# EXPERIMENTAL STUDY AND THERMODYNAMIC MODELING OF THE CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaF<sub>2</sub> SYSTEM

By DONG-GEUN KIM

# DEPARTMENT OF MINING AND MATERIALS ENGINEERING McGILL UNIVERSITY, MONTREAL



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#### Résumé

L'usage des poudres de coulée continue est une préoccupation majeure pour l'industrie sidérurgique. Actuellement, plus de 90% de l'acier est produit par le procédé de coulée continue, nécessitant impérativement l'emploi de poudres de coulée. Traditionnellement, le développement des poudres de coulée a été réalisé par la méthode d'essai et d'erreur depuis son introduction dans l'industrie dans les années 1960. Récemment, l'intérêt porté sur le fluor s'est accru car celui-ci présente d'importantes propriétés et fonctions pour le procédé de coulée continue, telles que son influence sur la cristallisation et la diminution du point de fusion et de la viscosité du laitier. Toutefois, la méthode conventionnelle de développement des poudres de coulée appropriées n'est pas efficace pour faire face aux exigences croissantes du procédé de coulée continue, telles qu'effectuer la coulée de brames minces et atteindre de plus grande vitesse de coulée. Par conséquent, l'étude fondamentale du diagramme de phase des systèmes de poudres de coulée est manifestement nécessaire, et la modélisation thermodynamique est le moyen le plus efficace pour concevoir de nouvelles poudres de coulée en termes d'économie de temps et d'argent. Les principaux composants des poudres de coulée, qui font partie du système CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaF<sub>2</sub>, sont examinés dans cette étude car ces quatre constituants affecteront le plus grand nombre de propriétés des poudres de coulée. Malheureusement, le fluor a une volatilité élevée à haute température et une réactivité élevée avec d'autres matériaux. Par conséquent, les résultats des expériences effectuées précédemment sur les systèmes contenant des fluorures sont caractérisés par des écarts importants en raison du c hangement de composition et de réactions inattendues lors des expériences. Comme les données disponibles dans la littérature rapportent des résultats contradictoires entre eux, des expériences ont été effectuées dans cette étude pour établir les diagrammes de phase. Ces expériences ont été menées avec la méthode de trempe dans des capsules de platine scellées pour empêcher la perte de fluor pendant les expériences. Les analyses ont été effectuées en utilisant un microscope électronique à b alayage (MEB) équipé d'un système d'analyse dispersive en énergie de rayons X (EDS), et une technique nouvellement développée qui produit des résultats plus précis lors de la quantification de la composition des phases à l'équilibre. La courbe du liquidus du CaO du système binaire CaO-CaF<sub>2</sub>, dont les données dans la littérature diffèrent entre elles jusqu'à environ 50 % atomique, a été confirmée. La solubilité de CaO dans CaF<sub>2</sub> à l'état solide a été trouvée pour la première fois et atteint environ 5 % atomique à la température eutectique. Les courbes de liquidus des systèmes CaO-Al<sub>2</sub>O<sub>3</sub>-CaF<sub>2</sub> et CaO-SiO<sub>2</sub>-CaF<sub>2</sub> ont été soigneusement étudiées et l'étendue de la lacune de miscibilité dans le système CaO-Al<sub>2</sub>O<sub>3</sub>-CaF<sub>2</sub> a été prouvée être beaucoup plus petite que celle rapportée dans la littérature. En outre, une analyse thermique a été réalisée par calorimétrie différentielle à b alayage (DSC) dans un creuset en platine. La température eutectique des systèmes CaO-CaF2 et CaAl2O4-CaF2 a été mesurée avec succès et la transition polymorphique de la forme α-CaF2 vers la forme  $\beta$ -CaF<sub>2</sub> a été confirmée. Sur base des nouvelles données expérimentales et des données fiables de la littérature, la modélisation thermodynamique du système CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaF<sub>2</sub> a également été réalisée. Les résultats de calcul thermodynamique peuvent être très bénéfiques pour la conception de nouvelles poudres de coulée.

#### Abstract

Mould flux for the continuous casting process is a major concern for the steelmaking industry. Nowadays, more than 90 % of steel is being produced by the continuous casting process, which requires mould flux as an essential additive. The development of mould flux has been achieved by the conventional trial and error approach since it was first introduced in industry in the 1960s. Recently, the interest on the properties of fluorine has increased a lot since it is reported that fluorine has important functions such as playing a critical role on the crystallization behavior, and decreasing the melting point and viscosity of slag. However, the conventional way to find a suitable mould flux is not efficient to face the increasingly stringent requirements of the continuous casting process such as thin slab casting and higher casting speed. Therefore, fundamental phase diagram study on mould flux systems is clearly necessary, and thermodynamic modeling is the most effective way to design new mould flux in terms of time and money saving. The major components of mould flux, the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaF<sub>2</sub> system, are investigated in this study as these four constituents will mostly affect the largest numbers of properties. Unfortunately, fluorine has high volatility at high temperature and high reactivity with other materials. Therefore, the results of previous experiments on F-containing systems are characterized by large discrepancies due to composition alteration and unexpected reactions during the experiment. As literature data show inconsistent results between each other, key phase diagram experiments were performed in this study. The phase diagram experiments were conducted with the quenching method in sealed Pt capsules to prevent fluorine loss during the experiment. The analyses were performed using a FE-SEM equipped with an EDS system, and a newly developed technique which produces more precise quantitative results for the equilibrium phase composition. The CaO liquidus of the CaO-CaF<sub>2</sub> binary system, which the literature data differ from each other by up to 50 mol %, was confirmed. The CaO solubility in solid CaF<sub>2</sub> was found for the first time and reaches about 5 m ol % at the eutectic temperature. The liquidus of the CaO-Al<sub>2</sub>O<sub>3</sub>-CaF<sub>2</sub> and CaO-SiO<sub>2</sub>-CaF<sub>2</sub> systems

were carefully studied and the miscibility gap in the CaO-Al<sub>2</sub>O<sub>3</sub>-CaF<sub>2</sub> system was proved to be much smaller than that reported in literature. Also, thermal analysis was performed using DSC in a Pt crucible. The eutectic temperatures of the CaO-CaF<sub>2</sub> and CaAl<sub>2</sub>O<sub>4</sub>-CaF<sub>2</sub> systems were successfully measured and the  $\alpha$  to  $\beta$ -CaF<sub>2</sub> polymorphic transition was confirmed. Based on the new experimental data and reliable literature data, thermodynamic modeling of the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaF<sub>2</sub> system was also carried out. The results of thermodynamic calculation can be very beneficial for new mould flux design.

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#### **Chapter 1: Introduction**

The oxy-fluoride systems have been used in various fields of metallurgical cement, glass industries, etc. In the steelmaking industry, for example, the fluorine (F) containing slag system is widely used in electro-slag remelting process and secondary refining process as well as continuous casting process. [70Hil] In particular, the use of fluorine containing mould flux plays a critical role in controlling the surface quality of cast products. Since the introduction of first continuous caster in 1901, the use of the continuous casting process has been increased a lot in a short period of time and now more than 90 % of steel is in these days produced by the continuous casting process. [11Kro] Therefore, the understanding of mould flux containing fluorine has been an important issue in steel industry. The purpose of the present study is to study the fundamental phase diagrams of the CaF<sub>2</sub> containing mould flux system, CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaF<sub>2</sub>, widely used in the steel casting process.

Two main functions of mould flux are the lubrication and the heat transfer control during the steel solidification. Fig. 1.1 shows the schematic diagram of the continuous casting process with emphasis on mould flux solidification. When mould powders are added into the mould, the powders in contact with liquid steel become molten and begin to infiltrate between the water-cooled Cu mould and liquid steel by oscillation force and gravity. After the infiltration, molten mould flux becomes crystallized on the mould side and is kept in liquid state in steel side. Glassy layer of mould flux can also be formed between the crystallized and molten layers. Depending on the thickness of the different mould flux layers forming between molten steel (later stage of solidification, molten steel is solidified to form solid shell near mould side) and mould, the heat flux can be varied. With the controls of the thickness of different layers and crystalline phases in crystallized mould flux layer, the heat extraction from molten steel can be effectively controlled. That is, the mould flux can highly influence the

solidification behavior of molten steel and transformation of  $\delta$ -iron to  $\gamma$ -iron. Also, the molten mould flux layer can act as a lubricant to assist the movement of the steel strand. Thus, understating of solidification of mould flux is very important for lubrication as well as heat flux control.

Fluorine (CaF<sub>2</sub>, NaF and LiF) is the element which has significant influence on the solidification behavior of mould flux. Typically, fluorine can decrease the melting temperature of mould fluxes and increase the flux fluidity. Thus, fluorine can enhance the homogeneous nucleation of crystalline phase in molten flux, which is important to obtain the uniform heat flux during the casting. The CaF<sub>2</sub> addition in CaO-SiO<sub>2</sub> containing mould flux can form cuspidine phase (Ca<sub>4</sub>Si<sub>2</sub>F<sub>2</sub>O<sub>7</sub>), which is the major crystalline phase in mould flux system. However, the solidification behavior of mould flux is still not well investigated due to the complexity of the oxy-fluoride system. Although phase diagrams are essential to understand solidification, the reported phase diagrams for oxyfluoride system are largely inconsistent with each other.

Presently, the experimental phase diagram study for the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaF<sub>2</sub> system; which is the fundamental system of mould flux, were carried out using a classical quenching technique followed by the FE-SEM/EDS phase analysis. In order to reduce the experimental error due to the volatility of F during the experiment, sealed Platinum (Pt) capsules were employed in all experiments. The DSC/TGA experiments for key compositions were also carried out to confirm the solidus and liquidus temperatures. Based on new experimental data and all available and reliable experimental data in literature, a thermodynamic database for mould flux system was developed. The details of experimental procedures and analytical techniques are discussed in Chapters 2 a nd 3, respectively. The experimental and thermodynamic modeling results for the CaO-CaF<sub>2</sub>, CaO-Al<sub>2</sub>O<sub>3</sub>-CaF<sub>2</sub> and CaO-SiO<sub>2</sub>-CaF<sub>2</sub> will be presented in Chapter 4, followed by the summary in Chapter 5.



Figure 1.1. Schematic diagram of the mould flux solidification, Thomas [01Tho].

#### **Chapter 2. Experiments**

2.1 Equilibration experiment: classical equilibration/quenching technique

#### 2.1.1. Materials preparation

Reagent grade calcium carbonate (CaCO<sub>3</sub>,  $\geq$  98.5 wt. %, Merck, Germany), calcium fluoride (CaF<sub>2</sub>,  $\geq$  97 wt. %, Merck, Germany), silicon oxide (SiO<sub>2</sub>, 99.995 wt. %, Alfa Aesar, Germany) and aluminum oxide (Al<sub>2</sub>O<sub>3</sub>, 99.97 wt. %, Alfa Aesar, Germany) were used for preparing the starting materials.<sup>(\*)</sup> CaCO<sub>3</sub> was used instead of CaO due to the hygroscopic behavior of lime. By the calcination reation, CaCO<sub>3</sub>  $\rightarrow$  CaO + C O<sub>2</sub>, CaO was obtained. Mixing was conducted by a mechanical mixer (Turbula, WEB, Switzerland, Fig. 2.1). Appropriate proportions of starting materials were carefully weighted, put in a vial and placed in the mixer. Batches of 3 to 10 g were mixed for more than an hour and stored in a desiccator. The compositions of the starting materials used in the present study are listed in Table 2.1.

Sample name	CaO	SiO <sub>2</sub>	$Al_2O_3$	CaF <sub>2</sub>
CF01 C	10			90
CF02 C	30			70
CF03 C	50			50
CF04 C	5			95
CF05 C	20			80
CF06 C	3			97
CF07 C	25			75
CSF01 C	30	60		10
CSF02 C	20	55		25

Table 2.1. Compositions of the starting materials (mol %).

CSF03 C	10	40		50
CSF06 C	45	40		15
CSF09 C	50	30		20
CSF10 C	70	20		10
CSF11 C	60	20		20
CAF03 C	45		5	50
CAF10 C	60		10	30

(\*): According to Merck specifications, the main impurities in  $CaCO_3$  (up to 1 wt. %) and  $CaF_2$  (up to 2.5 wt. %) is moisture.



Figure 2.1. Mechanical mixer machine for the preparation of the starting material mixtures.

