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Solubility of CaS in Molten CaCl₂

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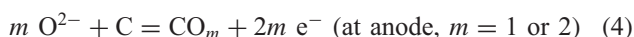
In order to check the solubility of CaS during sulfide reduction in molten CaCl₂, the mixture of CaCl₂ and a small amount of CaS was melted in Ar at the range from 1123 K to 1223 K. The melt was sampled by quartz tube and rapidly solidified. The solidified samples showed a lamella structure with CaS particles, which results in a simple eutectic reaction between CaCl₂ and CaS. Using ICP-AES analysis, the saturation of CaS was found to be completed within 1.8 ks, and $1.77 \pm 0.1 \text{ mol\%CaS}$ at 1173 K was measured as the solubility limit at the initial composition of 3.0 mol%CaS. A tentative phase diagram of CaCl₂–CaS binary system was proposed based on the solubility analysis in these temperatures and eutectic structure. [doi:10.2320/matertrans.MA201803]

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Keywords: solubility, CaCl₂–CaS binary system, molten calcium chloride, sulfur concentration, equilibrium phase diagram

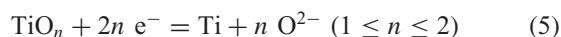
1. Introduction

Molten calcium chloride with addition of small amount of CaO has been often used to prepare pure metallic titanium from its oxides. Using this molten CaCl₂–CaO, the direct reduction from TiO₂ is extensively studied under the proposals such as FFC-Cambridge process¹⁾ and OS process.^{2,3)} For example, when only 3.0 V was applied between a carbon anode and cathodic oxide powder, CaO dissolved in the CaCl₂ melt is electrochemically decomposed to metallic Ca, which can react with TiO₂ at the cathode to form Ti. A sequence of this CaO decomposition and reduction of TiO₂ can be written as,³⁾



The CaCl₂ melt is a curious salt that can dissolve its constituting metal, Ca, in a range as wide as a few mol%,⁴⁻⁸⁾ and also dissolve CaO in a range as wide as 20 mol%.⁹⁻¹³⁾ No other metals and oxides in the halide melts can dissolve to such a high concentration except for the Ca–CaO–CaCl₂ system. This character is applicable for reduction of metallic oxide: Ca deposited from CaO can dissolve in the salt and react with the oxide powder as in eq. (3). The byproduct CaO will be easily and quickly removed from the reaction sites to the melt as in (1). This fast removal of CaO can enhance the oxide reaction, and it is an important key for industrial application, as reported in OS process.^{2,3)}

Chen *et al.* proposed another mechanism as known as FFC-Cambridge process¹⁾ that the oxide at the cathode releases O²⁻ to form the metal via the lower oxides. The oxide ions diffuse out from the oxides to the CaCl₂ melt. In case of titanium oxide, their proposal can be shown as,



Their process looks simple that it converts titanium oxide to metallic titanium directly. As the industrial impact is very large, many researchers have expected their realization.

The oxygen anion both from OS process and FFC process dissolves in the chloride melt and reacts with carbon anode to remove oxygen as CO or CO₂ gas out from the reaction vessel. Therefore, the behavior of oxygen dissolving into CaCl₂ is critical for successive reactions.

The solubility limits of CaO vary depending on solvent and temperature.⁹⁻¹⁴⁾ As a typical condition of oxide reduction, the experiments were often operated in CaCl₂ melt at 1173 K in Ar gas atmosphere. This condition is taken for comparison of solubility. Neumann *et al.* reported 22 mol%CaO⁹⁾ as the solubility limit, while Wenz *et al.* and Perry showed 19¹²⁾ and 20 mol%,¹⁰⁾ respectively. Wang *et al.* reported the largest value, about 26 mol%.¹⁴⁾ Although a large scatter can be found in the previous papers,⁹⁻¹⁵⁾ the solubility of CaO in CaCl₂ melt is much larger than the other combination of solid oxide-chloride melt.¹⁴⁾ Combining this wide solubility of CaO and a strong thermochemical reducibility of Ca in CaCl₂ melt,¹⁶⁾ the by-product CaO from the oxide reduction as shown in eq. (3) can be apart from the reaction site immediately, and promote the reduction toward the right side direction in eq. (3) without any interfere on the successive reduction.¹⁶⁾ The ternary phase equilibrium in Ca–CaO–CaCl₂ region was examined¹⁶⁾ and it is known that the solubility of Ca becomes smaller at the higher concentration range of CaO. This means that the supply of reductant Ca is weaker as the residual CaO increases.^{3,16)}

