Coupled experimental and thermodynamic modeling study of the $CaO-CaF_2$ system

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Abstract: A coupled experiment and thermodynamic modeling of the $CaO-CaF_2$ system is conducted. Equilibration experiments using sealed Pt capsules were performed to determine the CaO and CaF_2 liquidii and the solubility of CaO in solid CaF_2. In addition, the eutectic and the α- to β-CaF_2 polymorphic transition were investigated. For the first time, noticeable solubility of CaO in α- and β-CaF_2 solids is observed above 1000 °C. The maximum solubility of CaO in solid CaF_2 is about 5 mol % at the eutectic temperature (about 1363 °C). The discrepancies in the CaO and CaF_2 liquidii among the available experimental data were resolved. A critical evaluation of all available literature experimental data and thermodynamic optimization were conducted to obtain a set of thermodynamic functions which can reproduce all available and reliable experimental phase diagram and thermodynamic data. The results of thermodynamic modeling show that the binary liquid $CaO-CaF_2$ phase is an ideal ionic solution of O^{2-} and F^-. The thermodynamic properties of CaF_2 solid solutions are described using a simple defect solution model. Based on the thermodynamic modeling and the experimental study, it is concluded that the $CaO-CaF_2$ binary is a simple eutectic system with the eutectic reaction L (15.4 mol % CaO) → CaO (pure solid) + CaF_2 (solid solution with 4.9 mol % CaO) at 1363 °C. The α- to β-CaF_2 polymorphic transition is located at 1146 °C and the melting point of CaF_2 at 1420 °C.

Key words: $CaO-CaF_2$ system, phase diagram experiment, thermodynamic modeling.

1. Introduction

Oxy-fluoride systems have been used in various fields such as metallurgy, cement, glass, and refractory industries.[1] Although the $CaO-CaF_2$ system is one of the most fundamental systems, there are still large inconsistencies between available experimental data. One of the reasons is that oxy-fluoride systems form complex reciprocal systems where both cations and anions can mix together in the liquid state. Moreover, the evaporation of fluorine can change the composition of the charge during the experiment and the fluorine-containing liquid can be hardly quenched. In this work, high temperature equilibration experiments were carried out to measure the chemical compositions of coexisting phases by EDS compositional analysis and XRD phase analysis and DSC and TGA were used to determine the eutectic temperatures and phase transitions in CaF_2. Thermodynamic modeling of the binary $CaO-CaF_2$ system has been conducted based on our new experimental data and all available experimental data in literature. As a result, the large inconsistencies in the available experimental data were resolved and noticeable solubility of CaO in both α- and β-CaF_2 solids were observed above 1000 °C for the first time. In the thermodynamic "optimization" of a system, all available thermodynamic and phase-equilibrium data are evaluated simultaneously in order to obtain one set of model equations for the Gibbs energies of all phases as functions of temperature and composition. From these equations, all thermodynamic properties and phase diagrams can be back-calculated. In this way, all the data are rendered self-consistent and consistent with thermodynamic principles.

2. Literature Review

The phase diagram and activity of CaO in the CaO-CaF_2 system have been investigated by many researchers using various experimental techniques. All available experimental data in literature are plotted in Figs. 1 and 2.

As can be seen in Fig. 1, the experimental data for the liquidus of CaO are very scattered, but can be categorized into three groups depending on the liquidus positions. Budnikov and Tresvyatskii[2] reported the liquidus with eutectic composition at about 40 mol % CaF_2. The liquidus of CaO by Mukerji,[3] Schlegel,[4] Zhmoidin,[5] and Isaksson and Öberg[6] are similarly located with eutectic composition at about 60 mol % CaF_2. Other investigations including Davies and Wright,[7] Zhmoidin and Chatterjee,[8] Ries and Schwerdtfeger,[9] determined the liquidus with eutectic composition at about 80~85 mol % CaF_2. It should be also mentioned that indirect measurements of CaO liquidus from gas/slag equilibration for CaO activity (Hsu *et al.*,[10] Kor and Richardson,[11] Hawkins *et al.*,[12] and Edmunds and Taylor[13]) and high temperature mass spectrometry (Zaitsev *et al.*[14]) are also consistent with the liquidus with the eutectic composition at about 80~85 mol % CaF_2.