Due to the hygroscopic behavior of CaO and the possible moisture pickup from handling, decomposition of CaCO<sub>3</sub> was conducted just before the experiment using only the required amount of sample (20 to 40 mg). As gas tight capsule is essential to prevent F loss, a Pt tube was used by welding both sides. First, a partly welded (one side) Pt tube (10 mm in length, 4.6 mm O.D., 0.3 mm wall thickness) was used as a container in the calcination process. Welding was performed with an electric arc welder. Calcination of the starting materials was performed at 900 °C in a box f urnace (Nabertherm HT16, Keison, United Kingdom, as shown in Fig. 2.2 (a)) for more than 4 hours. The weights of the samples were measured before and after calcination to check the amount of

carbon dioxide loss. The measured  $CO_2$  loss confirmed the complete calcination in all samples. After the calcination, the samples were stored in a drying oven to cool down to 120 °C and again cooled down to room temperature in a dessicator. The materials were then crushed and packed to remove the air gaps among the grains. The other end of the Pt capsule was then gently crimped to remove the air space as much as possible, and cleaned to avoid possible hole formation during welding. Afterwards, the edge of crimped end was cut using a nipper, and then the capsule was welded to ensure gas-tight condition. All the welded tips were checked with an optical microscope before proceeding with the experiments.

#### 2.1.2 Experimental procedure

A high temperature vertical tube furnace (Gero HTRV, GERO Hochtemperaturöfen GmbH & Co.KG, Germany, with MoSi<sub>2</sub> heating elements, Fig. 2.2 (b)) was used for all equilibration experiments. An automated controlling system recorded the temperature during the experiment. The inside of the furnace is depicted in Fig 2.3. The temperature was measured using a type B thermocouple located at about 10 mm from the sample. Fluctuations were within  $\pm 5$  °C.



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Figure 2.2. (a) Box furnace used for the carbonate decomposition and (b) vertical tube furnace employed for the equilibration experiments.

For each experiment, Pt capsules containing the samples were placed in a Pt sample holder. The holder was held by thin Pt quench wires. The holder was then lowered from the top of the furnace to the hot zone. After the desired equilibration time at working temperature, the Pt wire holding the capsule was cut by an electric shock. The  $Al_2O_3$  disk was linked in the middle of the connection to prevent sticking between the wire and sample holder while applying current to the quench wire. The Pt capsules were then quenched as it fell into cold water. Samples that leaked during the experiment due to pressure build up larger than about 10 atm in the capsule (the maximum pressure a Pt capsule can withstand) were not considered in the analysis. The details of the experimental conditions for each experiment are listed in Table 2.2.

Sampla	Temperature	Duration	Samula	Temperature	Duration
Sample	(°C)	(h)	Sample	(°C)	(h)
CF01 C3	1300	24	CSF01 C1	1150	64
CF01 C4	1250	65	CSF02 C1	1150	2
CF01 C6	1050	260	CSF02 C2	1200	64
CF01 C7	1000	260	CSF03 C1	1500 (2 h), 1150	92
CF01 C9	1200	84	CSF06 C1	1150	64
CF02 C3	1390	2	CSF06 C3	1500 (1 h), 1300	87
CF02 C4	1650	1	CSF09 C1	1350	3
CF03 C4	1500	1	CSF09 C2	1500 (1 h), 1300	87
CF03 C5	1650	1	CSF10 C1	1500 (1 h), 1300	87
CF04 C1	1390	2	CSF11 C1	1350	3
CF04 C2	1300	76			
CF05 C1	1600	1	CAF03 C1	1550 (1 h), 1250	36
CF06 C1	1500 (1h), 1300	86	CAF10 C1	1250	2
CF07 C1	1600	1			

Table 2.2. Experimental conditions.



Figure. 2.3. Schematic drawing of the experimental setup for equilibration experiments.

2.2. Thermal analysis: Differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA)

#### 2.2.1. Materials preparation

Reagent grade calcium oxide (CaO, 99.95 wt. %, Alfa Aesar, USA), calcium fluoride (CaF<sub>2</sub>, 99.95 wt. %, Alfa Aesar, USA), and aluminum oxide (Al<sub>2</sub>O<sub>3</sub>, 99.99 wt. %, Alfa Aesar, USA) were used for preparing the starting materials. Batches of 5 to 10 g were mixed in an agate mortar for one hour. Due to hygroscopic character of CaO, mixing was performed in isopropyl alcohol to prevent moisture contact from air. The mixtures were then kept in a drying oven at 110 °C for more than 12 hours to dry off the alcohol, and cooled down to room

temperature in a desiccator. The compositions of the starting materials are listed in Table 2.3.

Sampla	Composition (mol %)					
Sample	CaO	$Al_2O_3$	CaF <sub>2</sub>			
CF01 M1	20		80			
CF02 M1	10		90			
CAF01 M1	30	30	40			
CAF02 M1	35	35	30			
CAF03 M1	32.5	32.5	35			

Table 2.3. Compositions of the starting materials.

#### 2.2.2. Calibration

Temperature and sensitivity calibrations were conducted by using the melting temperature and enthalpy of the reference materials. Biphenyl ( $C_{12}H_{10}$ ), benzoic acid ( $C_7H_6O_2$ ), rubidium nitride (RbNO<sub>3</sub>), potassium perchlorate (KClO<sub>4</sub>), caesium chloride (CsCl), potassium chromate ( $K_2CrO_4$ ), barium carbonate (BaCO<sub>3</sub>), and diopside (MgCaSi<sub>2</sub>O<sub>6</sub>) were used as reference materials. The corrected temperature and sensitivity curves with values are presented in Fig 2.4 and Fig 2.5.



(a)

	Substance	Temp. nom. ∥°C	Temp. exp. ∥°C	Mathematical Weight	Temp. corr. /°C
1	Diopside	1392.0	1385.9	1.000	1391.5
2	Benzoic acid	122.4	121.1	1.000	122.0
3	Biphenyl	69.2	68.3	1.000	69.3
4	RbNO3(trig>kub)	164.2	165.6	1.000	166.4
5	KCIO4	300.8	298.8	1.000	299.5
6	CsCl	476.0	473.5	1.000	474.2
7	K2CrO4	668.0	665.6	1.000	666.7
8	BaCO3	808.0	809.4	1.000	811.1

1	h	)
J	υ	J

Figure 2.4. (a) Temperature calibration curve and (b) the details of each element.



	Substance	Temp. /oC	Enthalpy J/g	Peak Area uV*s/mg	Sensit.Exp uV/mW	Mathem. Weighting	Sensit. Calc. uV/mW
1	Biphenyl	69.2	-120.500	-132.000	1.095	1.000	0.953
2	benzodic acid	122.4	-147.400	-94.740	0.643	1.000	0.939
3	RbNO3(trig>k	164.2	-26.600	-28.530	1.073	1.000	0.932
4	KCIO4	300.8	-104.900	-97.760	0.932	1.000	0.921
5	CsCl	476.0	-17.200	-15.210	0.884	1.000	0.888
6	K2CrO4	668.0	-35.000	-29.300	0.837	1.000	0.777
7	BaCO3	808.0	-94.900	-54.380	0.573	1.000	0.641
8	Diopside	1392.0	-635.880	-62.350	0.098	1.000	0.074

(b)

Figure 2.5. (a) Sensitivity calibration curve and (b) the details of each element.

#### 2.2.3. Experimental procedure

DSC (Differential Scanning Calorimetry) and TGA (Thermo Gravimetric Analysis) measurements were performed using Jupiter STA 449 F3 calorimeter (NETZSCH Instruments, Germany, Fig 2.6). The Pt-Rh crucibles (6.8 mm of O.D. with capacity up to 85  $\mu$ l) were used, to carry 20 to 40 mg of samples for each run.

Argon atmosphere with a gas flow rate of 20 ml min<sup>-1</sup> was used to avoid hydration of the sample. However, F loss could not be prevented because the crucibles were not gas tight. The composition change, according to F loss, was thoroughly monitored by TGA in order to track the actual composition of the samples. The annealing temperature for all samples were always set about 1000 °C to remove the moisture, homogenize the samples, and minimize the amount of F loss. Two to three heating and cooling cycles were run for each sample.



Figure 2.6. Jupiter STA 449 F3 calorimeter.

Due to F evaporation, the gas outlet must be checked occasionally to keep the accuracy of the TGA balance. Clogging of the outlet tube can cause unstable TG signals. The evaporated F gas can also cause sticking between the sample holder and the crucible. To avoid this, a 0.5 mm thick alumina lid was placed in between.

Between the different runs, the crucible containing the reference materials for the calibration was always cleaned using warm hydrofluoric acid (HF, 48 to 51 vol %). The crucibles used for F-containing materials were cleaned using the following procedure. First, the crucibles were filled with potassium bicarbonate

and fired for one minute under the flame. They were then soaked in warm hydrochloric acid (HCl, 36.5 to 38.0 vol %) for three minutes and then placed in warm distilled water for one minute.

### **Chapter 3. Analyses**

3.1. Equilibrium experiment

### 3.1.1. Sample preparation

The samples from the first few experiments in each binary and ternary system were embedded in epoxy resin with the Pt capsule to observe the phase distribution in the capsule. The mounted section was cut using a diamond saw and polished with water-free lubricant. The rest of the samples were taken out from the capsule and embedded in epoxy resin without the Pt capsule. All the polished sections were prepared just before microscopic observations to avoid hydration of CaO. Examples of polished sections are presented in Fig. 3.1 (a) and (b).



Figure 3.1. Samples prepared for the SEM-EDS phase analysis (six samples are mounted together with standard in the middle in (b), three samples are mounted together with Pt capsules and standard in (a)) and FE-SEM (JSM 7001F, JEOL, Japan, in (c)) used in the present study.

#### 3.1.2. Analysis procedure

Phase recognition and composition analysis were conducted with a Field Emission Scanning Electron Microscope (FE-SEM) equipped with an Energydispersive X-ray spectroscopy (EDS) system (JEOL JSM 7001F and EDS system from Thermo). Based on pre-analyses, the optimal EDS analysis conditions were achieved with an accelerating voltage of 7 kV and measurement area of ~477.5  $\mu$ m<sup>2</sup>. Also, other conditions such as working distance (10 mm) and aperture (3) were fixed. This ensures the consistency between the analysis results. The data acquisition requires 30 minutes per area and normally 5 to 10 a reas were measured for each phase to be quantified. The phases present in the sample and their distributions were checked before selecting the measurement areas. The Proza (Phi-Rho-Z) method was used for matrix correction and the background correction was done manually to increase the analysis accuracy. Internal standards were always used to minimize errors in quantitative analysis and were embedded with the samples (Fig. 3.1 (a) and (b)). Wollastonite (O), calcium fluoride (Ca and F), cuspidine (Ca, Si, F and O) and Krotite (Al and O) were employed as standards depending on the investigated system.

Optical microscopy (Imager Z1, Carl ZEISS, Germany) techniques were used for the phase distribution examination as well as SEM. X-Ray Diffraction (XRD, D8 Discover, Bruker axs, USA) was used for the identification of standard materials. All the data were processed by PARC (PhAse Recognition and Characterization) technique, developed by Corus (Tata steel Europe, Ijmuiden, The Netherlands). The details of PARC technique is in the following section (1.1.4 PARC (PhAse Recognition and Characterization) technique).

Fig. 3.2 shows the phase distribution homogeneity in the capsule for samples CF03 C3 (held at 1380 °C above solidus for 2 h) and CF01 C2 (held at 1340 °C below solidus for 3 h). Fig. 3.3 presents the phase distribution of samples CSF01 C2 (held at 1200 °C for 2 h) and CSF02 C1 (held at 1150 °C for 2 h) observed by SEM (BSE image). As can be seen in Figs. 3.2 and 3.3, the materials after the experiments were typically attached to the Pt capsule wall with the formation of a hole in the middle of the capsule due to interfacial tension.



Figure 3.2. Examples of phase distribution in samples equilibrated at 1380 °C, above solidus temperature (a, CF03 C3) and at 1200 °C, below solidus temperature (b, CF01 C2) observed by means of optical microscope.



(a)



(b)

Figure 3.3. Examples of phase distribution from samples equilibrated at 1200 °C (a, CSF01 C2) and at 1150 °C (b, CSF02 C1) observed BSE images using SEM.

### 3.1.2.1. Determination of optimal analysis condition

Because of high volatility of F, significant amount of F loss was found during the first test measurement. The first test was conducted on synthesized  $CaF_2$  under analytic conditions listed in Table 3.1. The accelerating voltage was fixed at 10 kV or 7 kV and the samples were analyzed with a given acquisition time (2, 5, 10, 15 and 20 sec). The acquisitions were continued up to 20 times to observe the F loss. T he influence of the acquisition time, number of measurements and accelerating voltage on the F counts is shown in Fig. 3.4.