On the other hand, the oxygen solubility in the solid valve metals such as Ti, V, Nb and Ta is generally very large; for example, 14 mass%O in α -Ti.¹⁷⁾ Titanium metal with such a high oxygen content is very brittle, and the complete removal of oxygen from Ti–O solid solution is required as proposed by Okabe *et al.*^{18,19)}



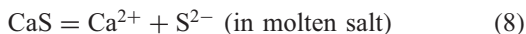
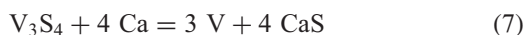
Because the oxygen diffusion in solid metal is relatively slow, the oxygen removal from the obtained metal has been a big issue in direct oxide reduction.

As an approach to avoid the oxygen contamination, the authors proposed a method as a kind of modification of OS process:²⁰⁻²²⁾ Once TiO₂ is converted to TiS₂, and the sulfide is reduced to metallic Ti using CaCl₂–CaS mixed liquid. This idea is inspired that sulfur locates below oxygen in periodic table, and that the chemical properties may be similar.

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However, sulfur has larger atomic radius than oxygen, and it is not easy to dissolve sulfur atoms in the metallic lattice. Therefore, the solubility of sulfur in any metal is generally much smaller than that of oxygen.¹⁷⁾ The authors found that sulfur removal from the Ti and V sulfides occurred more rapidly to form their metals, and that the concentrations of residual sulfur in the obtained metals were very low.^{20–22)}

V₃S₄ is one of the recycled products from the waste of secondary battery. In the example of vanadium metal formation, it was considered that the below-listed reactions are operated simultaneously.²²⁾



The mechanism consisting of these reactions is constructed using the analogy that the behavior of oxygen in CaCl₂–CaO melt is similar with that of sulfur in CaCl₂–CaS. The authors previously observed that solid particles of CaS floated on the top surface of CaCl₂ when 3 mol%CaS was added in the melt,²¹⁾ and they expected the added CaS in CaCl₂ will dissolve like CaO in CaCl₂. The solubility was considered less than 3 mol%CaO²¹⁾ in contrast with 19–26 mol%CaO.^{9–15)} There is no quantitative study on CaS solubility in CaCl₂.

The purpose of this work is to observe the dissolution behavior of CaS in liquid CaCl₂ (melting point is 1053 K²³⁾) when a small amount of CaS is added in CaCl₂, and to determine the saturation values of CaS concentration, i.e., the concentration of liquidus line. This information assists the basic understanding of electrochemical reaction mechanism of sulfides^{20–22)} in CaCl₂ melt.

2. Experimental

2.1 Preparation of the samples for analysis

The apparatus used for this experimental work is illustrated in Fig. 1. High purity of anhydrous CaCl₂ powder (Wako-Chemicals Co., Japan) and CaS (99%, Furuuchi Chemical

Co., Japan) were used. The samples with various composition of CaCl₂–CaS mixture (about 300 g) were filled in a dense and high purity Al₂O₃ crucible, and set in the reaction vessel. The temperature of salt mixture was measured by inserting a thermocouple sheathed in Al₂O₃ protection tube. The vessel made of stainless steel SUS316L was well evacuated and heated to 873 K at the rate of $8.33 \times 10^{-2} \text{ K s}^{-1}$. Then it was well dried for 25.2 ks in vacuum. The environment was replaced by 1 atm of highly purified Ar gas and the crucible was heated to a desired temperature. The holding time was counted after the stabilization of temperature. A part of the melted salt was soaked by a quartz tube (6 mm in outside diameter) and rapidly cooled without water, i.e., by blowing air from the outside of tube. The solidified salt was picked up after breaking the quartz tube.

2.2 Analysis of sulfur concentration

The terminal parts (about 30 mm) of the sample solidified in the quartz tube were cut off, and the central part with homogeneous color (milky white with light pink) was taken as the sample for analysis. The cross-section of the sample was polished without water, and immediately observed by optical microscope. The sample without coating could not be observed in scanning electron microscope (SEM) because of electrostatic charge. The platinum coating and successive SEM observation damaged the sample due to strong hygroscopic property. The optical microscope was useful to observe the sample quickly.