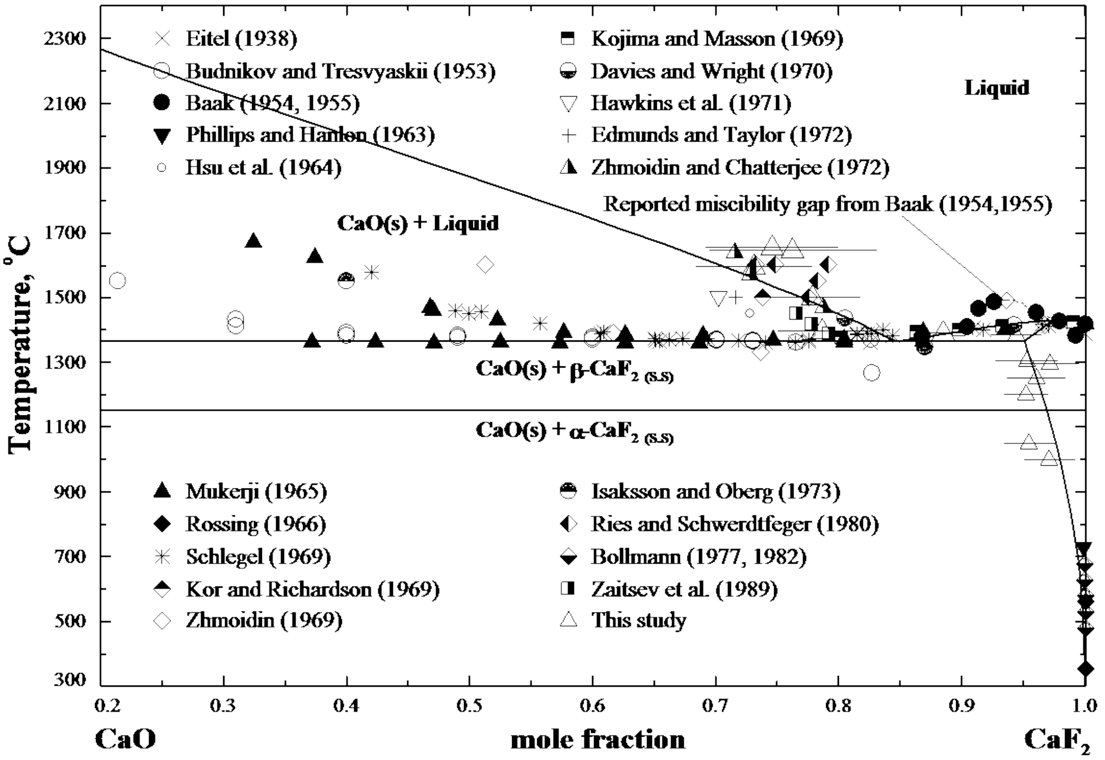


Figure 1. The optimized CaO-CaF_2 phase diagram.

All the experiments to determine the activities of CaO and CaF_2 employed the gas equilibration technique. However, the gas equilibration technique can cause a significant solubility of gas species in liquid CaO-CaF_2 solution, which can change the composition of the liquid during the experiments. This possible solubility of gas species is quite critical to the CaO-CaF_2 system. It is well known that the gas species such as C, CO_2 and S can be significantly dissolved into CaO- or CaF_2-rich liquid solution in the form of CaC_2, $CaCO_3$ and CaS. One of the evidences of this is the extended liquid region in all these experiments. For example, the liquidus of CaO at 1500 °C by Edmunds and Taylor[13] is at about 70 mol % CaF_2, Kor and Richardson[11] at 74 mol % CaF_2, Hawkins *et al.*[12] at 70 mol % CaF_2. Interestingly, however, most of the reported activity curves of CaO in Fig. 2 increase more or less linearly (strictly speaking, slightly exponential behavior) with increasing the CaO concentration in the liquid, which can be considered as an ideal ionic solution behavior of F^- and O^{2-} in the liquid CaO-CaF_2 solution. Kor and Richardson derived the activities of CaF_2 and CaO using the same ionic ideal solution concept which was proven for PbO-PbF_2 solution. However, the unity point of CaO activity (liquidus of CaO) is rather different in each study because the liquid region is varied due to the solubility of CaC_2, $CaCO_3$ or CaS in the liquid.