Sample	Acc. Vol. (kV)	Spot/Area	Beam current (nA)	Working dist. (mm)	Acquisition Time (sec)	Standard
Synthesized	10	anot	3.2	10	2 to 20	Nona
$CaF_2$	7	spot	3.61	10	2 10 20	none

 Table 3.1. The analysis conditions of accelerating voltage and acquisition time measurement.



(a)



Figure 3.4. The F loss according to different accelerating voltage (10 kV in (a), 7 kV in (b)) and acquisition time (the time is varying 2 to 20 seconds for each case).

As seen in Fig. 3.4, F loss is significant and it surely will affect the quantification of the F-containing phases during the measurement. The loss may result from the F evaporation due to the local heating generated by the electron beam. Apparently, if the electron beam stays a short time on one spot, in other words, with a short acquisition time, F loss can be minimized even the measurement is repeated many times. The alternative way to minimize the F loss is to use a lower accelerating voltage. With the consideration of minimum accelerating voltage for calcium analysis, 7 kV was considered as the minimum voltage applicable in the present study. Thus, the F loss tests were conducted at 10 kV and 7 kV accelerating voltage. By comparing the results at 10 kV and 7 kV, the analysis performed at 10 kV shows larger F loss than that at 7 kV with the same acquisition time. The difference is larger when longer acquisition time was applied. The results in Fig. 3.4 suggest that F measurement can be more accurate

with lower accelerating voltage and shorter acquisition time. Therefore in the present study, the composition analysis was performed with a short acquisition time and accelerating voltage of 7 kV. The way to have a short acquisition time on a same spot without having too low X-ray counts for quantitative analysis is attained by area measurement instead of spot measurement.

In order to find out the optimum area scanning condition (area size and scanning time for area), several different sized areas were tested with fixed scanning time per area. In the present study, the scanning time per area was fixed as 60 sec regardless the size to simplify the analysis condition. For example, six different area sizes were defined in the preliminary study for synthesized pure CaF<sub>2</sub> sample: ~10.6  $\mu$ m<sup>2</sup> (35000X), ~31.9  $\mu$ m<sup>2</sup> (20000X), ~123.3  $\mu$ m<sup>2</sup> (10000X), ~477.5  $\mu$ m<sup>2</sup> (5000X), ~11068.5  $\mu$ m<sup>2</sup> (1000X), and ~42855.0  $\mu$ m<sup>2</sup> (500X). The F counts were recorded during one scan of the given area (the scanning time for each area was always the same). The normalized F counts corresponding to each scanning area are presented in Fig. 3.5 and detailed condition in Table 3.2. Significant F loss was observed areas smaller than  $\sim 123.3 \text{ }\mu\text{m}^2$ . In the case of a scanned area of ~42855.0  $\mu$ m<sup>2</sup>, the F loss was negligible. For the area size of ~11068.5 to ~123.3  $\mu$ m<sup>2</sup>, a small (less than 2 %) F loss was detected but still negligible. The difference of the F loss is essentially originating from the electron beam stationary time in the given area. That is, as the scanning times for each area are the same regardless of their size, the beam stationary time for a given area increased with a decrease of the area size, resulting in an increased chance of F loss by evaporation as can be shown in the spot analysis in Fig. 3.4. From this result, selecting a large scanning area could reduce the F loss. However, in a real experimental sample, the size of homogeneous area containing a single phase is limited due to the formation of many different phases in a small area. Therefore, the size of the scanning area is restricted by the available size of the phase in a real sample. Based on the experience of many sample analyses, the size of the scanning area was fixed at  $\sim 477.5 \text{ }\mu\text{m}^2$  to minimize the interference by other neighboring phases during the phase analysis.



Figure 3.5. Normalized F counts by different size of scanning area.

Table 3.2. The analysis conditions of scanning area measurement.

G 1	Acc.		Beam	Working	Scanning	Standard
Sample	Vol. (kV)	Spot/Area	current (nA)	dist. (mm)	time (sec)	Stanuaru
Natural CaF <sub>2</sub>	7	Area	3.7	10	60 sec	None

Although the loss of F is small enough by using the above-mentioned EDS analysis condition (7 kV and ~477.5  $\mu$ m<sup>2</sup> scanning area with 60 sec scanning time per given area), the number of F count from the spectrum can be often less accurate and can mislead the composition. Therefore, 30 scans for the same area were performed to obtain statistically more accurate F and other element content. Unfortunately, it was found that more F can be lost during the continuous scan of the same area as can be seen in Fig. 3.6. The results of 30 minutes analysis (30 time of area scanning and each scan takes 60 sec) for the scan area of ~477.5  $\mu$ m<sup>2</sup>

shows about 5.77 % F loss during the analysis. In the case of an area scan of  $\sim$ 31.9 and  $\sim$ 10.6  $\mu$ m<sup>2</sup>, the F loss is 26.46, 29.99 %, respectively, which is too significant to give accurate composition analysis result. The results are summarized in Table 3.3.



Figure 3.6. F loss during 30 minutes analysis by different size of the area.

	area.	
Area size $(\mu m^2)$	Amount F loss (%)	F remaining (%)
447.5	5.77	94.23
31.9	26.46	73.54
10.6	29.99	70.01

Table 3.3. The percentage of F loss during 30 minutes by different size of the

The defined condition (7 kV and ~477.5  $\mu$ m<sup>2</sup> scanning area with 60 sec scanning time per given area x 30 times) was then applied to sample containing both CaF<sub>2</sub> and CaSiO<sub>3</sub> (CaF<sub>2</sub> and CaSiO<sub>3</sub> were used as standard materials for all samples from CaO-CaF<sub>2</sub> system). Ca standard spectrum can be obtained using either

CaSiO<sub>3</sub> or CaF<sub>2</sub>. The spectrum of F and O can be obtained from CaF<sub>2</sub> and CaSiO<sub>3</sub>, respectively. Then, two different approaches can be used to analyze the composition of CaSiO<sub>3</sub> and CaF<sub>2</sub> in the sample. In the first case (case-1), CaF<sub>2</sub> was used for the Ca and F standards and CaSiO<sub>3</sub> was used only for O standard. In the other case (case-2), CaSiO<sub>3</sub> was chosen for the standards of Ca and O, and CaF<sub>2</sub> was chosen as F standard. Based on each case (standard selections), the sample of pure CaF<sub>2</sub> and CaSiO<sub>3</sub> stoichiometries were analyzed. If F-loss is significant during the area scanning, the case-2 should give higher Ca amount for CaSiO<sub>3</sub> than its stoichiometric amount.

Table 3.4 shows the EDS analytic results for pure CaSiO<sub>3</sub> and CaF<sub>2</sub> with a scan area of ~477.5  $\mu$ m<sup>2</sup>. The stoichiometries of both CaSiO<sub>3</sub> and CaF<sub>2</sub> are almost exactly obtained for both case-1 and case-2 (small amount of oxygen in CaF<sub>2</sub> sample seems to be due to the surface hydration of CaF<sub>2</sub>, see the discussion below). On the other hand, with a scan area of ~31.9  $\mu$ m<sup>2</sup> (Table 3.5), the stoichiometry of Ca for CaSiO<sub>3</sub> is about 0.8% lower than the theoretical value (case-1).

The same approach was applied to real samples in the binary CaO-CaF<sub>2</sub> system. The results are summarized in Tables 3.4 and 3.5. As can be seen, the analysis obtained with scan area of ~477.5  $\mu$ m<sup>2</sup> shows the same composition for both case-1 and case-2. However, in the case of the analysis with a scan area of ~31.9  $\mu$ m<sup>2</sup>, both Ca and F concentrations show about 1 mol % difference depending on the standard selection. Although this error seems to be small, it can become significant in ternary and multicomponent systems. Moreover, since the solubility of CaO in CaF<sub>2</sub> is less than several mol %, this 1 mol % analysis error by can induce a significant experiment inaccuracy when determining solubilties. Therefore, obtaining the most reliable EDS analytic conditions is critical for the present study.
Table 3.4. Comparison between two cases, and two real samples in the optimal analytical conditions (7 kV,  $\sim$ 477.5  $\mu$ m<sup>2</sup> area measurement).

Case I
--------

## Case 2

CaF <sub>2</sub>		CaSiO <sub>3</sub>		CaF <sub>2</sub>		CaSiO <sub>3</sub>	
Element	mol %	Element	mol %	Element	mol %	Element	mol %
0	1.307	0	59.992	0	1.302	0	59.995
F	66.374	F		F	66.384	F	0
Si	0.052	Si	20	Si	0.051	Si	20.003
Ca	32.267	Ca	20.007	Ca	32.262	Ca	20.002
				<b>O</b> 1	<b>71 7</b>	177 5	$2 \mathbf{a} \mathbf{a} \mathbf{b}$

Condition: 7 kV,  $\sim$ 477.5  $\mu$ m<sup>2</sup>, 30 min

CF06 C1

CF07 C1

Case 1		Case 2		Case 1		Case 2	
Element	mol %						
0	2.812	0	2.807	0	9.622	0	9.618
F	64.743	F	64.754	F	55.751	F	55.76
Si	0.05	Si	0.05	Si	0.041	Si	0.041
Ca	32.394	Ca	32.389	Ca	34.586	Ca	34.581

Condition: 7 kV,  $\sim$ 477.5  $\mu$ m<sup>2</sup>, 30 min

Table 3.5. Comparison between two cases, and two real samples in the optimal analytical conditions (7 kV,  $\sim$ 31.9  $\mu$ m<sup>2</sup> area measurement).

Case 1	Case 2							
CaF <sub>2</sub>		CaSiO <sub>3</sub>		CaF <sub>2</sub>		CaSiO <sub>3</sub>		
Element	mol %	Element	mol %	Element	mol %	Element	mol %	
0	1.004	0	60.381	0	1.108	0	59.994	
F	66.55	F	0	F	65.4	F	0	
Si	0.049	Si	20.411	Si	0.05	Si	20.003	
Ca	32.397	Ca	19.208	Ca	33.441	Ca	20.002	
				a 1.	· – 1 x z	21.0	2	

Condition: 7 kV,  $\sim$ 31.9  $\mu$ m<sup>2</sup>, 30 min

Case 1		Case 2		Case 1		Case 2	
Element	mol %	Element	mol %	Element	mol %	Element	mol %
0	2.411	0	2.505	0	8.381	0	8.398
F	64.816	F	63.672	F	56.38	F	55.296
Si	0.041	Si	0.043	Si	0.014	Si	0.016
Ca	32.732	Ca	33.779	Ca	35.225	Ca	36.29
				Condit	ion: 7 kV.	~31.9 µm <sup>2</sup>	$^{2}$ , 30 min

CE07 C1

In summary, in the present study, an accelerating voltage of 7 kV, area scan of  $\sim 477.5 \ \mu m^2$ , and 30 minutes acquisition time (30 time of area scanning and each scan takes 60 sec) was established as the optimum EDS analytic conditions for F containing oxide systems. Apart from this, several other factors explained below were important to obtain accurate phase analysis results.

## 3.1.2.2. Standard materials and background correction

 $CaF_2$  is usually used as standard material for F and/or Ca. In the present study, both natural and synthetic  $CaF_2$  were tested for standard materials. Small amount of oxygen was analyzed during the analysis. In order to characterize the oxygen and find the way to eliminate the error induced by the unexpected oxygen,  $CaF_2$ standard materials were carefully examined.

Fig. 3.7 shows the behavior of F loss for natural and synthetic  $CaF_2$  under optimal analysis conditions. As expected, both samples showed continuous F loss during the 30 minutes measurement, and the rates of F loss from natural and synthetic  $CaF_2$  are very similar. This means either natural or synthetic  $CaF_2$  can be used as standard material. In the present study, therefore, natural  $CaF_2$  was used as standard materials for F and/or Ca.

CF06 C1



Figure 3.7. F loss comparison between natural CaF<sub>2</sub> and synthetic CaF<sub>2</sub>.

As mentioned earlier and can be seen in Tables 3.4 and 3.5, a small amount of oxygen (typically about  $1.0 \pm 0.5 \text{ mol }\%$ ) was detected in CaF<sub>2</sub> standard materials. This oxygen contamination can slightly affect the quantification in a real sample. In order to find out the source of the oxygen, several different tests were carried out. It is well known that CaF<sub>2</sub> can be easily hydrated to form Ca(OH)<sub>2</sub> or CaO. If this happened, most of the oxygen should exist at the surface of CaF<sub>2</sub> rather than inside the CaF<sub>2</sub> matrix. In fact, in the CaO-CaF<sub>2</sub> samples in the present study, Ca(OH)<sub>2</sub> was often observed at the CaO / CaF<sub>2</sub> boundary when the samples were kept several days even in a desiccator.

