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Solubility of CaS in CaCl₂–LiCl Eutectic Melt

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Solubility of CaS in molten CaCl₂–65 mol% LiCl eutectic salt was examined by sampling of CaS saturated salt and ICP analysis. The handling in dried environment and an adequate mass of melt were applied for reliable measurements, in addition to suppression of inclusion of CaS particles. The solubility limit was found to be 0.22 ± 0.05, and 0.31 ± 0.05 mol%CaS at 873 K and 973 K, respectively. This saturation value was less than 1.77 ± 0.1 mol%CaS in pure CaCl₂ at 1173 K. [doi:10.2320/matertrans.MA201809]

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1. Introduction

Molten calcium chloride containing a small amount of CaO or CaS is useful media to produce pure metals from its oxides or sulfides, respectively.1–15 Many authors have studied the reduction of various oxides using CaCl₂–CaO. Similarly using molten CaCl₂–CaS, the reduction of sulfide5–15 can be expected under the concepts known as FFC-Cambridge process1) and OS process,2–4 although the reports on sulfide reduction are not so many at present. The reduction of Cu₂S,5,6,8 CuFeS₂,2,8,9 W₂S₃,9,10 and MoS₂11,12 was electrochemically studied considering FFC-mechanism, namely, the decomposition of these sulfides, MSₙ, in the molten chloride melt, RCl, such as CaCl₂ and the successive ionic diffusion of sulfur between two electrodes (R = alkali or alkaline metal originated from salt, M = metal from sulfide). However the formation of RSₙ and R₂MSₙ phases was often reported in these studies as intermediate phase during reduction.6–9,12 This strongly suggests a contribution of R as the reductant in the melt. The authors examined the molten salt electrolysis of TiS₂13,14 and V₂S₄15 under the concept of calciothermic reduction as based on OS process. For example, when 3.0 V was applied between a carbon anode and the sulfide powder in the cathode basket, CaS dissolved in the CaCl₂ melt is electrochemically decomposed to metallic Ca (≡ R), and it reacts with metallic sulfide such as TiS₂ at the cathode to form its metal such as Ti. These reactions can be written as,

\[
\text{CaS} = \text{Ca}^{2+} + \text{S}^{2-} \quad \text{(in the melt)} \quad \text{(in the melt)} \quad (1)
\]

\[
\text{Ca}^{2+} + 2e^- = \text{Ca} \quad \text{(at cathode)} \quad \text{(in the melt)} \quad (2)
\]

\[
\text{Ca} \quad \text{(at cathode)} = \text{Ca} \quad \text{(in the melt)} \quad (3)
\]

\[
2 \text{Ca} \quad \text{(in the melt)} + \text{TiS}_2 \quad \text{(inside the cathodic basket)} = \text{Ti} \quad \text{(inside the cathodic basket)} \quad + 2 \text{CaS} \quad \text{(on Ti particle)} \quad \text{(4)}
\]

\[
\text{S}^{2-} \quad \text{(anode)} = 1/2 \quad \text{S}_2(g) + 2 \quad e^- \quad \text{(5)}
\]

The key of these reactions is that CaCl₂ melt dissolves both the reductant Ca6–20 and the byproduct CaS.21 This feature is suitable for reduction of metallic sulfide: Ca electrochemically deposited at the cathode surface from Ca₂⁺ as shown in eq. (2), and dissolves into the salt as shown in eq. (3). Then it reacts with the sulfide powder as in eq. (4). The byproduct CaS is quickly removed from the reaction sites to the melt as given in (1). This fast removal of CaS from the sulfide surface can enhance the sulfide reduction because the unreacted Ti sulfide in the original particles is freshly exposed to the Ca-containing melt. The fast supply of Ca to the reaction front is another important key for industrial application, as reported in OS process.2–4

Another mechanism, FFC-Cambridge process,1) requires ionization of sulfide and S²⁻ dissolution because the sulfide at the cathode should release S²⁻ to form the metal6–12 via the lower sulfides,7,12 and that S²⁻ diffuses out from the sulfides to the CaCl₂ melt. If we apply this mechanism to titanium sulfide, their proposal can be written as,

\[
\text{TiS}_2 + 2n \quad e^- = \text{Ti} + n \quad \text{S}^{2-} \quad (1 \leq n \leq 2) \quad (6)
\]

In both mechanisms, S²⁻ should dissolve into the CaCl₂ melt and react with carbon anode to remove sulfur as S₂5–15 (or CS₂,5,13) gas from the reaction vessel. Therefore, the dissolution of S²⁻ (eq. (1) or eq. (6)) and anodic behavior as shown in eq. (5) are critical for the sulfide reduction.