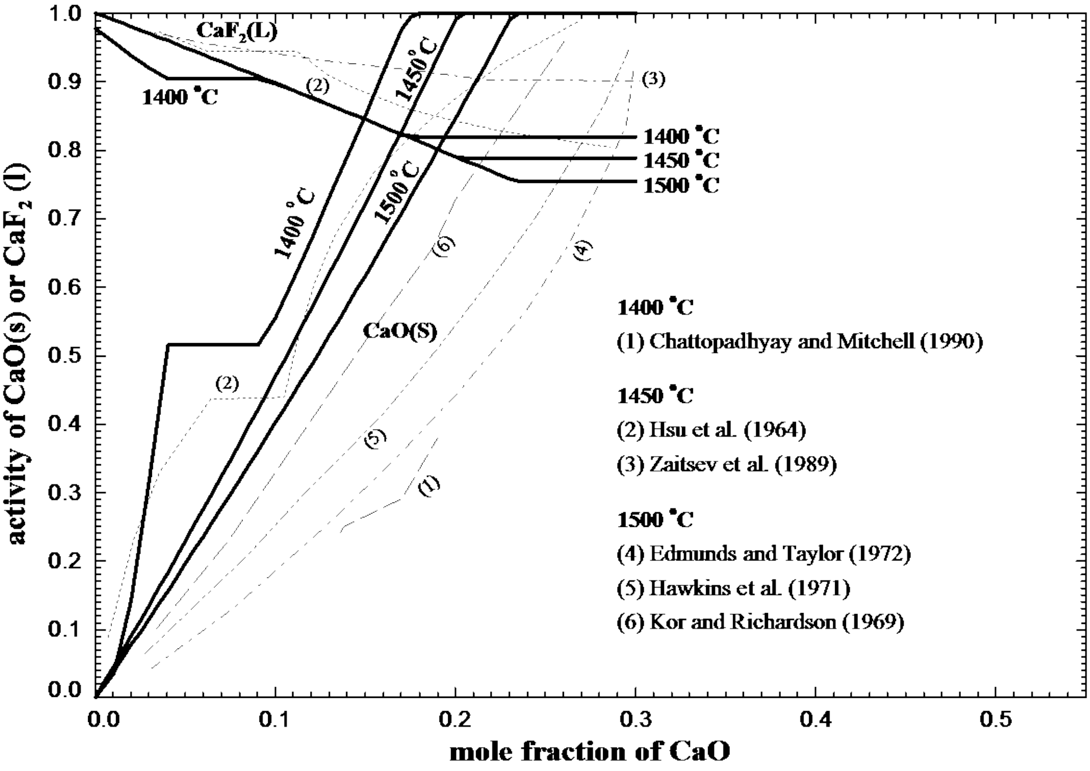


Figure 2. Activities of CaO and CaF_2 at various temperatures in the CaO-CaF_2 system.

The previous experimental attempts to measure the solubility of CaO in CaF_2 were limited below 727 °C and the reported solubility is less than 0.5 mol % (Phillips and Hanlon,[15] Schlegel,[4] Rossing,[16] and Bollmann,[17, 18]) In fact, if the CaO solubility data for α-CaF_2 reported by Bollmann[17, 18] are extrapolated to the β-CaF_2 region in the phase diagram without distinguishing the structural change of CaF_2, the solubility of CaO would be 5.8 mol % at the eutectic temperature (1363 °C). All experimental data for the homogeneity range of CaF_2 solid solution and its liquidus are plotted in Fig. 1.

In the case of the liquidus of CaF_2, Bääk[19, 20] based on electrical resistivity measurements, found a miscibility gap between 90.4 and 99.2 mol % CaF_2, with a consolute temperature of 1485 °C at 92.6 mol % CaF_2 (Fig. 1). On the contrary, Kojima and Masson,[21] Mukerji,[3] Davies and Wright,[7] and Schlegel[4] did not find any evidence of liquid immiscibility in the CaF_2-rich region. According to Zhmoidin and Chatterjee,[8] the presence of non-equilibrium crystalline CaO could mislead the immiscibility by Bääk. In addition, Bääk used graphite crucible to perform their experiments, which might cause a large solubility of CaC_2 (maximum 22 mol % at 1500 °C according to the note by Edmunds and Taylor[13]) and formation of CaC_2 during the experiments, which could subsequently influence the conductivity measurements.