Two different accelerating voltages, 7 kV and 3 kV, were used to check the oxygen counts on the CaF<sub>2</sub> standard materials. The results are plotted in Fig. 3.8. As can be seen in the figure, the oxygen count with 3 kV is much higher than that with 7 kV. The Monte-Carlo simulations (Casino version 2.42) were conducted to predict the beam interaction volumes with two acceleration voltages as shown in Fig. 3.9. Typically, when the accelerating voltage is higher, X-rays are generated

deeper inside the sample. On the other hand, when lower voltage is used, only X-rays from the surface are detected. Thus, larger counts of oxygen with 3 kV in Fig. 3.8 can only be explained by the presence of oxygen on the surface in the form of Ca(OH)<sub>2</sub>, CaO, or H<sub>2</sub>O. Also, under the optimal EDS-analytic conditions setup in the previous section (accelerating voltage of 7 kV, area scan of ~477.5  $\mu$ m<sup>2</sup>, and 30 m inutes of acquisition time), the oxygen content continuously changed as well. Certainly, the oxygen is decreasing during 30 m in acquisition time. This shows the forms of Ca(OH)<sub>2</sub> and H<sub>2</sub>O were presented on the surface.



Figure 3.8. Comparison of oxygen counts at accelerating voltages of 3 kV and 7  $\,$ 

kV.



Figure 3.9. Distribution of the generated X-ray counts in the interaction volume of  $CaF_2$  at accelerating voltages of 3 kV (a) and 7 kV (b) (Monte-Carlo simulations).

There is always a small amount of oxygen detected due to the formation of  $Ca(OH)_2$  or  $H_2O$  on the surface of standard materials and real samples after sample preparation. This surface oxygen is not real dissolved oxygen in the materials and should be removed from the analysis to obtain more accurate oxygen content in the sample. In the present study, the amount of  $Ca(OH)_2$  or

 $H_2O$  formed after the sample preparation was assumed to be propositional to the amount of CaF<sub>2</sub>. Based on this assumption, the oxygen amount was corrected during the EDS analysis.

To minimize the influence of the small oxygen peak analyzed from the standard, a Gaussian fit method was used in the EDS Noran system. This technique avoids adding the small oxygen peak into the F peak (as these two peaks overlap near the background level). The Gaussian fit method consists in the zero full width at half maximum (FWHM) as a reference to calculate the FWHM of detected elements' peaks, taking the peak position of each element presented, and calculating the Gaussian shape of the peak. In this way, the small oxygen peak can be analyzed more precisely without interference from the F peak. Fig. 3.10 presents the concept of the Gaussian fit method.



Figure 3.10. Schematic diagram of peak analyzed by Gaussian fit method.

Strangely, in most of the samples containing F, the background of the X-ray spectra was not accurately corrected by the EDS Noran system itself. For example, Fig. 3.11 (a) shows the actual background on t op of the calculated background for a CaO-CaF<sub>2</sub> sample. As can be seen, the background is much underestimated and the resultant total wt. % from elements analyzed in EDS

analysis can become variable. Typically when the total wt% of EDS analysis is  $100 \pm 2$  wt. %, the analyzed elemental concentration is reliable. Therefore, the background should be manually corrected for all the samples containing F in the present study as shown in Fig. 3.11 (b) to obtain more accurate elemental analysis. In the analysis, the same correction for background was applied to both standard materials and samples.



Figure 3.11. The background correction, (a) automatic correction by Noran and (b) manual background correction.

## 3.1.2.3. PARC (PhAse Recognition and Characterization) technique

Preliminary experimental results showed that all the melts containing considerable amount of F exhibit phase separation during quenching. The melts are difficult to quench because the liquid phase is highly fluid. For example, a single liquid phase in the CaO-CaF<sub>2</sub> system at a given temperature becomes a mixture of liquid and exsolved CaO upon c ooling. In order to determine the accurate original liquid composition, both liquid (amorphous) and exsolved CaO should be counted together in the EDS analysis. In order to obtain the accurate elemental analysis using EDS (average composition of the area), the two different phases should be analyzed separately based on the matrix correction for each phase and then averaged based on the volume of each phase in the specified analyzed volume. Usually, the EDS elemental analysis for area mapping is

performed without considering the matrix correction for different phases, which can induce error in the analysis.

# 3.1.2.3.1. Liquid phase with exsolved solid phase

The analysis technique used in this study is called PARC developed by Corus (Tata Steel Europe, Ijmuiden, The Netherlands). The principle of this technique is to divide a given area (in this case 5000X of magnification, ~477.5  $\mu$ m<sup>2</sup>) into 512 (width) × 384 (height) pixels and collect the individual spectrum of each pixel. Each pixel spectrum (~0.0024  $\mu$ m<sup>2</sup>) is analyzed separately considering the appropriate matrix correction. About 200,000 c ollected pixels can be sorted by elements, and also be grouped based on any given user defined condition. Fig. 3.12 shows the BSE image of a liquid (amorphous) phase containing exsolved CaO during quenching, and the corresponding element distribution obtained by PARC analysis technique.



Figure 3.12. BSE image of liquid phase (a) and element distribution (b) obtained by PARC analysis technique.

In order to obtain the bulk composition of the analyzed area, the individual pixels should be grouped into the liquid and CaO phase. Fig. 3.13 (a) shows the

classified two groups using PARC. Then, the adequate matrix correction can be applied to correct the intensity of elements in each group of pixels. Another advantage of PARC is the automatic area fraction calculation of each phase, without using an image analyzer program. In this way, the accuracy of averaged elemental analytical results of an inhomogeneous matrix can be increased using the PARC system.



Figure 3.13. Grouped pixels for both liquid and exsolved CaO phase (a) and separated boundary pixels (b).

However, in order to obtain the accurate composition of the solid and liquid area, the spectrum near the boundary area were not counted in the determination of the composition of each phase. To calculate the averaged composition of the entire area, the area fraction of each phase analyzed above is corrected by its density and then multiplied by the composition of each phase. The error induced by the area separation of the two phases was calculated based on the amount of boundary pixels.

## 3.1.2.3.2. Sub-solidus sample with small holes

Fig. 3.15 shows the various morphology of the solid  $CaF_2$  surface depending on the thermal history of the samples. The details of the experiemental conditions are summarized in Table 3.6. In the case of solid  $CaF_2$  equilibrated with the liquid phase above the solidus temperature (Fig. 3.15 (a)), small exsolved CaO particles were observed, which seems to be formed during the quenching process. However, in the sample equilibrated at sub-solidus temperature (Fig. 3.15 (b)), no exsolved CaO were found but lots of small holes in solid CaF<sub>2</sub> were observed. When the samples were completely melted (Fig. 3.15 (c)) or partially melted (Fig. 3.15 (d)) and subsequently equilibrated at in sub-solidus temperature, the shape of the holes in solid CaF<sub>2</sub> was different from the case in Fig. 3.15 (b). Smaller holes were found in the completely melted samples.





Figure 3.15. The surface of solid CaF<sub>2</sub> samples with different thermal history. (a) equilibrated above solidus temperature, (b) equilibrated at sub-solidus tempature, (c) completely melted and equilibrated at sub-solidus temperature and (d) partially melted and equilibrated at sub-solidus temperature.

Sample	Composition	Temperature (°C)	Duration (h)
CF04 C1 (a)	95 mol % CaF2	1390	2
CF01 C5 (b)	90 mol % CaF <sub>2</sub>	1200	66
CF01 C9 (c)	90 mol % CaF <sub>2</sub>	1500 (1 hr), 1200	84
CF01 C8 (d)	90 mol % CaF2	1400 (5 min), 1200	66

Table 3.6. Experimental conditions.

It is possible to conclude that the pores are mainly due to an incomplete sintering process of the powder or shrinkage during quenching rather than exsolution of CaO from the solid  $CaF_2$  crystals. Consequently, in the composition analysis using PARC technique, the holes were excluded.

#### 3.2. DSC and TGA experiments

Typically 2 to 3 heating/cooling cycles at the rate of 10 K/min were repeated for each sample to obtain reliable results. Among them, the second or third heating cycle results were taken for analysis because the starting materials can be inhomogeneous and not well reacted in the first heating cycles. Also, samples preannealed in a box furnace were used in some cases for the same reason. Cooling curves were excluded as they often show super cooling effects. Solidus and liquidus temperatures were determined by the onset temperature (a in Fig. 3.16) and peak temperature (b in Fig. 3.16) of the DSC peaks, respectively, during the heating cycle.



Figure 3.16. Heating/Cooling curves from DSC.



Figure 3.17. TGA curve from DSC.

In each analysis, the F loss was recorded (Fig. 3.17) by the TGA and the actual composition of the sample was corrected to take into account the F loss. Accordingly, the compositions of experimental points are more accurate. One of the examples for the analysis result with the composition changes is shown in Fig. 3.18, (result from the pseudo binary CaAl<sub>2</sub>O<sub>4</sub>-CaF<sub>2</sub> system). According to Zaisev *et al.* [90aZai], CaF<sub>2</sub> and AlF<sub>3</sub> are two main volatile gas species in the CaO-Al<sub>2</sub>O<sub>3</sub>-CaF<sub>2</sub> system (strictly, reciprocal system CaO-Al<sub>2</sub>O<sub>3</sub>-CaF<sub>2</sub>-AlF<sub>3</sub>). Zaisev measured partial pressures of CaF<sub>2</sub> and AlF<sub>3</sub> by means of the Knudsen effusion method in combination with mass-spectral analysis. The CaF<sub>2</sub> was reported as a

major gas species through the composition  $(30 - 50 \text{ mol } \% \text{ CaF}_2)$  and temperature (1337 and 1450 °C) ranges. Thus, F loss was corrected as CaF<sub>2</sub> loss in the pseudo binary system. Strictly speaking, some discrepancies on the composition and the temperature are expected because the experiments were in the reciprocal system. As the super cooling effect was significant, the liquidus and solidus phase transition temperatures were significantly lower than the results obtained from the heating cycles.



Figure 3.18. DSC peaks and composition change monitored by TGA. (1), (2), (3) on the phase diagram indicate the 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup> heating cycle.

### **Chapter 4. Results**

4.1. CaO-CaF<sub>2</sub>

#### 4.1.1. Literature review

Since the study of Eitel [38aEit and 38bEit] in 1938, m any researchers have studied the phase diagram and thermodynamic properties of the CaO-CaF<sub>2</sub> system using various techniques. Although the system is generally accepted as a simple binary eutectic system, the experimental studies of CaO and CaF<sub>2</sub> liquidus are largely inconsistent with each other. The eutectic composition is determined is between 17.5 mol % and 26 mol % of CaF<sub>2</sub> at about 1360 °C. [38aEit, 53Bud, 65Muk, 69Sch, 69Kor and 72Zhm] Very limited solubility of CaO in  $\alpha$ -CaF<sub>2</sub> was reported in low temperature region (about 352 t o 727 °C), [63Phi, 66Ros and 77aBol] but no da ta were reported in high temperature region with  $\beta$ -CaF<sub>2</sub> (polymorph transition of  $\alpha$ -CaF<sub>2</sub>  $\leftrightarrow \beta$ -CaF<sub>2</sub> occurs at 1151 °C). All the literature data and preliminary calculation are presented in Fig 4.1.

Liquidus of CaO and CaF<sub>2</sub> were firstly measured by Eitel [38aEit and 38bEit] using a thermal analysis technique. Schlegel [67Sch and 69Sch] and Mukerji [65Muk] also used the thermal analysis technique. In the case of Mukerji, the samples were contained in the sealed Pt capsules for thermal analysis and some samples were also quenched to perform phase analysis using XRD. Budnikov and Tresvyatskii [53Bud] performed the classical quenching experiment to determine the liquidus. Ries and Schwerdtfeger [80Rie] quenched the samples contained in sealed capsules after equilibration. Then, the liquidus of CaO was determined by EPMA compositional analysis. Cryoscopic method was used by Kojima and Masson [69Koj]. Bääk [54Baa and 55Baa] investigated the liquidus of CaF<sub>2</sub> by

means of electrical conductivity measurement and reported a liquid miscibility gap in the CaF<sub>2</sub> rich region.

The liquidus of the system was also determined by indirect methods. Hsu *et al.* [64Hsu], Hawkins *et al.* [71Haw] and Edmunds and Taylor [72Edm] determined the activity of CaO and CaF<sub>2</sub> by gas equilibrium measurement and determined the liquidus of CaO indirectly from the change in the activity. Kor and Richardson [69aKor], Isaksson and Öberg [73Isa] and Zaitsev and Korolev [89Zai] used gas pressure measurement, slag/metal equilibrium, and high temperature Knudsen mass spectrometry, respectively. Zhmoidin [69Zhm] and Davies and Wright [70Dav] roughly determined the liquidus using viscosity measurements. Zhmoidin and Chatterjee [72Zhm] determined CaO liquidus using capillary method which measured the pressure increment during the solidification at liquidus temperature.