Oxygen solubility in the solid metals such as Ti, V, Nb and Ta (so-called valve metals) is very large; for example, 14 mass%O in α-Ti.22) Ti metal containing such a high oxygen content is very brittle, and the complete removal of oxygen from Ti–O solid solution is required for production of the reliable structural metal. Because the oxygen diffusion in solid metal is slow, the oxygen removal from the obtained metal was a big issue in direct oxide reduction.2–4

Especially in order to avoid the oxygen contamination as a solid solution of oxygen, the authors proposed the sulfide reduction in the molten CaCl₂–CaS.13–15 The solid solubility of sulfur in any metal is generally much smaller than that of oxygen.21 It is expected that the concentration of residual sulfur in the metals reduced from their sulfides is very low.13–15 For example, our previous study on vanadium sulfide reduction examined V₂S₄ as a starting material.15 Using CaCl₂–CaS, a very low concentration of residual sulfur such as 210 ppm sulfur could be achieved starting from 45.6 mass%S in V₂S₄.15 For material balance and electric neutrality in the melt, the effect of CaS should be examined more precisely. The dissolution rate and solubility of S²⁻ in the CaCl₂ melt are needed to design an industrial application.

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The authors previously observed that solid particles of CaS floated on the top surface of CaCl₂ when 3 mol% CaS was added to pure CaCl₂ melt at 1173 K. Successive study showed the solubility of CaS to CaCl₂ melt was only 1.77 ± 0.1 mol%CaS in contrast with 20 mol%CaO. This small solubility of S²⁻, however, seems enough to remove S²⁻ electrochemically from the sulfides. The operating temperature was normally set as high as 1148 K. The working at the lower temperature is desired for energy saving. As shown in Fig. 1, the eutectic temperature of 758 K is one of the targets. The electrochemical stability of LiCl is stronger than CaCl₂ and it is expected that LiCl does not decompose prior to CaCl₂ at the electrode voltage as low as 3.0 V. Ca is more favorable than Li as the reductant because of stronger stability of Ca even in sulfide systems. Additionally both CaCl₂ and LiCl can dissolve O₂⁻ in the melt, which may be favorable for possible contamination due to oxygen. The studied conditions are illustrated in the phase diagram of CaCl₂–65 mol%LiCl binary system and of pure CaCl₂ and LiCl binary system is one of the targets. The electrochemical stability of LiCl is stronger than CaCl₂ and it is expected that LiCl does not decompose prior to CaCl₂ at the electrode voltage as low as 3.0 V. Ca is more favorable than Li as the reductant because of stronger stability of Ca even in sulfide systems. Additionally both CaCl₂ and LiCl can dissolve O₂⁻ in the melt, which may be favorable for possible contamination due to oxygen.

The purpose of this work is to observe the dissolution behavior of CaS in liquid mixture of CaCl₂ and LiCl when a small amount of CaS is added in the melt. The saturation value of CaS is determined at 923 K using the molten CaCl₂–65 mol%LiCl. (The salt having this composition is hereafter called as eutectic salt.) This information assists the basic understanding of electrochemical reaction mechanism of sulfides at the low temperature electrolysis using CaCl₂–LiCl based molten salt.