3. Experimental phase diagram determination

3.1. Equilibrium experiments

Reagent grade calcium carbonate ($CaCO_3$, ≥ 98.5 wt. %, Merck, Germany) and calcium fluoride (CaF_2, ≥ 97 wt. %, Merck, Germany) were used for preparing the starting materials. The main impurity in $CaCO_3$ and CaF_2 is moisture. $CaCO_3$ was used instead of CaO due to the hygroscopic behavior of lime. Appropriate proportions of starting materials were carefully weighed, mixed by a mechanical mixer. The calcination of $CaCO_3$ to obtain CaO was conducted just before the experiments and the sample weights were measured before and after calcination to confirm the completion of the reaction. To prevent F loss during high temperature experiments, sealed Pt capsules were used which were checked with an optical microscope before performing the experiments.

A vertical one-atm tube furnace with $MoSi_2$ heating elements (Gero HTRV, Germany) was used for all phase equilibrium experiments. Temperatures were measured using type B thermocouples located at about 10 mm from the sample and independently controlled within ± 5 °C by an automated system which also logged the temperatures during the experiments. For each experiment, several Pt capsules with different bulk compositions along the CaO-CaF_2 binary were placed in a Pt sample holder held by a thin Pt wire. 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 was melted by an electric current, such that the capsules fell into a crucible filled with water in the bottom part of the furnace for rapid quenching.

Phase recognition and composition analysis was conducted with a Field Emission Scanning Electron Microscope (FE-SEM, JEOL JSM 7001F, Japan) equipped with an Energy-dispersive X-ray spectrometer (EDS, Thermo Scientific, USA) system. Based on preliminary analyses,[22] the optimal EDS conditions for compositional analyses of F-containing samples were obtained with an accelerating voltage of 7 kV and a measurement area of about 500 μm^2. All the FE-SEM EDS data were processed with the PARC (PhAse Recognition and Characterization) technique, developed by Corus (Tata Steel Europe, The Netherlands). Details regarding the PARC technique can be found elsewhere.[23] Internal standards embedded with the samples were always used to minimize errors in the quantitative EDS analysis. The standards were wollastonite (O) and calcium fluoride (Ca and F).

3.2. DSC and TGA experiments

Reagent grade calcium oxide (CaO, 99.95 wt. %, Alfa Aesar, USA) and calcium fluoride (CaF_2, 99.95 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 the hygroscopic character of CaO, mixing was performed in isopropyl alcohol to prevent moisture pickup from the 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.

DSC and TGA measurements were performed using a Jupiter STA 449 F3 thermal analyser (NETZSCH Instruments, Germany). Pt-Rh crucibles with lids were used to carry 20 to 40 mg of sample for each run. Temperature and sensitivity calibrations were conducted by using the phase transition temperature and enthalpy of melting of the following reference materials: biphenyl ($C_{12}H_{10}$), benzoic acid ($C_7H_6O_2$), rubidium nitride ($RbNO_3$), potassium perchlorate ($KClO_4$), caesium chloride (CsCl), potassium chromate (K_2CrO_4), barium carbonate ($BaCO_3$), and diopside ($CaMgSi_2O_6$). F loss could not be avoided because the crucibles were not sealed. The composition change resulting from F loss was monitored by TGA in order to track the actual composition of the samples during experiments. The annealing temperature was always set to about 1000 °C to remove the moisture and homogenize the samples with minimum amount of F loss. Two to three heating and cooling cycles were run for each sample to obtain reliable thermal signal results.