Figure 4.1. All available phase diagram experimental data in literature along with the phase diagram (dotted lines) calculated from the thermodynamic modeling.

As seen from the Fig. 4.1, the experimental data for the liquidus of CaO are very scattered, but can be categorized into three groups depending on the liquidus composition. Budnikov and Tresvyatskii [53Bud] reported the liquidus with eutectic composition at about 0.4 mole fraction of CaF<sub>2</sub>. The liquidus of CaO by Mukerji [65Muk], Schlegel [67Sch], Zhmoidin [69Zhm], and Isaksson and Öberg [73Isa] are similarly located with eutectic composition at about 0.6 mole fraction of CaF<sub>2</sub>. The others including Hsu *et al.* [64Hsu], Kor and Richardson [69aKor], Davies and Wright [70Dav], Hawkins *et al.* [71Haw], Edmunds and Taylor [72Edm], Zhmoidin and Chatterjee [72Zhm], Ries and Schwerdtfeger [80Rie], and Zaitsev and Korolev [89Zai] determined the liquidus with eutectic composition of about 0.85 mole fraction of CaF<sub>2</sub>. Probably the uncertainties in CaO liquidus resulted from F evaporation during both experiment and chemical analysis. However, the eutectic temperature was determined to be about 1360 °C by all studies, which is less influenced by the evaporation of F.

The miscibility gap on  $CaF_2$  liquidus was measured by Bääk [54baa], and Korpachev *et al.* [69bKor]. However, Kojima and Masson [69Koj], Mukerji [65Muk], Schelgel [67Sch], and Davies and Wright [70Dav] did not report any miscibility gap. Zhmoidin and Chatterjee [72Zhm] mentioned that the experimental data of Bääk [54Baa] based on the electric conductivity measurement could be affected by the formation of  $CaC_2$  due to the usage of graphite crucible.

The solubility of CaO in solid  $CaF_2$  was studied by Phillips and Hanlon [63Phi] using the micrographic method which measured penetration depth of oxygen and Schlegel [67Sch] using dynamic thermal analysis. Rossing [66Ros] and Bollmann

[77Bol and 82Bol] used the electrical conductivity measurement. All the measurements were done at temperatures below 727 °C and the determined solubility is less than 0.5 at %. Delbove *et al.* [65Del] investigated solubility of CaO into CaF<sub>2</sub> using cryometric technique at liquidus temperature and reported the possibility of noticeable solubility. All experiments except Delbove *et al.* [65Del] were performed with  $\alpha$ -CaF<sub>2</sub> (low temperature polymorphic form of CaF<sub>2</sub>). However, possible CaO solubility in high temperature polymorph  $\beta$ -CaF<sub>2</sub> was discussed by considering the similarity of crystal structure of CaO and CaF<sub>2</sub>. The structure of  $\alpha$ -CaF<sub>2</sub> is cubic *fcc* space group, and the structure of  $\beta$ -CaF<sub>2</sub> belongs to the tetragonal *bct* space group which has one slightly elongated fold than cubic structure according to Mirwald [77Mir]. This indicate the possibility of CaO solubility into  $\beta$ -CaF<sub>2</sub>. Naylor [45Nay] measured the transformation of  $\alpha$ -CaF<sub>2</sub> at 1151 °C with heat of transition of 4769.76 J mol<sup>-1</sup>.



Figure 4.2. Activities of CaO (s) and CaF<sub>2</sub> (l) determined by previous studies.

The activities of CaO and  $CaF_2$  in liquid phase were calculated by several researchers from the equilibration results between CaO-CaF<sub>2</sub> melt and gas mixture. Hsu et al. [64Hsu] used the H<sub>2</sub>O/HF gas mixture at 1450 °C, the activity ratio of CaO/CaF<sub>2</sub> was determined based on thermodynamic reaction CaF<sub>2</sub>(l) + H2O(g) = CaO(1) + 2HF(g). Kor and Richardson [69aKor] and Hawkins *et al.* [71Haw] equilibrated CaO-CaF<sub>2</sub> slag with CO-CO<sub>2</sub>-SO<sub>2</sub>-50%N<sub>2</sub> gas mixtures at 1500 °C. Then, Kor and Richardson estimated the CaO saturation from the trend of S solubility at different initial compositions of CaO-CaF<sub>2</sub>, derived the activity of CaO and CaF<sub>2</sub>. However, Hawkins et al. calculated CaO activity from the reaction  $CaO(l) + \frac{1}{2}S_2(g) = CaS(l) + \frac{1}{2}O_2(g)$  based on determined CaS solubility and controlled S<sub>2</sub> and O<sub>2</sub> gas pressure. Chattopadhyay and Mitchell [90Cha] used the equilibration of liquid CaO-CaF2 and CO2 gas (1 atm) at 1400 °C, the CaO activity was estimated using the reaction  $CaO(1) + CO_2(g) = CaCO3(1)$ . Edmunds and Taylor [72Edm] determined the activity of CaO by measuring the partial pressure of CO(g) for the CaO +  $3C = CaC_2 + CO(g)$  reaction. Zaitsev *et al.* [89Zai] employed the high temperature Knudsen mass spectrometry technique to determine the activities of CaO(1) and CaF<sub>2</sub>(1) in the temperature range of 1093 °C to 1450 °C. The experimental results are plotted in Fig. 4.2.

The measured activity from Edmunds and Taylor [72Edm] could have large errors because of the solubility of  $CaC_2$  in  $CaF_2$ . Kor and Richardson [69aKor] and Hawkins *et al.* [71Haw] may have similar problem due to the dissolution of  $CaCO_3$ , CaS,  $CaN_2$  into molten slag.

### 4.1.2. Experimental results and discussion

As discussed in the previous section, there is a large discrepancy between available experimental data on the liquidus of CaO and  $CaF_2$  in the bianry CaO-CaF<sub>2</sub> system. Moreover, although there is a possibility to have a noticeable amount of CaO solubility in  $\beta$ -CaF<sub>2</sub> phase, no experimental study on the solubility has been carried out. Therefore, this study focused especially on these two aspects of the phase diagram.

4.1.2.1. Liquidus of CaO and CaF2

All analyzed liquid samples showed phase separation during the quenching process due to high fluidity of CaO-CaF<sub>2</sub> melt. That is, solid CaO phase was exsolved during the quenching of liquid samples. The amount of exsolved CaO varied depending on its equilibration temperature (superheat from liquidus) and composition. The more exsolved CaO particles were observed with the higher equilibrium temperature at given composition. Normally 5 areas in the samples were selected to analyze liquid compositions. But, 10 areas were analyzed for the samples equilibrated at 1650  $^{\circ}$ C, because the distribution of exsolved phases at high temperature was less homogeneous than other samples. Fig. 4.3 shows the examples of exsolved CaO in the samples equilibrated at 1650  $^{\circ}$ C and 1390  $^{\circ}$ C.



Figure 4.3. Examples of the quenched liquid samples. (a) CF02 C4and (b) CF02 C3.

The details of experimental conditions are listed in Table 4.1, and the experimental results are plotted in Fig. 4.4.

Sample	Ini compo (mo	tial osition 1 %)	Temp. (°C)	Duration (h)	Phases	Analyzed liquid composition (mol %)	
	CaO	CaF <sub>2</sub>	(-)			CaO	CaF <sub>2</sub>
CF02 C4	30	70	1650	1	CaO+Liquid	23.8 (6.8)	76.2 (6.8)
CF03 C5	50	50	1650	1	CaO+Liquid	25.5 (5.3)	74.5 (5.3)
CF05 C1	20	80	1600	1	Liquid	<b>`</b>	
CF07 C1	25	75	1600	1	CaO+Liquid	26.9 (4.7)	73.1 (4.7)
CF03 C4	50	50	1500	1	CaO+Liquid	22.2 (3.8)	77.8 (3.8)
CF02 C3	30	70	1390	2	CaO+Liquid	21.4 (3.6)	78.6 (3.6)
CF04 C1	5	95	1390	2	CaF <sub>2</sub> +Liquid	11.5 (1.7)	88.5 (1.7)

Table 4.1. Experimental results for the liquidus of CaO and  $CaF_2$  in the present

study.

Values in parentheses show errors (mol %).



Figure 4.4. Experimental results for the CaO and CaF<sub>2</sub> liquidus in the present study along with the phase diagram (dotted lines) calculated from the thermodynamic modeling.

The dotted lines in Fig. 4.4 represent the estimated phase diagram based on the present experimental results. The symbols with error bars are liquidus compositions analyzed by PARC system. The indicated errors are the combined errors from analyzed spectrums, area separation for liquid and exsolved CaO phase, and discrepancy among analyzed areas. As shown on the diagram, the error increases as temperature increases. Like previously mentioned, the larger amount of exsolved CaO phase were observed at higher temperature region, which can increase the uncertainty due to the larger boundary area between liquid and exsolved CaO. The liquidus of  $CaF_2$  was also measured at 1400 °C.

The present experimental data on CaO liquidus are in good agreement with the results from Hsu *et al.* [64Hsu], Kor and Richardson [69aKor], Davies and Wright [70Dav], Hawkins *et al.* [71Haw], Edmunds and Taylor [72Edm], Zhmoidin and Chatterjee [72Zhm], Ries and Schwerdtfeger [80Rie], and Zaitsev and Korolev

[89Zai], as shown in Fig. 4.5, which indicates the eutectic composition of about 0.85 CaF<sub>2</sub>. In the case of liquidus of CaF<sub>2</sub>, the data are in agreement with experimental data without liquid miscibility gap.



Figure 4.5. Comparison of the present liquidus experimental data with the previous studies along with the phase diagram (dotted lines) calculated from the thermodynamic modeling.

4.1.2.2. Solid solution

Fig. 4.6 shows the typical microstructure of sub-solidus experiments. As mentioned in the Chapter 3 for analysis, many small holes (pores) were observed in solid samples. From the preliminary experiments with different heat treatments, the holes were concluded as pores formed during powder sintering process at high temperature and during cooling due to density change from high temperature to room temperature. Therefore, the holes were excluded in the PARC analyses for all sub-solidus samples. X-ray Rietveld analysis was also conducted to determine the amount of CaO and CaF<sub>2</sub> phases, which is independent of the holes (pores) in

the samples. Based on the quantitative analysis and the known starting composition, the chemical composition for the CaF<sub>2</sub> solid solution could be estimated. The solubility of CaF<sub>2</sub> in CaO is virtually zero, which was confirmed by EDS analysis of all samples. The error of this analysis is typically several % (~3 mol % error). Similarly, the solubility of CaO in CaF<sub>2</sub> was also estimated using the image analysis on BSE image by axio-vision software. Because the BSE image of the sample was taken in a wide area and CaO has no solubility of CaF<sub>2</sub>, the composition of CaF<sub>2</sub> solid solution can be relatively well estimated. These results were compared in Fig. 4.7 with the PARC analysis in the present study.



Figure 4.6. Sample equilibrated at sub-solidus temperature (CF01 C9).



Figure 4.7. The solubility of CaO in CaF<sub>2</sub> analyzed by various techniques.

As can be seen in Fig. 4.7, the results of PARC and image analysis are in good agreement. X-ray Rietveld analysis shows the smaller solubility of CaO than the PARC or image analyses. However, all analyses certainly show noticeable solubility of CaO in solid  $CaF_2$  phase.

All the sub-solidus samples were analyzed using the PARC system assuming the holes in the sample are sintering pores. The results of the sub-solidus experiments are summarized in Table 4.2 and the solubility of CaO in the CaF<sub>2</sub> is plotted in Fig. 4.8.

Table 4.2. Experimental results for the CaO solubility in  $CaF_2$  in the present

study.

Sample	Composition (mol %)		Temperature	Duration	Phases
	CaO	CaF <sub>2</sub>	(C)	(11)	
CF04 C1	5	95	1390	2	CaF <sub>2</sub> +Liquid

CF06 C1	3	97	1500 (1h)	86	$CaF_2$
CF04 C2	5	95	1300	76	CaO+CaF <sub>2</sub>
CF01 C3	10	90	1300	24	CaO+CaF <sub>2</sub>
CF01 C4	10	90	1250	65	CaO+CaF <sub>2</sub>
CF01 C9	10	90	1500 (1h)	84	CaO+CaF <sub>2</sub>
CF01 C6	10	90	1050	260	CaO+CaF <sub>2</sub>
CF01 C7	10	90	1000	260	CaO+CaF <sub>2</sub>



Figure 4.8. Experimental results for the CaO solubility in CaF<sub>2</sub> in the present study.