About 100 mg of the sample was dissolved in ethylenediaminetetraacetic acid (EDTA) solution. The EDTA-glycerin method is popular for fixing sulfuric ions in an aqueous solution to analyze hydrogen sulfide concentration in water.^{24–26)} 2 g NaOH, 25 mL glycerin and 0.2 g EDTA.2Na were diluted in 500 g distilled water purified highly. EDTA is active as masking reagent of iron which may act as catalysis of oxidization of S^{2–}.^{24–26)} Basic solution using NaOH was taken to suppress the possible scattering due to H₂S gas evolution from the acidic solution.

The sulfur concentration was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using the standard solutions.²⁶⁾ The emission at 180.7 nm was taken because of the best reproducibility and linearity in the measurable 5 strong peaks. The analytical values of ionic sulfur concentration in aqueous solution, C_{S^{2–}}, was converted to the sulfur concentration in the solidified sample, C_{CaS} using

$$C_{\text{CaS}} = C_{\text{S}^{2-}} \frac{M_{\text{CaS}}}{M_{\text{S}^{2-}}} \frac{V_{\text{solvent}}}{W_{\text{sample}}} \quad (11)$$

where V_{solvent} , W_{sample} , M_{CaS} and $M_{\text{S}^{2-}}$ represent the volume of EDTA solution (500 mL), mass of dissolved salt, molar mass of CaS and S^{2–}, respectively.

3. Results and Discussion

3.1 Dissolution of CaS

Figure 2 shows (a) the appearance of solidified sample and (b) the cross-sectional view of the solidified sample using the optical microscope. Homogeneous white color was observed over the cross sections, as shown in Fig. 2(a), although the

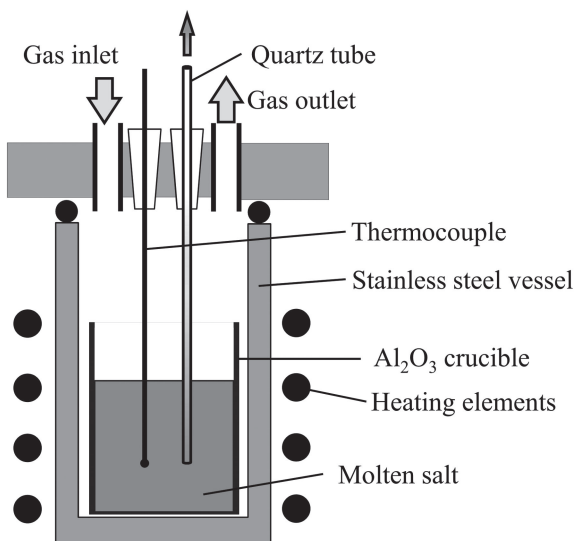


Fig. 1 Schematic diagram of solubility measurement of CaS in molten salt.

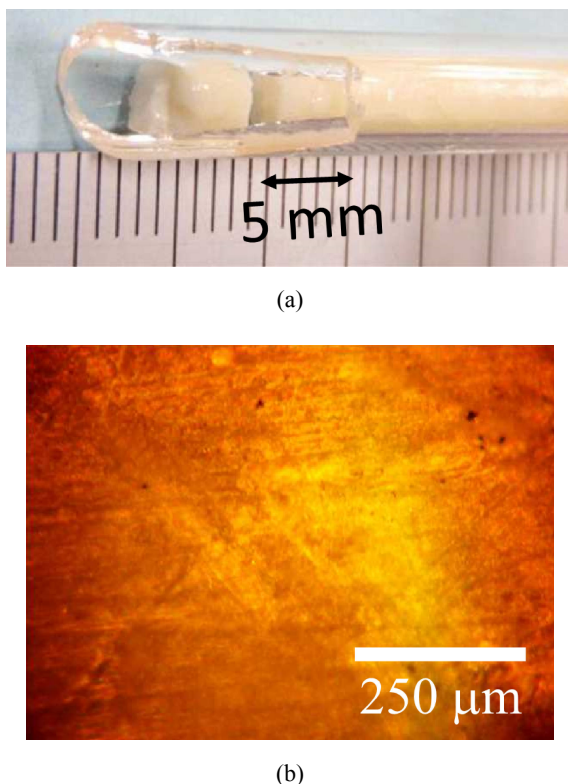


Fig. 2 (a) Photograph and (b) optical microscopic image of sample soaked from CaCl_2 -2.0 mol%CaS melt after melting at 1173 K for 21.6 ks, where the initial concentration was 2.0 mol%CaS.