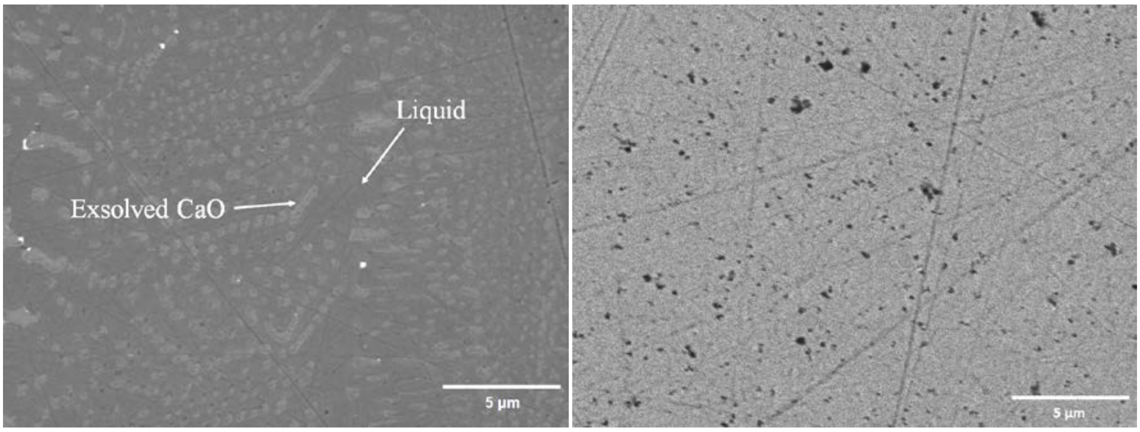
3.3. Experimental phase diagram

All quenched liquid samples show small CaO quench crystals (CaO particles exsolved from liquid during the quenching of the samples). The amount and distribution of exsolved CaO vary according to the equilibration temperature of the charge. The largest amount of exsolved CaO particles is observed and distributed more inhomogeneously at the highest equilibration temperatures for a given composition. Typical microstructures obtained for the CaF_2-rich liquid are shown in Fig. 3(a). Fortunately, the primary crystalline CaO particles in equilibrium with the liquid are typically larger than about 20 μm, which can be easily distinguished from the exsolved CaO particles. Experimental results obtained for the liquidii are shown on the phase diagram of Fig. 1. For the CaO liquidus, the error in liquid composition is relatively large (about 3 to 7 %) due to the inhomogeneous nature of the exsolved CaO particles. Moreover, the initial composition of the samples might be slightly shifted toward the CaO-rich side of the phase diagram due to possible F loss during sample preparation.

A significant amount of sintered pores (holes) in solid CaF_2 can be seen as shown in Fig. 3(b). The microstructures observed in four solid CaF_2 crystals with different thermal histories were compared. In the case of solid CaF_2 equilibrated with liquid, small exsolved CaO particles, which seems to have formed during the quenching process, are present in solid CaF_2. In the sample equilibrated at sub-solidus temperature, no such exsolved CaO particles are visible but a significant amount of sintered pores (holes) in solid CaF_2 can be seen. When the samples are partially melted and subsequently annealed at sub-solidus temperature, the shape of the holes in solid CaF_2 is different from that in the samples equilibrated only at sub-solidus temperature. Moreover, the size of the holes becomes smaller and smaller as the sample is more and more melted. From these observations, it is possible to conclude that the pores observed in solid CaF_2 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, the pores were excluded in the PARC analyses of all sub-solidus samples. Results of these solubility measurements are shown in Fig. 1. The solubility of CaO in solid CaF_2

at sub-solidus temperatures ranges between 2.9 and 5.6 mol % between 1000 and 1390 °C, respectively. One of the samples showed only CaF_2 crystals and no CaO phase, which supports the noticeable solubility of CaO in CaF_2. According to the present experimental data, the maximum solubility of CaO in CaF_2 reaches about 5 mol % at the eutectic temperature, and decreases gradually with decreasing temperature. Furthermore, the change of solubility in CaF_2 seems to be continuous with temperature regardless of the CaF_2 structure (α or β) within the experimental error range.

Temperatures of the CaO-CaF_2 eutectic and the α/β-CaF_2 transition were measured by DSC and TGA. Unfortunately, while equilibration experiments employed sealed Pt capsules to prevent F loss, DSC and TGA experiments used Pt crucibles and lids which did not prevent the F loss. Fortunately, this problem had no impact on the results since the determination of the eutectic and polymorphic transition temperatures are independent of the composition. The results are depicted in the phase diagram of Fig. 1. The eutectic temperature was determined to be 1361 ± 1 °C and the α/β-CaF_2 polymorphic transition was located at 1146 ±6 °C, which is the same as the polymorphic transition temperature of pure CaF_2. The solubility of CaO has therefore no effect on the transition temperature of CaF_2.