In order to confirm the solubility of CaO in the CaF<sub>2</sub>, one sample (CF06 C1) with 0.97 mole fraction of CaF<sub>2</sub> was annealed at 1300 °C for 86 hours after being melted for 1 hour at 1500 °C. The samples showed the single CaF<sub>2</sub> phase without CaO, which supports the solubility of CaO in CaF<sub>2</sub>. The solid CaF<sub>2</sub> equilibrated with liquid phase at 1400 °C showed about 5 mol % solubility of CaO in CaF<sub>2</sub>. According to the present experimental data, the maximum solubility of CaO in

CaF<sub>2</sub> reaches about 5 mol % at eutectic temperature and decreases gradually with decreasing temperature. Furthermore, the change of the solubility in CaF<sub>2</sub> seems to be continuous with temperature regardless of the structure of CaF<sub>2</sub> ( $\alpha$  and  $\beta$ ) within the experimental error range. This means the dissolution behaviors of CaO in  $\alpha$  and  $\beta$ -CaF<sub>2</sub> are similar to each other. For the first time, the solubility of CaO in CaF<sub>2</sub> is experimentally determined.

### 4.1.2.3. Eutectic and polymorphic transition temperatures

The eutectic temperature and polymorphic transition of  $\alpha$  to  $\beta$ -CaF<sub>2</sub> were measured by DSC/TGA. Unfortunately, while the equilibration experiment employed sealed Pt capsule to prevent F loss, Pt crucible containing sample covered with Pt lid was used for the DSC experiments. Therefore, it was not possible to prevent the F loss during the experiments. However, as the eutectic temperature and polymorphic transition temperature are independent of the composition varied with F loss, they could be easily determined in DSC/TGA experiments.

The DSC thermal graph and TGA weight loss graph for the sample CF01 M2 are plotted together in Fig. 4.9 to explain the volatility of F. As shown by temperature curve, the sample was first heated up to 1508 °C, and cooled down to 967 °C where the sample was annealed for 3 hours and heated to 1508 °C for second cycle. The experiment was carried out under inert gas atmosphere (Ar) and the heating and cooling rate was 10 K min<sup>-1</sup>. During the thermal cycles, the F loss was monitored by TG curve, which shows the amount of loss at given temperature. From the loss of F, it is possible to calculate the compositional change of sample during the experiment. As noticed in the figure, the F loss is significant above 1360 °C, which is coincident with the eutectic temperature of the system.

The thermal peak analyses from the second cycle of DSC curve are presented in Fig. 4.10. The cooling curve was not used for analysis due to the possible super cooling effect. The transition temperatures from heating curve can be taken from its onset temperatures as the reaction starts from the onset point. Therefore,  $\alpha$  to  $\beta$ -CaF<sub>2</sub> polymorphic transition temperature was found at 1150.5 °C (indicated as a in Fig. 4.10.), and the solid to liquid transition, eutectic temperature, was found at 1360.6 °C (indicated as b in Fig. 4.10.). The attempt to investigate the liquidus temperature was failed as the amount of phase transformation is too small to recognize its thermal signal.

The details of the experimental results are listed in Table 4.3. Literature data regarding eutectic temperature and  $\alpha$  to  $\beta$ -CaF<sub>2</sub> polymorphic transition temperature were presented in Fig. 4.11.



Figure 4.9. DSC, TG, Temperature curves from DSC/TGA experiment on sample CF01 M2.



Figure 4.10. The analyzed peaks from second DSC curve (CF01 M2).

Table 4.3. Experimental results for the solidus and polymorphic transitiontemperatures in the present study.

Sample	Com (m	position .ol %)	Solidus	Polymorphic transition (°C)	
	CaO	CaF <sub>2</sub>	- (()		
CF01 M2	20	80	1360.6	1150.5	
CF02 M1	10	90	1361.4	1142.0	
Pure CaF <sub>2</sub>	0	100	-	1146.4	



Figure 4.11. Result from DSC/TGA experiments and literature data along with the phase diagram (dotted lines) calculated from the thermodynamic modeling.

The present DSC experimental data for the eutectic temperature are in good agreement with previous studies by Schlegel [67Sch] and Mukerji [65Muk]. The  $\alpha$  to  $\beta$ -CaF<sub>2</sub> transition temperature from the binary CaO-CaF<sub>2</sub> samples (0.8 and 0.9 mole fraction of CaF<sub>2</sub>) is about 1146 ±4 °C, which is the same as that of pure CaF<sub>2</sub>. This means the solubility of CaO does not change the transition temperature of CaF<sub>2</sub>.

4.1.3. Thermodynamic models

4.1.3.1. Stoichiometric compounds

All the pure substance data for solid and liquid CaO and CaF<sub>2</sub> were taken from FactSage database.

## 4.1.3.2. Liquid (molten CaO-CaF<sub>2</sub> solution)

The Modified Quasichemical Model (Pelton *et al.* [00Pel]), which takes into account short-range ordering of second-nearest-neighbor cations or anions in the ionic melt, is used for modeling liquid phase. The following short-range ordering quasichemical reaction is taken into account:

$$(A - A) + (B - B) = 2(A - B) \qquad \Delta g_{AB}$$

In the present study for the CaO-CaF<sub>2</sub> liquid solution, Ca<sup>2+</sup> is common cation in both components of the liquid phase. Thus, actual quasichemical reaction is assuming short-range-ordering of anion species, O<sup>2-</sup> and F<sup>-</sup>. That is, A and B in above equation are O<sup>2-</sup> and F<sup>-</sup>, and (A – B) represents a second-nearest-neighbor pair (O<sup>2-</sup>–F<sup>-</sup>). The Gibbs energies of this reaction  $\Delta g_{AB}$  are the model parameters, which can be expanded as empirical functions of composition. Coordination numbers of the liquid components used in the model are 1.3774 f or O<sup>2-</sup> and 0.6887 for F<sup>-</sup>. As will be discussed below, no parameter was required to reproduce the thermodynamic properties of the liquid solution in the present study.

### 4.1.3.3. Solid solution (CaF<sub>2</sub> solid solution)

Both solid  $\alpha$  and  $\beta$ -CaF<sub>2</sub> have noticeable solubility of CaO. No solubility of CaF<sub>2</sub> in solid CaO was found from EDS analysis. In order to describe the thermodynamic properties of the CaF<sub>2</sub> solid solution, simple thermodynamic model considering the replacement of 2F by O and Vacancy was considered in the present study:  $(Ca^{2+})[F^-, (O^{2-}Va^+)^-]_2$ . Then, the molar Gibbs energy of the CaF<sub>2</sub> solution is modeled as ideal ionic substitutional Henrian solutions by the following expressions:

$$G_{CaF_2}^m = \left(X_A G_A^o + X_B (G_B^o + C_B^o)\right) + 2RT(X_A ln X_A + X_B ln X_B)$$

where A and B are CaF<sub>2</sub> and CaO,  $G_A^o$  and  $G_B^o$  are the Gibbs energies of pure CaF<sub>2</sub> and CaO,  $X_A$  and  $X_B$  are the component mole fractions, and  $C_B^o$  is model parameter.  $C_B^o$  can be considered as the Gibbs energy of transition of pure CaO with the fcc cubic structure to hypothetical pure CaO with  $\alpha$  or  $\beta$ -CaF<sub>2</sub> structure. In order to reproduce the solubility of CaO in CaF<sub>2</sub>,  $C_B^o$  was optimized to be 81.797 kJ mol<sup>-1</sup> for both  $\alpha$  and  $\beta$ -CaF<sub>2</sub> solid solutions.

### 4.1.4. Critical evaluation/optimization

In the present study, all phase diagram data and thermodynamic data were critically reviewed. Then, the present phase diagram experimental data and other reliable experimental data in literature were considered for the thermodynamic modeling of the CaO-CaF<sub>2</sub> system.

The calculated phase diagram of the CaO-CaF<sub>2</sub> system from the optimized model parameters is shown with the experimental data in literature (Fig. 4.12) and with present experimental study (Fig. 4.13). The present liquidus data of CaO are in good agreement with the experimental data by Hsu *et al.* [64Hsu], Kor and Richardson [69aKor], Davies and Wright [70Dav], Hawkins *et al.* [71Haw], Edmunds and Taylor [72Edm], Zhmoidin and Chatterjee [72Zhm], Ries and Schwerdtfeger [80Rie], and Zaitsev and Korolev [89Zai]. The other studies show liquidus of CaO with much lower CaF<sub>2</sub> composition, which might results from evaporation of F and hygroscopic nature of CaO and CaF<sub>2</sub>. These liquidus data with lower CaF<sub>2</sub> liquidus are in general good agreement with the present experimental data except for the data from Bääk [54Baa], based on electrical

resistivity measurements. He found a liquid miscibility gap between 89.2 and 99.3 mol % CaF<sub>2</sub>, which is impossible to be reproduced in thermodynamic modeling.

The solubility of CaO in  $\alpha$  and  $\beta$ -CaF<sub>2</sub> solid solutions were modeled based on the present experimental data. As can be seen in the Fig. 4.12, the maximum solubility of CaO in the CaF<sub>2</sub> is calculated to be about 5 mol % at eutectic temperature. In order to reproduce the transition temperature for  $\alpha$  and  $\beta$ -CaF<sub>2</sub> solid solution, which is the same as pure CaF<sub>2</sub>, and the continuous change in the solubility of CaO in the CaF<sub>2</sub> regardless of its structure, the Henrian excess Gibbs energy model parameter ( $C_B^o$  in equation (2)) was set to be the same value.

The calculated eutectic temperature is 1363 °C, which is in agreement with the present DSC data and previous experimental data in literature.

Fig. 4.14. shows the activity of CaO and CaF<sub>2</sub> in liquid solution. As can be seen in the figure, available activity data of CaO (s) are rather inconsistent with each other. For example, Edmunds and Taylor [72Edm] at 1500 °C reported much lower CaO activities than those of Kor and Richardson [69aKor]. All experiments employed gas equilibration technique. The gas equilibration technique can cause solubility of gas species in liquid CaO-CaF<sub>2</sub> solution, which can change the composition of liquid during the experiments. It is well known that the gas species such as C, CO<sub>2</sub> and S can be significantly dissolved into CaO-rich liquid melt in forms of CaC<sub>2</sub>, CaCO<sub>3</sub> and CaS. One of the evidence of this is the extended liquid region in all these experiments. For example, the liquidus of CaO at 1500 °C by Edmunds and Taylor is at about 0.7 mole fraction of CaF<sub>2</sub> which should be at about 0.75 according to the present study. However, interestingly, most of the activities of CaO in all studies increase linearly with increasing CaO concentration in the liquid, which can be considered as an ideal solution behavior. The calculated activity of the present study is in good agreement with Kor and Richardson [69aKor] and Hsu et al. [64Hsu] considering the possible solubility of gas species in their experimental condition.



Figure 4.12. Calculated phase diagram along with experimental data in literature.



Figure 4.13. Calculated phase diagram with present experimental data.



Figure 4.14. Calculated activities of CaO (s) and CaF<sub>2</sub> (l) with experimental data in literature. Solid lines are calculated activity lines from present thermodynamic modeling.

 $4.2.\ CaO\text{-}Al_2O_3\text{-}CaF_2$ 

4.2.1. Literature review

Since the first experiment on this system by Eitel [41Eit], this ternary system has been studied by many researchers. Liquid miscibility gap was found by Rie and Schwerdtfeger [80Rie] in the CaF<sub>2</sub> rich region close to the Al<sub>2</sub>O<sub>3</sub>-CaF<sub>2</sub> side almost in contact. The system has two ternary compounds; Ca<sub>4</sub>Al<sub>6</sub>O<sub>12</sub>F<sub>2</sub> (Calfidine) and Ca<sub>12</sub>Al<sub>14</sub>O<sub>32</sub>F<sub>2</sub> which were proven by many studies. Rie and Schwerdtfeger [80Rie] studied liquidus isotherm at 1600 °C and the miscibility gap between 1600 °C and 1725 °C. Zhmoidine and Chatterjee [86Zhm] investigated liquidus of CaO and CaO-Al<sub>2</sub>O<sub>3</sub> compounds at 1600 °C and 1800 °C. The isothermal sections of 1600 °C and 1800 °C in two studies are in good agreement each other. Nafziger [73Naf] studied the liquidus of the ternary system but the reliability of the data was suspected as the miscibility gap and one of the ternary compounds (Calfidine) were not found in his work.

Many other researchers have studied the phase diagram of this ternary system using various experimental techniques. The experimental techniques are summarized below.

