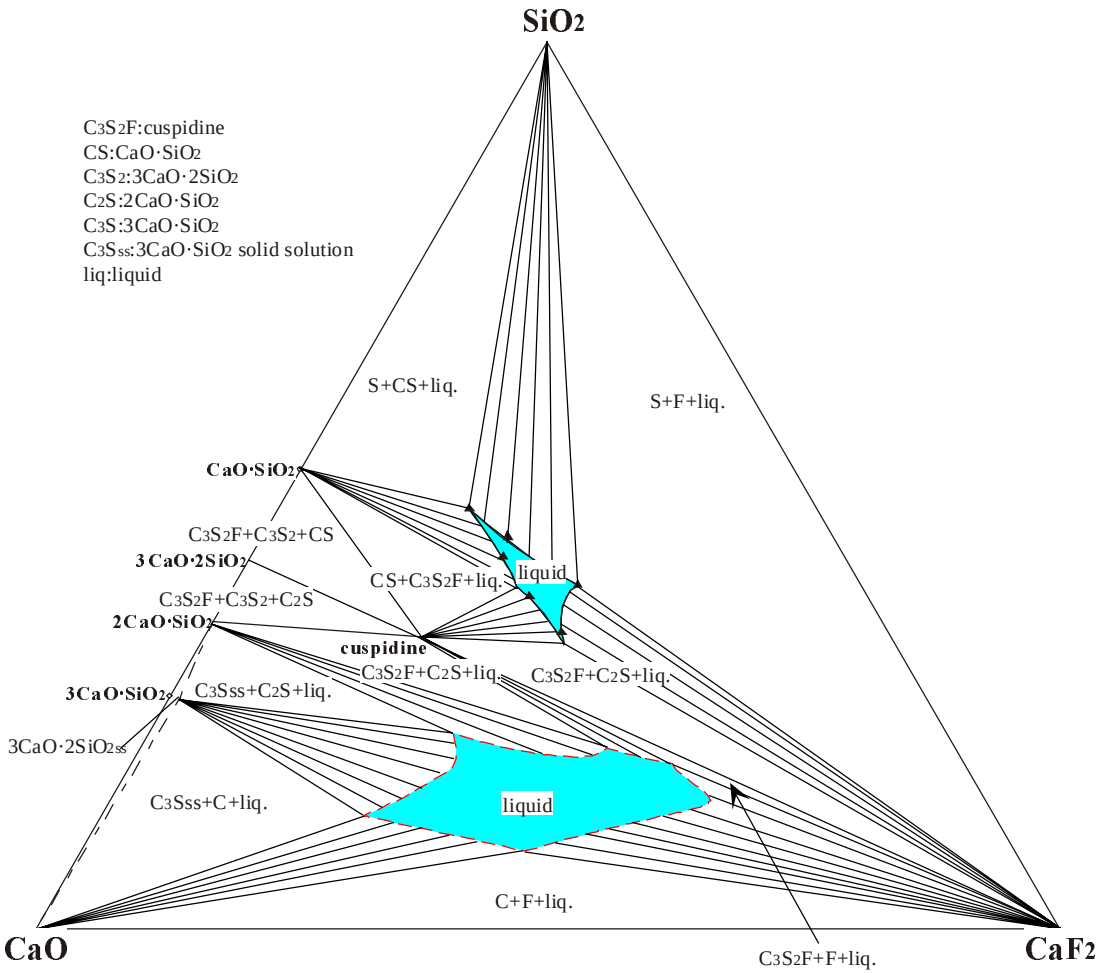


Fig.3 Phase equilibria in the system CaO-SiO_2-CaF_2 at 1473K