(a) (b)

Figure 3. Examples of microstructures from (a): quenched liquid phase and (b): quenched solid CaF_2 phase.

4. Thermodynamic Modeling

4. 1. Thermodynamic model

The Modified Quasichemical Model[24] which takes into account short-range ordering of second-nearest-neighbor cations or anions in the ionic melt, is used for modeling the liquid phase. In the present study, Ca^{2+} is the common cation in both components of the CaO-CaF_2 liquid phase. Thus, the actual quasichemical reaction is assuming short-range-ordering of anion species, O^{2-} and F^-:

$$(\mathrm{A}-\mathrm{A})+(\mathrm{B}-\mathrm{B})=2(\mathrm{A}-\mathrm{B}) \qquad \Delta g_{\mathrm{AB}} \qquad (1)$$

where A and B are O^{2-} and F^-, and (A-B) represents a second-nearest-neighbor pair (A-Ca^{2+}-B). The Gibbs energy of this reaction Δg_{AB} is the model parameter, which can be expanded as an empirical function of composition and temperature. Coordination numbers of the anions used in the model are 1.3774 for O^{2-} and 0.6887 for F^- with respect to the charge difference between the anions. Note that the coordination number of Ca^{2+} is 1.3774. The details of the model can be found elsewhere.[24]

A noticeable solubility of CaO in both α and β-CaF_2 was found in this study while no solubility of CaF_2 in solid CaO was found. In order to describe the thermodynamics of the CaF_2 solid solutions, a simple thermodynamic model considering the replacement of two F^- anions by one O^{2-} anion was employed in the present study. Once two F^- are replaced by one O^{2-}, one of the F^- sites should be replaced by a vacancy (Va), which can be modeled by assuming that two F^- can be replaced by two $(Va^+O2^-)^-$. Then, the molar Gibbs energy of the CaF_2 solution is described as an ideal ionic substitutional Henrian solution:

$$G_{CaF_2} = \left(X_{CaF_2} G^o_{CaF_2} + X_{CaO} G^o_{CaO}\right) + 2RT(X_A \ln X_A + X_B \ln X_B) \qquad (2)$$

$$G^o_{CaO} = G^o_{CaO\,(pure)} + RT\ln \gamma^o_{CaO\ (in\ CaF_2)} \qquad (3)$$

X_i is the mol fraction of i. A and B represents F^- and $(Va^+O^{2-})^-$, respectively. $G^o_{CaF_2}$ and G^o_{CaO} are the Gibbs energies of pure CaF_2 and CaO, respectively, in the CaF_2 structure. The henrian activity coefficient of CaO in the CaF_2 solution, $\gamma^o_{CaO\ (in\ CaF_2)}$, which is the model parameter of the solution, is determined to reproduce the solubility of CaO in the CaF_2 solid solution. No excess Gibbs energy parameters were necessary.

4.2 Thermodynamic modeling results

All the experimental activity data of CaO and CaF_2 are compared with calculated activities from the present model in Fig. 2. In the present study, an ideal ionic solution behavior of F^- and O^{2-} in liquid CaO-CaF_2 solution was assumed. It should be noted that the ideal solution of ionic species F^- and O^{2-} are different from ideal solution of molecular CaO and CaF_2, because CaF_2 can produce two F^- ions. This ideal solution assumption can reproduce the liquidus of CaO of recent experimental studies and our new experimental study without any further complication. Obviously, the calculated activity of CaO increases almost linearly with increasing CaO concentration in the liquid until the CaO saturation.

The liquid CaO-CaF_2 solution shows an ideal ionic solution behavior. Because solid CaO exists as a pure stoichiometric compound, the liquidus of CaO can be easily predicted from the ideal liquid solution. The predicted liquidus of CaO agrees very well this experimental study and those by Kor and Richardson,[11] Davies and Wright,[7] Zhmoidin and Chatterjee,[8] Ries and Schwerdtfeger,[9], Zaitsev *et al.*[14] In the thermodynamic modeling, it was found that the CaO liquidus determined by Budnikov and Tresvyaskii,[2] Mukerji,[3] and Schlegel[4] with rather peculiar liquidus shape (the slope of the liquidus curve becomes less steep with decreasing temperature) can hardly be reproduced with reasonable Gibbs energy of the liquid solution. The eutectic temperature cannot be reproduced with these experimental data. All the experimental data are compared with calculated liquidus from the present model in Fig. 1.