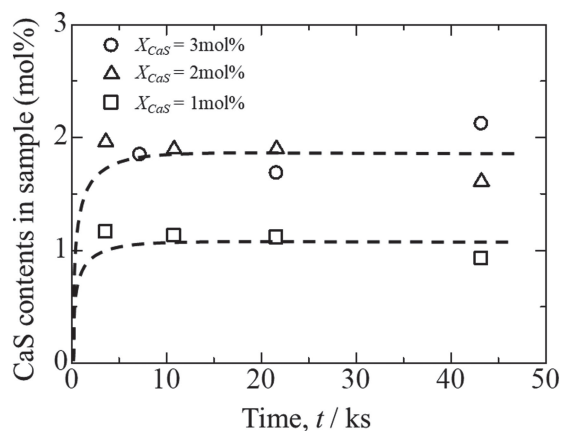


Fig. 3 Time dependency of CaS concentration in the samples quenched from the molten CaS - CaCl_2 at 1173 K. Three initial concentrations, X_{CaS} , were used as the starting compositions.

top surface of the sample was hygroscopic. A white lath-like structure in the microscopic cross-sectional view was often found in addition to the polishing damages, especially in the samples with high concentration of CaS. The matrix shows the characteristic eutectic structure, as shown in Fig. 2(b).

Figure 3 shows the time dependency of CaS concentration in the rapidly solidified sample. The analytical values approached to the constant values within 3.6 ks in the samples that 1 and 2 mol%CaS were initially added. These steady values of CaS concentration are close to the initial values, respectively. In contrast, in the series of 3 mol%CaS, the CaS concentration in the bath did not arrive at the initial concentration (3.0 mol%CaS), and saturated at about 2 mol%.

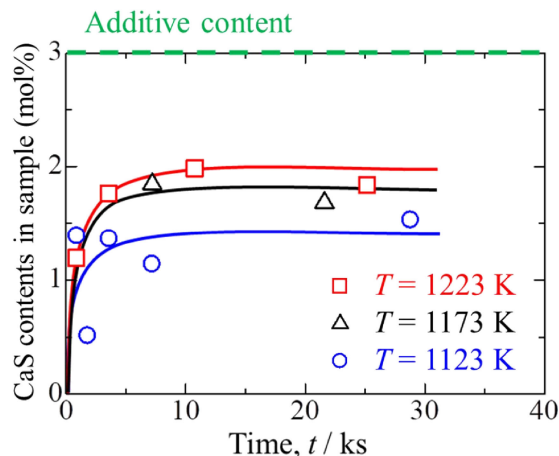


Fig. 4 Time dependency of CaS content in the quenched samples at various temperatures. The initial concentration of CaCl_2 -3 mol%CaS was melted.

In the sampling on CaS analysis, if the undissolved CaS particles were picked up in the soaked samples homogeneously, the measured value should be constant at 3.0 mol%. However, the analyzed value (2.0 mol%) was lower than the initial concentration. This means that the undissolved CaS does not affect the bulk concentration when the initial concentration exceeds a saturation value. The maximum concentration of CaS dissolution could be reproducibly measured at 3.0 mol% when the equilibrium was achieved at 1173 K. Therefore, the solubility of CaS in CaCl_2 melt at 1173 K was concluded as 1.77 ± 0.1 mol% by considering a strong weight on the concentration analysis at 3.0 mol%.

In order to examine the solubility at 1123 and 1223 K, the concentration of the quenched samples was analyzed only at 3.0 mol%CaS (initial), assuming that the solid CaS coexisted in equilibrium with the saturated melt at this concentration. Figure 4 shows the time dependency of analyzed concentration of the samples quenched from various temperatures using CaCl_2 -3.0 mol%CaS mixture. The concentrations approached to a certain value at any conditions within a short time.

3.2 Side reactions

Figure 5 shows the appearance of quenched samples from 1223 K. The inner parts of solidified samples were homogeneously white solid, but turned gray at the longer holding time. The sample quenched after holding for 25.2 ks was analyzed by X-ray diffraction (XRD). CaCl_2 and CaS were detected and the dissolution of Al_2O_3 crucibles and SiO_2 tubes was not found, and any phases containing Al and Si were not detected in the solidified salt by XRD. It is noted that the excess amount of CaS did not form the other compounds such as CaSO_4 , but that it remained as CaS.