2. Experimental

2.1 Preparation of the samples for analysis

The apparatus used for this experimental work was the same as that in the previous report and the experimental procedure was also similar with the previous one. High purity of anhydrous CaCl₂ and LiCl powders (Wako-Chemicals Co., Japan), and CaS (99%, Furushchi Chemical Co., Japan) were used. The samples with various composition of CaCl₂–65 mol%LiCl–X mol%CaS mixture (about 150 g or 300 g, X = 0.2–1.5) were filled in an Al₂O₃ crucible (90 mm ID, 100 mm OD and 200 mm tall), and set in the reaction vessel. The temperature of molten salt was measured with imnerted stirring by inserting a K-type thermocouple. The stainless steel vessel was evacuated and heated to 723 K. The sample was well dried for 25.2 ks in vacuum. The environment was replaced by 1 atm of Ar gas, and the crucible was heated to a desired temperature. The holding time was started to count after temperature stabilization. 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 of the sample solidified in the quartz tube were cut off, and the central part was taken as the sample for analysis. The cross-section of the sample was polished without water, and immediately observed by optical microscope. X-ray diffraction analysis and observation by scanning electron microscopy were failed due to strong hygroscopic nature in the open environment.

About 100 mg of the sample was dissolved in ethylenediaminetetraacetic acid (EDTA) solution (0.2 g EDTA, 25 mL glycerin and 2 g NaOH were dissolved in 500 mL H₂O) for fixing sulfuric ions in water. The sulfur concentration was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) as reported previously. The analytical values of ionic sulfur concentration in aqueous solution, C₅⁻ (g/mL), was converted to the sulfur concentration in the solidified sample, C₅⁻ in (mass ratio) using

\[
C_{CaS} = C_{S^2^-} \frac{M_{CaS}}{M_{S^2^-}} \frac{V_{solvent}}{M_{solvent}}
\]

where \(V_{solvent}, W_{sample}, M_{CaS} \) and \(M_{S^2^-} \) represent the volume of EDTA solution (mL), mass of dissolved salt (g), molar mass of CaS and S²⁻ (g/mol), respectively. The obtained C₅⁻ was then converted in molar % in the salt.

3. Results and Discussion

3.1 Dissolution of CaS

When the excess amount of CaS was added to the melt over the saturation limit, the residual CaS particles precipitated and floated to the top surface of melt due to density difference. The position for sampling by the quarts tube was carefully selected not to include these CaS precipitates, and all the sampling was done from a supernatant melt through a clean surface area.

Figure 2 shows the samples solidified rapidly from the melt of CaCl₂–65 mol%LiCl–0.2 mol%CaS and 0.5 mol%CaS, respectively, after holding at 923 K for 21.6 ks. Figure 2(a) shows the appearance of solidified sample in the quartz tubes, and (b) the cross-sectional view of the sample using the optical microscope. Homogeneous reddish color
was observed over the cross sections, as shown in Fig. 2(b), although the top surface of the sample was hygroscopic. The lamellar structure was often found pale red in addition to the larger red particles, especially in the samples with higher concentration of CaS. Because CaS used in this study is red and consists of fine grains, the matrix of solidified samples contained a lot of red CaS. A fairly large amount of CaS did not dissolve in the melt and existed as the red particles as a kind of suspension, when 1.0 mol% CaS was examined. When too much amount of CaS was added, the residual undissolved particles were picked up in the quartz tube. The terminal parts of solidified sample (about 10 mm) were cut off for analysis, but significant disturbance was found in ICP analysis when these particles were included. The sample soaked from the melt of CaCl$_2$–65 mol% LiCl–0.5 mol% CaS were white in the whole body and did not show any red spot, as shown in Fig. 2. Therefore, most of experiments used a certain concentration of CaS lower than 0.5 mol% CaS.