The calculated liquidus of β-CaF_2 solid solution shows a maximum at about 1.5 mol % CaO. Interestingly, the experimental data of Schlegel[4] show this trend, as can be seen in Fig. 1. This is due to the defect structure of the CaF_2

solid solution. More precisely, when very small amount of CaO is added to pure solid CaF_2, the Gibbs energy of the solid CaF_2 solution can be more stable than that of the liquid CaF_2-CaO solution at the same composition because the addition of CaO induces more entropy in solid CaF_2 (one O^{2-} replaces two F^- with generation of a vacancy in the pseudo-anion sites) than in liquid CaF_2 (one O^{2-} replace two F^- without generation of vacancy in the liquid). Therefore, the liquidus of CaF_2 solid solution increases with the CaO content up to a certain value and then naturally decreases. This is a well-known phenomenon for solid solutions with defect formation.[25]

The Henrian activity coefficient, $\gamma^{o}_{\mathrm{CaO\ (in\ CaF_2)}}$ was determined to reproduce the solubility of CaO in solid CaF_2. As there is no discontinuity in the experimental solubility of CaO between α- and β-CaF_2 and the phase transformation temperature for α/β CaF_2 solid solution is the same as pure CaF_2, the same Henrian activity coefficient was assumed for both α- and β-CaF_2 solutions:

$$RT\ln \gamma^{o}_{\mathrm{CaO}} = 81.797 \text{ kJ mol}^{-1} \qquad (5)$$

The calculated maximum solubility of CaO in CaF_2 from this study is about 4.9 mol % at the eutectic temperature.

5. Summary

The classical quenching method was used with sealed Pt capsules to determine the position of the liquidii in the CaO-CaF_2 system and the solubility of CaO in solid CaF_2. The solubility was measured by FE-SEM EDS analysis using the PARC technique. In addition, DSC and TGA experiments were performed to locate the temperatures of the eutectic and the α/β-CaF_2 polymorphic transition. For the first time, noticeable solubility of CaO in both α- and β-CaF_2 solids were observed above 1000 °C. The maximum solubility of CaO is about 5 mol % at 1363 °C, the eutectic temperature, while no solubility of CaF_2 in solid CaO is detected. The α/β-CaF_2 polymorphic transition temperature is located at 1147 ± 5 °C, which is the same temperature as pure CaF_2. The critical evaluation and optimization of all available phase diagram and thermodynamic data was carried out to obtain one set of thermodynamic functions describing the Gibbs energies of all phases in the CaO-CaF_2 system. It is found that the liquid CaO-CaF_2 solution is essentially an ideal solution. The CaF_2 solid solution was modeled with the defect solution model considering the possible vacancy formation with addition of CaO replacing CaF_2. The discrepancies in the available experimental liquidus data of CaO and CaF_2 were resolved by both the thermodynamic modeling and experimental study. The CaO-CaF_2 system can be concluded as a simple binary eutectic system with an eutectic reaction, L (15.4 mol % CaO) → CaO (pure solid) + CaF_2 (solid solution with 4.9 mol % CaO) at 1363 °C.

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References

[1] Hillert, L.H., Effect of alkaline earth fluorides on some oxide of technical importance. Phase relations between the

fluorides of one of the metals calcium, magnesium, strontium, and barium, the corresponding oxide, and one or two of the oxide of silicon, aluminum, and titanium. Acta Polytech. Scand., Chem. Incl. Met. Ser., 1970, No. 90, p 208

[2] Budnikov, P.P. and S.G. Tresvyatskii, Melting-point diagram of the system calcium oxide-calcium fluoride. Dokl. Akad. Nauk SSSR, 1953, 89, p 479-82.

[3] Mukerji, J., Phase equilibrium diagram CaO-CaF_2-$2CaO.SiO_2$. J. Am. Ceram. Soc., 1965, 48(4), p 210-13.

[4] Schlegel, E., System calcium oxide-magnesium oxide-calcium fluoride. Silikattechnik, 1969, 20, p 93-5.