A small amount of FeO existed mainly at the gray area. The reason of FeO existence may be related with a higher partial pressure of CaCl_2 at a higher temperature. CaCl_2 melt hardly reacts with water or iron oxides, but its gas can react with the stainless steel vessel. The equilibrium vapor pressure of CaCl_2 is evaluated as 0.25 Pa and 0.79 Pa at 1173 K and 1223 K, respectively.²³⁾ The higher vapor pressure of CaCl_2 may cause the side reactions more significantly at 1223 K.

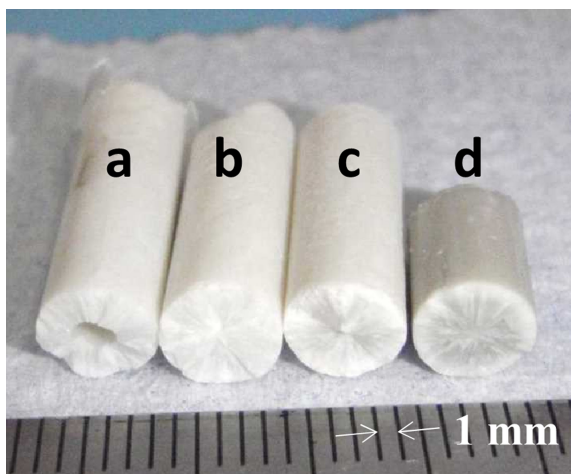


Fig. 5 Photograph of samples extracted from CaCl₂-3.0 mol%CaS melt at 1223 K. Holding time are (a) 1.8 ks, (b) 3.6 ks, (c) 10.8 ks and (d) 25.2 ks.

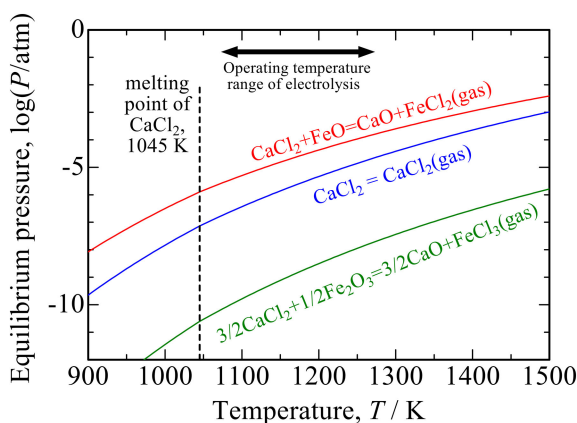
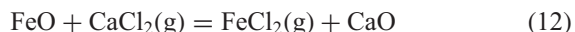


Fig. 6 Equilibrium vapor pressure of CaCl₂ gas under coexisting with liquid CaCl₂. Vapor pressures of iron chlorides gas were evaluated under the same equilibrium, considering that iron oxides react CaCl₂ gas and produce FeCl₂ or FeCl₃.

For example, the evaporated CaCl₂ may react on the stainless steel wall as,



The other reactions can be considered, but iron, the main component of stainless steel, was taken for simplification. The valence change of iron was not considered in the above-listed reactions. Equilibrium partial pressures of gaseous FeCl₂, CaCl₂ and FeCl₃ were evaluated²³⁾ as shown in Fig. 6. It was assumed that the other substances are pure and hold a unit thermochemical activity. Namely it is expected that gaseous FeCl₂ could be generated during the equilibrium experiments. Because the sampling of molten salt might contaminate the Ar gas environment by partial opening to air, faint amounts of water and oxygen were introduced into the reaction vessel, and they oxidized FeCl₂ gas to form FeO, which dropped on the top surface of melt.