3.2 Scattering of analyzed values

Figure 4 shows the time dependency of analytical concentration of sulfur in the samples quenched from CaCl$_2$–65 mol% LiCl–0.2 mol% CaS. The data scatter was well suppressed at 923 K. The amount of dissolved CaS approached to 0.20 ± 0.05 mol%, which agrees with the added CaS concentration. At 873 K, lower by 50 K, however, the analytical value was equivalent with the added CaS concentration, or sometimes it exceeded over the added value. Although the saturation at 873 K approached to 0.27 ± 0.10 mol%, it can not be taken as an equilibrium value. Because the solubility at the lower temperature may be very small in eutectic salt, and the analysis becomes the more sensitive against small deviations. Any slight experimental errors may disturb reliable measurement. One of the significant reasons is inhomogeneous distribution of S$^{2-}$ in the melt because of slow diffusion at the lower temperature. The light nature of CaS may float S$^{2-}$ upwards. The thermal convection is suppressed at a lower temperature and the gravity effect becomes more apparent, as illustrated in Fig. 5. Considering homogeneity in the melt, the downward flow of the added concentration of CaS was 0.5 mol% CaS. Therefore, the solubility of CaS at 923 K may locate at 0.2 mol%. However, the analytical data at 973 K scattered largely. The excess value from the solubility limit can be considered due to the mixing with the CaS precipitate on the top surface or with the suspended CaS particles. The possible reason why the lower values were obtained is hygroscopic nature of this salt mixture solidified after sampling procedure. During handling in open air, the salt reacts with the moisture in air and the mass of sample increase. It is noted that mass of CaCl$_2$ and LiCl can increase to 197% and 142%, respectively, when they completely converts to the most stable hydrates. This water contamination decrease true W$_{\text{sample}}$ in eq. (7) and causes the error in analysis. Therefore, the most of handling was hereafter done in the glove box with the dried Ar gas circulation (dew point was kept <203 K).

The sample pick-up from the quartz tube, grinding, mass measuring and sample storage were operated in dried Ar gas, before dissolving the sample in the aqueous solution for ICP analysis.
solid CaS particles should be minimized but the distribution of S\textsuperscript{2-} in the melt should be more homogeneous in a crucible.

### 3.3 Control of depth

The charge in the crucible was halved from 300 g to 150 g in order to shorten the depth of melt (55 mm when 300 g is charged) and to be homogenized in a shorter period. Figure 6 shows the results using 150 g melt. The depth is estimated as 23 mm. Assuming the solubility limit locates near 0.2–0.3 mol%CaS, the added concentration of CaS was set at 0.4 mol%. The analyzed concentrations from the quenched samples did not arrive at the added concentration, and they converged to 0.31 ± 0.05 mol%CaS at 973 K, and 0.22 ± 0.05 mol% at 873 K. The authors would like to report these values are true saturation limits of this melt.

### 3.4 Applicability for sulfide reduction

Our previous work\textsuperscript{21)} reported that pure CaCl\textsubscript{2} could dissolve 1.77 ± 0.1 mol%CaS in at 1173 K. At the higher temperature, the saturation value of CaS may increase in eutectic salt as those in CaCl\textsubscript{2}–CaS system.\textsuperscript{21)} However, at those temperature region, the evaporation of LiCl becomes significant\textsuperscript{30}) and the concentration change during long time holding is worried. Because the low temperature electrolysis is a target when eutectic salt is selected, such a high temperature operation is not favorable.

The dissolution of CaS looked fast as shown in Fig. 3, 4 and 6. Within 3.6 ks (or much shorter) in these temperature range, various concentrations of CaS in the initial setting approached to an equilibrium value. This fast dissolution may enhance the quick removal of electrochemically deposited CaS from the reaction site to the melt. Considering the homogeneity of CaS in the melt, it is recommended that the smooth operation temperature should be set above 923 K. A very low saturation limit of CaS in this eutectic melt may suppress the sulfide reduction, but the authors expect that fast removal of CaS can enhance the reduction.

### 4. Conclusion

The solubility of CaS in the molten eutectic salt of CaCl\textsubscript{2}–65 mol% LiCl was measured by sampling and ICP analysis, and the data scattered in a range of 0.2–0.5 mol%. No clear temperature dependency was found in the first stage, and some analytical data exceeded the added concentration. The handling in dried environment and an adequate mass of melt were applied for reliable measurements. Achievement of homogeneous CaS concentration and suppression of inclusion of CaS particles were key for repeatable measurement. The analytical values converged to 0.31 ± 0.05 mol%CaS at 973 K, and 0.22 ± 0.05 mol% at 873 K. It is expected that the sulfide reduction can be operated under this small solubility of CaS because the dissolution rate is quite high even at the low temperature.

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