[5] Zhmoidin, G.I., Fusibility of fluorine-containing slags. Izv. Akad. Nauk SSSR, Metal., 1969, p 9-16.

[6] Isaksson, I. and K.E. Oberg, Activity of silicon dioxide in the ternary slag system calcium fluoride-calcium oxide-silicon dioxide at 1550 °C from equilibrium masurements. Scand. J. Met., 1973, 2, p 1-4.

[7] Davies, M.W. and F.A. Wright, Viscosity of calcium fluoride-based slags. Chem. Ind. (London), 1970, p 359-63.

[8] Zhmoidin, G.I. and A.K. Chatterdzhi, Use of a capillary method for determining the liquidus line of a calcium oxide-calcium fluoride system. Zavod. Lab., 1972, 38, p 186-9.

[9] Ries, R. and K. Schwerdtfeger, Contribution to the phase diagram calcium fluoride-calcium oxide-alumina. Arch. Eisenhuettenwes., 1980, 51(4), p 123-9.

[10] Hsu, Y.-S., C. Yuan-Hsi, and L. Fu-Lien, A study of the equilibrium between HF-H_2O gas and slags of the CaO-CaF_2 and CaO-SiO_2-CaF_2 system. Acta Metall. Sin., 1964, 7, p 24-31.

[11] Kor, G.J.W. and F.D. Richardson, Sulfide capacities of basic slags containing calcium fluoride. Trans. Met. Soc. AIME (Amer. Inst. Mining, Met., Petrol. Eng.), 1969, 245, p 319-27.

[12] Hawkins, R.J., S.G. Meherali, and M.W. Davies, Activities, sulfide capacities, and phase equilibriums in calcium fluoride-based slags. J. Iron Steel Inst., London, 1971, 209, p 646-57.

[13] Edmunds, D.M. and J. Taylor, Reaction calcium oxide + carbon = calcium carbide + carbon monoxide. Activity of lime in calcium oxide-aluminum oxide-calcium fluoride. J. Iron Steel Inst., London, 1972, 210, p 280-3.

[14] Zaitsev, A.I., N.V. Korolev, and B.M. Mogutnov, Thermodynamic properties of calcium fluoride-calcium oxide slags. Rasplavy, 1989, p 58-64.

[15] Phillips, W.L., Jr. and J.E. Hanlon, Oxygen penetration into single crystals of calcium fluoride. J. Am. Ceram. Soc., 1963, 46, p 447-9.

[16] Rossing, B.R., Lattice disorder in calcium fluoride. Ph.D. thesis, MIT, 1966, p1-94.

[17] Bollmann, W., Solubility of calcium oxide in calcium fluoride crystals. Krist. Tech., 1977, 12(9), p 941-4.

[18] Bollmann, W., Solubility and distribution coefficient of oxygen in calcium fluoride. Cryst. Res. Technol., 1982, 17, p 107-108.

[19] Baak, T., The system CaO-CaF_2. Acta Chem. Scand., 1954, 8, p 1727.

[20] Baak, T., The electrical conductivity of the system CaO-CaF_2. Acta Chem. Scand., 1955, 9, p 1406.

[21] Kojima, H. and C.R. Masson, Cryoscopic studies with molten fluorides. I. Depression of the freezing point of calcium fluoride by alkaline-earth fluorides and oxide and calcium silicates. Can. J. Chem., 1969, 47, p 4221-8.

[22] Kim, D.-G., Experimental study and thermodynamic modeling of the CaO-SiO_2-Al_2O_3-CaF_2 system. Master's thesis, McGill University, Canada, 2011, p 1-80.

[23] van Hoek, C.J.G., M. de Roo, G. van der Veer, and S.R. van der Laan, A SEM-EDS Study of Cultural Heritage Objects with Interpretation of Constituents and Their Distribution Using PARC Data Analysis. Microscopy and Microanalysis, 2011, FirstView, p 1-5.

[24] Pelton, A.D., S.A. Degterov, G. Eriksson, C. Robelin, and Y. Dessureault, The modified quasichemical model I - binary solutions. Metall. Mater. Trans. B, 2000, 31B, p 651-659.

[25] Pelton, A.D. Solution models. 1997. Academic.