When the melt contained these impurities, the mass of solid sample for ICP analysis was measured heavier than the true value. This error increases W_{sample} in eq. (11), and the solubility is evaluated a little smaller than true value. Therefore, the analyzed concentration for 10.8 ks was taken

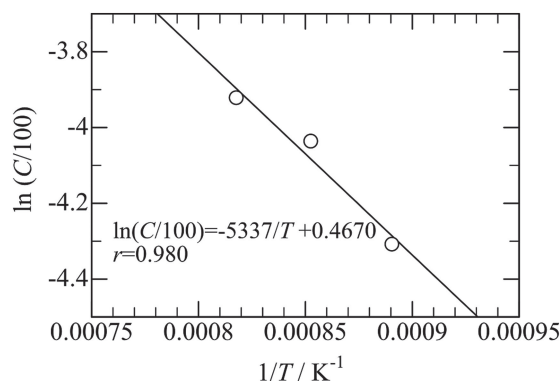


Fig. 7 Arrhenius-type plot of CaS concentration (C in mol%) with inversed temperature ($1/T$).

as the saturation value at 1223 K, where the contribution of FeO did not affect the solubility of CaS significantly.

3.3 Temperature dependency

The solubility of CaS increased slightly as the holding temperature increased. Figure 7 shows the temperature dependency of solubility. The solubility, C , was approximated by Arrhenius type dependency as^{14,15)}

$$C = C_0 \exp(-E/RT) \quad (14)$$

where T and E are temperature and apparent activation energy, respectively. When C is expressed as the molar fraction ($0 < C < 1$),

$$\ln C = 0.4670 - 5337/T \quad (15)$$

Of course, the solubility of CaS is related with the liquidus line in the binary phase diagram, where the balance between partial free energy of CaS and that of CaCl₂ plays a main role. Therefore, eq. (15) shows only an experimental approximation in this system.

Using the solubility of CaS, the liquidus line of CaS and the simple phase diagram were estimated. When all CaS added initially could dissolve in the melt, its region should be in a single phase of liquid in the binary phase diagram. By increasing the CaS content in the bath, however, the saturation was achieved. When the excess amount of CaS precipitates or the undissolved CaS remains, such conditions should be called as two-phase region of solid CaS and liquid.

Figure 8 illustrates the phase diagram using the melting point of CaCl₂ and the solubility limits of CaS, in addition to the experimental conditions. Because the eutectic solidification was observed and no other compounds were found, the simple eutectic melting is expected. The eutectic temperature was not studied here, but it should be lower than the melting point of CaCl₂. Figure 8 was thus drawn.

The liquidus of CaS in CaS-CaCl₂ system locates closer to CaCl₂ than that of CaO in CaO-CaCl₂ system.⁹⁻¹⁵⁾ Namely, the solubility of CaS is much smaller than that of CaO (nearly 20 mol%CaO at 1173 K⁹⁻¹⁵⁾). It is known that a compound CaO_xCl_y exists in CaCl₂-CaO binary system,^{9,11)} and that it affects the liquidus of CaO. However, a stable compound in CaCl₂-CaS system was not found in this work, and a simple eutectic reaction as shown in Fig. 8 does not contribute to expand CaS solubility to a wider range. It is clear from the

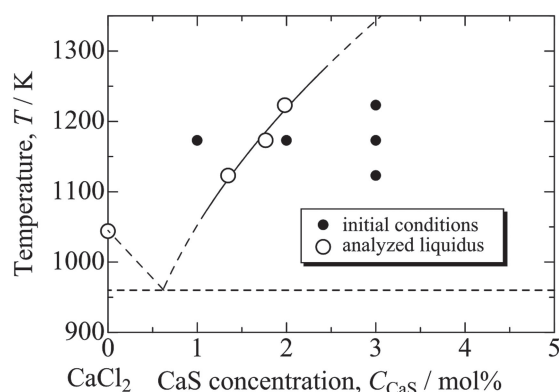


Fig. 8 Phase diagram of CaCl_2 - CaS system estimated by CaS solubility in CaCl_2 . Closed and open circles show the initial conditions and the analyzed liquidus position, respectively.

physical view that the different solubility is due to the differences of ionic radius of oxygen and sulfur, and of interaction force among oxygen, sulfur and CaCl_2 . A detailed quantitative study is expected in future.

A relatively large solubility of CaS in CaCl_2 melt supports the proposed mechanism in our previous reports that the dissolved CaS decomposes electrochemically to form Ca in CaCl_2 melt. The equilibrium solubility of CaS can predict the maximum soluble amount of CaS in the reaction crucible, which is helpful to assess the applicability of OS process of the sulfides.