The experimental data obtained from Eitel [41Eit] by thermal analysis with optical microscopy, and Zhmoidin [69Zhm] by means of conductivity measurement in the temperature range between 1150 °C and 1650 °C. Mitchell and Cameron [71Mit] measured electrical conductivity, Gutt *et al.* [70aGut], Zhmoidin and Chatterjee [71bZhm], Chatterjee and Zhmoidin [72aCha and 72bCha], and Smirnov *et al.* [73Smi] by means of equilibration experiment in a gas-tight capsule with optical microscope and X-ray analysis, [73Naf] used DTA in helium atmosphere, Rie and Schwerdtfeger [80Rie] using quenching experiment with both open and closed capsules with EPMA, Zhmoidin and Chatterjee [86Zhm] by quenching experiment in sealed cells, Zaitsev *et al.* [90aZai] using Knudsen cell and mass spectrometry in a temperature range 1327 to 1557 °C. Also, thermodynamic studies using other's experimental data by Nikitin [70Nik] and Zaitsev *et al.* [90bZai and 91Zai].

The ternary compounds were investigated by several researchers, the Ca<sub>4</sub>Al<sub>6</sub>F<sub>2</sub> O<sub>12</sub> (Calfidine) examined by Leary [62Lea] by optical microscopy and XRD, found that it crystallize in the hexagonal system and melt congruently at 1507 °C, Jacques [63Jac] and Brisi and Rolando [67Bri] determined  $H_{f(298.15 K)}^{o} =$ -7720.7352 *kJ mol*<sup>-1</sup> and  $\Delta H_{f at 1100 °C} = 30.543 kJ mol^{-1}$ , respectively using solution calorimetry. The compound Ca<sub>12</sub>Al<sub>14</sub>F<sub>2</sub>O<sub>32</sub>, was studied by Brisi and Rolando [66Bri], Williams [68Wil], Nafziger [73Naf], and Costa and Ballirano [00Cos] by means of XRD. They found that it has cubic space group *I43d*  structure. Chatterjee and Zhmoidin [72bCha] and Zhmoidin and Chatterjee [86Zhm] determined the melting temperature of the compound as 1577 °C and 1627 °C, respectively.

The critical evaluation and optimization of all available and reliable phase diagrams and thermodynamic data were performed by Jung *et al.* [CRD report #3] to prepare preliminary thermodynamic database for the CaO-Al<sub>2</sub>O<sub>3</sub>-CaF<sub>2</sub> system. The calculated miscibility gap is actually smaller than the experimental data from Rie and Schwerdtfeger [80Rie]. Tendency of liquid vitrification and difficulties of conducting experiment in two liquid phase area at high temperature region can cause such errors. However, the calculation is supported by Zaitsev *et al.* [90bZai] who reported smaller miscibility gap by investigating the liquidus and iso-activity lines.

One of the pseudo binary sections from this ternary,  $CaAl_2O_4-CaF_2$  is presented in Fig. 4.15. Both Gutt *et al.* [70aGut] and Rie and Schwerdtfeger [80Rie] indicated the large miscibility gap located in the range between 48 and 95 mol %. Also, Gutt *et al.* [70aGut] shows almost flat liquidus between  $Ca_4Al_6O_{12}F_2$  (calfidine) and  $CaF_2$  followed by the eutectic temperature at 1472 °C. This is controversial compare with the data from Zaitsev *et al.* [90Zai], who suggested about 100 °C lower eutectic temperature in the same region of the phase diagram. Consequently, the liquid immiscibility is much smaller than those data reported by Gutt *et al.* [70aGut] and Rie and Schwerdtfeger [80Rie]. The experimental data of Zaitsev *et al.* [90Zai] indicating smaller liquid miscibility gap, which is thermodynamically more preferable and reliable with other thermodynamic properties reported in the present study. Therefore, the preliminary thermodynamic modeling by Jung *et al.* [CRD report #3] considered the experimental data of Zaisev *et al.* [90Zai] more reliable data than others.


Figure 4.15. Pseudo binary section of CaAl<sub>2</sub>O<sub>4</sub>-CaF<sub>2</sub>. The lines represent the calculated phase diagram from the preliminary thermodynamic modeling.

## 4.2.2. Results from DSC/TGA experiments

The DSC experiment on pseudo binary section,  $CaAl_2O_4-CaF_2$ , was performed in the present study. Three samples with different compositions were investigated to determine the solidus and liquidus of calfidine compound ( $Ca_4Al_6F_2O_{12}$ ). Overall DSC/TGA profile of one of the samples is presented in Fig. 4.16. The sample was annealed at 1070 °C for four hours before taking three heating and cooling DSC profiles. All samples were measured in three sets of cycles. The first cycle and initial sintering stage were considered to be enough time to form calfidine ( $Ca_4Al_6F_2O_{12}$ ) and  $CaF_2$ . As in the experiments for binary CaO-CaF<sub>2</sub> system, the composition change due to F loss was monitored by TGA. The second and third DSC profiles were used for peak analysis. For example, the third heating and cooling cycles are depicted in Fig. 4.17 to show peak analysis. The solidus temperature, 1355.9 °C was taken from the onset (indicated as a in Fig. 4.17), and the liquidus, 1405.5 °C was taken from peak temperature (indicated as b in Fig. 4.17). The cooling cycle was not used as it often showed super cooling effect.



Figure 4.16. Overall profiles of DSC/TGA experiment for CAF01 M2 sample.



Figure 4.17. The analysis of thermal peaks for the third DSC cycle (CAF01 M2).

All the results from the present DSC analyses in the CaAl<sub>2</sub>O<sub>4</sub>-CaF<sub>2</sub> pseudo binary system are listed in Table 4.4 and presented with the optimized phase diagram in Fig. 4.18.

	Compos	ition				
Sample	(mol 9	%)	Second	cycle (°C)	Third cycle (°C)	
	CaAl <sub>2</sub> O <sub>4</sub>	CaF <sub>2</sub>	Solidus	Liquidus	Solidus	Liquidus
CAF01 M1			1356.1	1402.6	1382.3	-
CAF01 M2	43	57	1384.9	1406.1	1355.9	1405
CAF01 M3			1384	1403	1384.2	1403
CAF02 M1			1383.3	-	1384	-
CAF02 M2	54	46	1384.1	-	1385	-
CAF02 M3			1384.9	-	1385.1	-
CAF03 M1			1369.2	-	1364.3	-
CAF03 M2	48	52	-	1445.3	-	1443.4
CAF03 M3			1383.4	-	1383.3	-
					· fail to de	toot moole

Table 4.4. Solidus and liquidus analyzed in DSC/TGA experiments.

- : fail to detect peaks



# Figure 4.18. Result of DSC/TGA experiments with literature data and calculated phase diagram.

The compositions of final experimental points are different from their starting compositions as F loss was corrected using TG analysis. This DSC/TGA experiments confirmed that the eutectic temperature of the system is about 1380 °C. Liquidus data obtained in the present DSC experiment are also similar to the results of Zaitsev *et al.* [90Zai]. Present experimental data confirmed the calculated phase diagram from the preliminary thermodynamic database.

### 4.2.3. Results from equilibration experiments

The equilibration experiments were performed at 1250 °C to confirm the calculated phase diagram in the present study. The PARC analysis was used to analyze the liquid compositons. As can be seen in Fig. 4.19, a lot of phase separations were observed due to the high fluidity of the melt.





Figure 4.20. The PARC analysis of liquid composition from sample CAF03 C1:(a) BSE image, (b) calculated phase proportion, (c) combined pixels for liquid phase, and (d) combined pixels for exsolved phase.

Fig. 4.20 (b) shows the phase proportion obtained from the PARC analysis. The proportion was calculated based on num ber of pixels which belongs to each phase. Fig. 4.20 (c) and (d) present the filtering boundary area when the composition analysis is applied for each phase.

Three phase assemblage was obtained for CAF03 C1 composition at 1250 °C: CaO, CaF<sub>2(s.s)</sub>, and liquid. For CAF10 C1 sample, three phase assemblage of CaO, Ca<sub>12</sub>Al<sub>14</sub>F<sub>2</sub>O<sub>32</sub>, and Liquid was obtained. The analyzed liquid compositions are listed in Table 4.5 and the experimental data are plotted in Fig. 4.21 along with calculated phase diagram from the preliminary thermodynamic modeling.



Figure 4.21. Calculated isothermal section of the ternary CaO-Al<sub>2</sub>O<sub>3</sub>-CaF<sub>2</sub> system at 1250 °C from the preliminary thermodynamic database along with equilibrium experimental results in the present study.

Sample	Composition (mol %)			Temp.	Time	Phases	Liquid comp. (mol %)		
	С	А	F	(°C)	(h)		С	А	F
CAF03 C1	45	5	50	1250	36	C + F + Liq	32	10	58
CAF10 C1	60	10	30	1250	2	$C + C_{11}A_7F + Liq$	40	11	49
C: CaO, A: $Al_2O_3$ , F: CaF <sub>2</sub>									

Table 4.5. Experimental results for the liquidus of the CaO-Al<sub>2</sub>O<sub>3</sub>-CaF<sub>2</sub> system.

From these two experimental points, a small liquid single phase region can be expected between two liquid compositions as depicted in Fig. 4.21. In comparison with calculated diagram, the remaining liquid region at 1250 °C is slightly shifted toward to higher CaF<sub>2</sub> region. However, in general, the calculated phase diagram can reasonably reproduced the phase equilibria of the CaO-Al<sub>2</sub>O<sub>3</sub>-CaF<sub>2</sub> system.



Figure 4.22. BSE image of the sample CAF10 C1. C<sub>11</sub>A<sub>7</sub>F, CaO, and liquid phases were determined by the EDS analysis.

From the comparison with the present experimental results, it is found that the phase diagrams calculated from the preliminary thermodynamic database are quite reliable. But in the CaO-rich side, there is small margin to improve the database.

4.3. CaO-SiO<sub>2</sub>-CaF<sub>2</sub>

#### 4.3.1. Literature review

Although many experimental studies have been conducted for the CaO-SiO<sub>2</sub>-CaF<sub>2</sub> system, still, there are large discrepancies among the available phase diagrams. The recent experimental phase diagram data from Selin *et al.* [90Sel], Zaitsev *et al.* [93Zai], and Watanabe *et al.* [02Wat] were different from the data reported previously by Mukerji [63Muk and 65Muk], Hillert [70Hil], and Sommerville and

Kay [71Som]. The recent experimental data has smaller liquid homogeneity field, which is more consistent with other thermodynamic property data. Consequently, liquidus isotherms at 1200, 1300, 1350, and 1427 °C from more recent data, Selin *et al.* [90Sel], Zaitsev *et al.* [93Zai], and Watanabe *et al.* [02Wat] were used for the thermodynamic modeling by Jung *et al.* [CRD report #3].

The Fig. 4.23 shows the phase diagrams for CaSiO<sub>3</sub>-CaF<sub>2</sub>, Ca2<sub>s</sub>iO<sub>4</sub>-CaF<sub>2</sub> and Ca<sub>3</sub>SiO<sub>5</sub>-CaF<sub>2</sub> pseudo binary sections calculated from the preliminary thermodynamic database along with experimental data in literature. The experimental data in the pseudo binary CaSiO<sub>3</sub>-CaF<sub>2</sub> system show noticeable discrepancies in terms of liquidus shape. The calculated diagram mainly followed the results from Bääk and Olander [55Baa] and Suito and Gaskell [76Sui]. According to the liquidus shape from Bääk and Olander [55Baa] and Suito and Gaskell [76Sui], the eutectic temperature is lower than the result from Shiraishi and Saito [65Shi] who showed quite different liquidus than the others. The calculated liquidus is also supported by the eutectic temperature measured by Karandéeff [11Kar] who reported the eutectic temperature at 1130 °C, which is similar to the value from Bääk and Olander [55Baa] at 1127 °C. Other pseudo binary sections of Ca<sub>2</sub>SiO<sub>4</sub>-CaF<sub>2</sub> and Ca<sub>3</sub>SiO<sub>5</sub>-CaF<sub>2</sub> were investigated by Mukerji [63Muk], Gutt and Osbone [66Gut and 70bGut], and Suito and Gaskell [76Sui]. Both the liquidus and the eutectic point in each system are well reproduced by the calculated phase diagrams.



(a)



(b)



(c)

Figure 4.23. Calculated phase diagrams for the pseudo binary sections (a) CaSiO<sub>3</sub>-CaF<sub>2</sub>, (b) Ca2<sub>8</sub>iO<sub>4</sub>-CaF<sub>2</sub>, and (c) Ca<sub>3</sub>SiO<sub>5</sub>-CaF<sub>2</sub>.