4. Conclusion

The solubility of CaS in CaCl_2 melt was measured experimentally in order to confirm the solution mechanism of CaS as an important reaction in the cycle of proposed reduction. By soaking the melt into the silica tube and rapid cooling, the solubility was analyzed by ICP-AES method. When 3 mol% CaS was added to CaCl_2 , a constant solubility of 1.77 ± 0.1 mol% CaS was measured after 3.6 ks holding at 1173 K. Within a short period of 0.9 ks, the soluble CaS arrived to the saturation value. This confirms that the byproduct CaS in the sulfide reduction quickly dissolves in the CaCl_2 - CaS melt and diffuses to the bulk.

Using temperature dependency of the maximum solubility of CaS and structural analysis of solidified salt, a binary phase diagram of CaCl_2 - CaS system was sketched as shown in Fig. 8.

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REFERENCES

- 1) G.Z. Chen, T.W. Farthing and D.J. Fray: *Nature* **407** (2000) 361–364.
- 2) K. Ono and R.O. Suzuki: *JOM* **54**(2) (2002) 59–61.
- 3) R.O. Suzuki, K. Teranuma and K. Ono: *Metall. Mater. Trans. B* **34** (2003) 287–295.
- 4) R.A. Sharma: *J. Phys. Chem.* **74** (1970) 3896–3900.
- 5) V. Dosaj, C. Aksaranan and D.R. Morris: *J. Chem. Soc., Faraday Trans. 71* (1975) 1083–1098.
- 6) L.-I. Staffansson and D. Sichen: *Scand. J. Metall.* **21** (1992) 165–171.
- 7) A.S. Dworkin, H.R. Bronstein and M.A. Bredrig: *Discuss. Faraday Soc.* **32** (1961) 188.
- 8) S. Shaw and R. Watson: *ECS Trans.* **16**(49) (2009) 301–308.
- 9) B. Neumann, C. Kröger and H. Jüttner: *Z. Elektrochem.* **41** (1935) 725–736.
- 10) G.S. Perry and L.G. MacDonald: *J. Nucl. Mater.* **130** (1985) 234–241.
- 11) W.D. Threadgill: *J. Electrochem. Soc.* **112** (1965) 632–633.
- 12) D.A. Wenz, I. Johnson and R.D. Wolson: *J. Chem. Eng. Data* **14** (1969) 250–252.
- 13) V. Dosaj, C. Aksaranan and D.R. Morris: *J. Chem. Soc., Faraday Trans. 71* (1975) 1083–1098.
- 14) S. Wang, F. Zhang, Z. Liu and L. Zhang: *Thermochim. Acta* **470** (2008) 105–107.
- 15) V.L. Cherginets and T. Rebrova: *Thermochim. Acta* **654** (2017) 51–53.
- 16) R.O. Suzuki and S. Inoue: *Metall. Mater. Trans. B* **34** (2003) 277–286.
- 17) H. Okamoto: *Desk Handbook, Phase Diagrams for Binary Alloys*, (ASM International, Materials Park, OH, USA, 2000).
- 18) T.H. Okabe, R.O. Suzuki, T. Oishi and K. Ono: *Mater. Trans. JIM* **32** (1991) 485–488.
- 19) T.H. Okabe, M. Nakamura, T. Oishi and K. Ono: *Metall. Trans. B* **24** (1993) 449–455.
- 20) N. Suzuki, M. Tanaka, H. Noguchi, S. Natsui, T. Kikuchi and R.O. Suzuki: *ECS Trans.* **75**(15) (2016) 507–515.
- 21) N. Suzuki, M. Tanaka, H. Noguchi, S. Natsui, T. Kikuchi and R.O. Suzuki: *Mater. Trans.* **58** (2017) 367–370.
- 22) T. Matsuzaki, S. Natsui, T. Kikuchi and R.O. Suzuki: *Mater. Trans.* **58** (2017) 371–376.
- 23) A. Roine and P. Kobaylin: *HSC Chemistry*, ver. 8.0.8, (Outotec Research Center, Poli, Finland, 2014).
- 24) R.A. Day, *et al.*: *Quantitative Analytical Chemistry*, Revised Ed., (Fubaikan, Tokyo, 1999) (in Japanese).
- 25) M. Yano: *Research Report at Hyogo Prefectural Institute for Healthy Life Science*, (Hyogo, Japan, 2002) (in Japanese).
- 26) Japan Industrial Standard, JIS K0108 9.1.2.7, Methylene blue absorption method—Standard solution of sulfide ion, (Tokyo, Japan, 2010).