Three ternary compounds  $Ca_4Si_2O_7F_2$  (Cuspidine),  $Ca_5Si_2O_8F_2$ , and  $Ca_{10}Si_3O_{15}F_2$ were reported. In particular, many researchers investigated the mineral Cuspidine since 1877. Scacchi [77Sca] and Zambonini [10Zam] indentified the cuspidine phase from natural minerals. Smirnova *et al.* [55Smi] found that it crystallizes in the monoclinic *P2*<sub>1</sub>/*c* space group, and Andrews [61And] synthesize it for the first time. Brisi [57Bri] and Gutt and Osbone [66Gut] reported the melting of cuspidine (Ca<sub>4</sub>Si<sub>2</sub>O<sub>7</sub>F<sub>2</sub>) but they are not consistent with the recent results by Watanabe *et al.* [00Wat and 02Wat], and Fukuyama [08Fuk] who determined the congruent melting at 1407 °C.

Jacques [63Jac] investigated the heat of formation at 298 K ( $\Delta H_{f(298.15 K)}^{o}$ ) and suggested the value of -5104.06 ±18.83 kJ mol<sup>-1</sup>. Maruo *et al.* [00Mar] determined the enthalpy change ( $\Delta H$ ) in a temperature range between 831 and

1554 °C, and reported that  $\Delta H_{cuspidine} = 0.382 T - 135 \pm 15 \text{ kJ mol}^{-1}$ . Fukuyama *et al.* [03Fuk and 04Fuk] reported the standard Gibbs energy of formation,  $\Delta G_{f,cuspidine}^{o} = -5198 + 0.825 T (\pm 12) \text{ kJ mol}^{-1} \text{ K}$  by EMF measurement (CaF<sub>2</sub> as a solid electrolyte) in the temperature range from 1040 °C to 1056 °C, and  $\Delta G_{f,cuspidine}^{o} = -5178 + 0.813 T (\pm 19) \text{ kJ mol}^{-1} \text{ K}$  by means of gas transpiration method for the reaction (3CaO·2SiO<sub>2</sub>·CaF<sub>2</sub>(s) + H<sub>2</sub>O(g) = 2(2CaO·SiO<sub>2</sub>)(s) + 2 HF(g)) in the temperature range from 948 °C to 1196 °C. All these thermodynamic data were considered to determine the Gibbs energy of cuspidine phase in the preliminary thermodynamic modeling by Jung *et al.* [CRD Report #3].

The details of experimental techniques for all previous phase diagram experimental studies are summarized below. The investigations for this ternary CaO-SiO<sub>2</sub>-CaF<sub>2</sub> system were conducted by Scacchi [77Sca] and Zambonini [10Zam] using goniometric measurements on natural crystals, Karandéeff [11Kar], Eitel [38aEit and 38bEit] using thermal analysis, Bääk and Olander [55Baa] performed electrical conductivity measurement, Smirnova et al. [55Smi] used X-ray analysis, Brisi [57Bri] using chemical analysis and XRD, Ershova and Ol'shanskii [57Ers] by means of immersion technique, which measures refraction indexes of quenched glasses in oil, Andrews [61And] by means of microradiographic method and XRD, Jacques [63Jac] using solution calorimetry, Mukerji [63Muk and 65Muk] by quenching experiment in closed capsules as well as DTA, Shiraishi and Saito [65Shi] by means of thermal analysis, Gutt and Osbone [66Gut and 68Gut] using DTA in gas-tight crucibles and XRD, Hillert [66Hil] using quenching experiment in sealed capsules, Akaiwa *et al.* [66Aka and 68Aka] by DTA and EPMA, Kojima and Masson [69Koj] by means of cryoscopic method, Sommerville and Kay [71Som] by means of quenching experiment, Suito and Gaskell [76Sui] by measuring depressions of freezing temperatures, Selin et al. [90Sel] using combustion and ion selective methods, spectrophotometry, and X-ray analysis, Zaitsev et al. [92Zai] using Knudsen-effusion method followed by mass-spectrometric analysis, Zaitsev et al. [93Zai] by equilibration experiment in

closed cells with microscopic examination and chemical analysis, Maruo *et al.* [00Mar] used drop calorimetry in a temperature range between 831 and 1554 °C, Watanabe *et al.* [00Wat] by quenching experiment and DTA in closed capsules, Watanabe *et al.* [02Wat] by DTA and quenching experiment in vacuumed silica crucibles followed by XRD and EPMA, Fukuyama *et al.* [03Fuk and 04Fuk] by electromotive force (EMF) measurement and gas transpiration method followed by XRD, Choi *et al.* [04Cho] using quenching experiment followed by XRF and chemical analysis, and Fukuyama [08Fuk] using DTA.

#### 4.3.2. Results from equilibration experiments

The equilibration experiments were performed at 1150, 1200, 1300, and 1350 °C. All equilibration experimental conditions and results are listed in Table 4.6. The experimental results were compared with calculated phase diagrams in Figs. 4.24, 26, and 27.

Sample	Composition (mol %)			Temp. (°C)	Time	Phases	Liquid comp. (mol %)		
	С	S	F	1 ( )	(h)		С	S	F
CSF06 C1	45	40	15	1150	64	CS + Cus + liq	32	40	28
CSF03 C1	10	40	50	$\begin{array}{c} 1500 \text{ (2h)} \rightarrow \\ 1150 \end{array}$	92	S + F + Liq	32	41	27
CSF06 C3	45	40	15	$\begin{array}{c} 1500 \ (1h) \rightarrow \\ 1300 \end{array}$	87	CS + Cus + liq	43	43	14
CSF09 C2	50	30	20	$\begin{array}{c} 1500 \ (1h) \rightarrow \\ 1300 \end{array}$	87	Cus + Liq	45	26	29
CSF10 C1	70	20	10	$\begin{array}{c} 1500 \ (1h) \rightarrow \\ 1300 \end{array}$	87	C + C3S + Liq	47	21	32
CSF02 C1	20	55	25	1150	2	S + F + Liq		-	
CSF02 C2	20	55	25	1200	64	S + F + Liq		-	
CSF01 C1	30	60	10	1150	64	S + CS + Liq		-	

Table 4.6. Experimental results for the liquidus of the CaO-SiO<sub>2</sub>-CaF<sub>2</sub> system.

CSF11 C1	60	20	20	1350	3	C + Liq	-
CSF09 C1	50	30	20	1350	3	Cus + Liq	-
C.	CoO	C . C	SO	E: CoE CS: Co	S: O	$C2S$ , $C_2S$ ; $O$	Cus: Ca Si E O

C: CaO, S: SiO<sub>2</sub>, F: CaF<sub>2</sub>, CS: CaSi<sub>2</sub>O<sub>4</sub>, C3S: Ca<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>, Cus: Ca<sub>4</sub>Si<sub>2</sub>F<sub>2</sub>O<sub>7</sub>

- : The chemical compositions at liquid were not analyzed properly

Fig. 4.24 shows the calculated iso-thermal section of the CaO-SiO<sub>2</sub>-CaF<sub>2</sub> system at 1150 °C along with present experimental results. Although the phase assemblage of two samples, CSF03 C1 and CSF06 C1, are well predicted, the compositions of liquid phase in both samples are quite different from the calculated diagram. Interestingly, the liquid compositions from two samples are almost the same each other, which indicates that the size of liquid single phase region is much smaller than the calculated diagram and the liquid composition should be much low in CaF<sub>2</sub> content. In order to confirm the experimental liquid area, two more samples, CSF01 C1 and CSF02 C1 were prepared. The result of the two samples also confirmed the small liquid single phase region.



Figure 4.24. Calculated isothermal section of the ternary CaO-SiO<sub>2</sub>-CaF<sub>2</sub> system at 1150 °C from the preliminary thermodynamic database along with equilibrium experimental results from the present study.

In order to check the phase assemblage at high  $SiO_2$  region, CSF02 C2 sample was equilibrated at 1200 °C. The equilibrium phases were  $CaF_2 + SiO_2 + Liquid$  (see Fig. 4.25), while the calculation tells that  $SiO_2 + Liquid$  phase equilibrium. Therefore, it seems that the calculated liquid single phase region in  $SiO_2$  rich region is rather wider than reality.



Figure 4.25. BSE image of the sample CSF02 C2 equilibrated at 1200 °C.

The isothermal section of the CaO-SiO<sub>2</sub>-CaF<sub>2</sub> at 1300 °C is calculated in Fig. 4.26 along with present experimental results. The phase assemblages of all three samples are well matched with the calculated phase diagram. However, the compositions of liquid are somewhat different from calculations. For example, the experimental liquidus near to CaSiO<sub>3</sub> is somewhat lower in CaF<sub>2</sub> content than calculated value. In the case of Ca<sub>3</sub>SiO<sub>5</sub> liquidus, the experimental results are slightly richer in CaF<sub>2</sub> than the calculated value.



Figure 4.26. Calculated isothermal section of the ternary CaO-SiO<sub>2</sub>-CaF<sub>2</sub> system at 1300 °C along with present experimental results.

However, the experiments performed at 1350 °C showed somewhat different results than the results at 1300 °C. The experimental results of CSF09 C1 and CSF11 C1 are in good agreement with calculated phase diagram as shown in Fig. 4.27.

In summary, the present experimental results of the CaO-SiO<sub>2</sub>-CaF<sub>2</sub> system show the calculated phase diagram in SiO<sub>2</sub> rich region predicts more wide liquid region than reality. However, the other regions of the phase diagram are well predicted by the preliminary thermodynamic database.



Figure 4.27. Calculated isothermal section of the ternary CaO-SiO<sub>2</sub>-CaF<sub>2</sub> system at 1350 °C along with the present experimental results.



Figure 4.28. BSE images of the samples (a) CSF09 C1 and (b) CSF11 C1 equilibrated at 1350 °C.

#### **Chapter 5. Summary**

This study was aimed to achieve a fundamental understanding of the mould flux systems widely used in the continuous steel casting process. The CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaF<sub>2</sub> system was investigated using a coupled phase diagram experiment and thermodynamic modeling.

The EDS characterization methodology for F content in oxy-fluoride samples was setup by preliminary test analyses for optimum conditions (such as variation of electron voltage (eV) and data acquisition time etc). The results were integrated with PARC analysis (developed by Tata Steel Europe, Ijmuiden, the Netherlands) to perform the chemical composition analysis of oxy-fluoride samples. In order to prevent the F loss during experiments at high temperature, the sealed Pt capsules are used for all equilibration/quenching experiments in the present study. In order to detect the transition temperatures such as solidus, liquidus and solid state phase transformation, DSC/TGA technique was also employed.

For the first time, the solubility of CaO in the  $CaF_2$  solid was determined in the present study. The solubility of CaO reaches up to about 5 mol % at eutectic temperature. The liquidus of CaO and CaF<sub>2</sub>, which showed large contradiction between previous experimental studies, were clearly determined. Based on the present experimental data and the reliable literature data, the thermodynamic modeling of the CaO-CaF<sub>2</sub> system was performed. The optimized model parameters can reproduce all the reliable experimental data.

Key experiments on the ternary CaO-Al<sub>2</sub>O<sub>3</sub>-CaF<sub>2</sub> and the CaO-SiO<sub>2</sub>-CaF<sub>2</sub> systems were also performed. The results were compared with the phase diagram constructed by the preliminary thermodynamic modeling. In the pseudo binary section of CaAl<sub>2</sub>O<sub>4</sub>-CaF<sub>2</sub>, the solidus and liquidus of Ca<sub>4</sub>Al<sub>6</sub>F<sub>2</sub>O<sub>12</sub> were experimentally determined, which can resolve a long time argument on the existence of wide liquid miscibility gap in this system. The experimental results

convey less probability of liquid miscibility gap in the CaAl<sub>2</sub>O<sub>4</sub>-CaF<sub>2</sub> section. The comparison between the key experiments and the modeling pointed out that the database for the CaO-Al<sub>2</sub>O<sub>3</sub>-CaF<sub>2</sub> is quite reliable but just small adjustment for the liquid in CaO-rich side is necessary. For the CaO-SiO<sub>2</sub>-CaF<sub>2</sub> system, the calculated diagram shows a rather large discrepancy with the experimental data in SiO<sub>2</sub>-rich region. However, the calculated phase diagram is in good agreement with present experimental results in other areas of the system. Overall, the accuracy of the preliminary thermodynamic database can be judged to be quite reliable but still needed to be improved for more accurate calculations in future.

The results of the experimental data and the thermodynamic modeling in the present study has already been incorporated with a large thermodynamic database for mould flux, which can be used to understand the mould flux solidification behavior and will be applied for new mould flux design.

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