



Title	Solubility of CaS in CaCl <sub>2</sub> -LiCl Eutectic Melt
Author(s)	Matsuzaki, Takahiro; Suzuki, Ryosuke O; Natsui, Shungo; Kikuchi, Tatsuya; Ueda, Mikito
Citation	MATERIALS TRANSACTIONS, 60(3), 411-415 <a href="https://doi.org/10.2320/matertrans.MA201809">https://doi.org/10.2320/matertrans.MA201809</a>
Issue Date	2019-03-01
Doc URL	<a href="http://hdl.handle.net/2115/73964">http://hdl.handle.net/2115/73964</a>
Type	article
File Information	60_MA201809.pdf



[Instructions for use](#)

## Solubility of CaS in CaCl<sub>2</sub>-LiCl Eutectic Melt

Takahiro Matsuzaki, Ryosuke O. Suzuki\*, Shungo Natsui, Tatsuya Kikuchi and Mikito Ueda

Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan

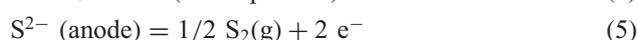
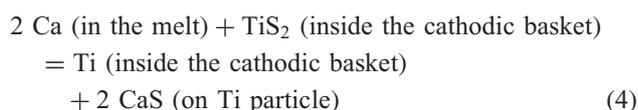
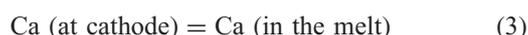
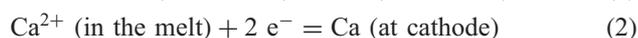
Solubility of CaS in molten CaCl<sub>2</sub>-65 mol%LiCl eutectic salt was examined by sampling of CaS saturated salt and ICP analysis. The handling in dried environment and an adequate mass of melt were applied for reliable measurements, in addition to suppression of inclusion of CaS particles. The 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 CaCl<sub>2</sub> at 1173 K. [doi:10.2320/matertrans.MA201809]

(Received September 18, 2018; Accepted December 10, 2018; Published January 25, 2019)

**Keywords:** solubility, calcium sulfide, CaCl<sub>2</sub>-LiCl eutectic salt

### 1. Introduction

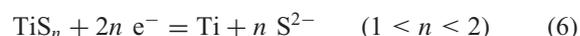
Molten calcium chloride containing a small amount of CaO or CaS is useful media to produce pure metals from its oxides or sulfides, respectively.<sup>1-15)</sup> Many authors have studied the reduction of various oxides using CaCl<sub>2</sub>-CaO. Similarly using molten CaCl<sub>2</sub>-CaS, the reduction of sulfide<sup>5-15)</sup> can be expected under the concepts known as FFC-Cambridge process<sup>1)</sup> and OS process,<sup>2-4)</sup> although the reports on sulfide reduction are not so many at present. The reduction of Cu<sub>2</sub>S,<sup>5,6)</sup> CuFeS<sub>2</sub>,<sup>7,8)</sup> WS<sub>2</sub>,<sup>9,10)</sup> and MoS<sub>2</sub><sup>11,12)</sup> was electrochemically studied considering FFC-mechanism, namely, the decomposition of these sulfides, MS<sub>x</sub>, in the molten chloride melt, RCl, such as CaCl<sub>2</sub> 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 RS<sub>x</sub> and R<sub>x</sub>M<sub>y</sub>S<sub>z</sub> phases was often reported in these studies as intermediate phase during reduction.<sup>6-9,12)</sup> This strongly suggests a contribution of R as the reductant in the melt. The authors examined the molten salt electrolysis of TiS<sub>2</sub><sup>13,14)</sup> and V<sub>3</sub>S<sub>4</sub><sup>15)</sup> 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 cathodic basket, CaS dissolved in the CaCl<sub>2</sub> melt is electrochemically decomposed to metallic Ca (= R), and it reacts with metallic sulfide such as TiS<sub>2</sub> at the cathode to form its metal such as Ti. These reactions can be written as,<sup>13,14)</sup>



The key of these reactions is that CaCl<sub>2</sub> melt dissolves both the reductant Ca<sup>16-20)</sup> and the byproduct CaS.<sup>21)</sup> This feature is suitable for reduction of metallic sulfide: Ca electrochemically deposited at the cathode surface from Ca<sup>2+</sup> 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.<sup>2-4)</sup>

Another mechanism, FFC-Cambridge process,<sup>1)</sup> requires ionization of sulfide and S<sup>2-</sup> dissolution because the sulfide at the cathode should release S<sup>2-</sup> to form the metal<sup>6-12)</sup> via the lower sulfides,<sup>7,12)</sup> and that S<sup>2-</sup> diffuses out from the sulfides to the CaCl<sub>2</sub> melt. If we apply this mechanism to titanium sulfide, their proposal can be written as,



In both mechanisms, S<sup>2-</sup> should dissolve into the CaCl<sub>2</sub> melt and react with carbon anode to remove sulfur as S<sub>2</sub><sup>5-15)</sup> (or CS<sub>2</sub><sup>5,13)</sup> gas from the reaction vessel. Therefore, the dissolution of S<sup>2-</sup> (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.<sup>22)</sup> 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.<sup>2-4)</sup>

Especially in order to avoid the oxygen contamination as a solid solution of oxygen, the authors proposed the sulfide reduction in the molten CaCl<sub>2</sub>-CaS.<sup>13-15)</sup> The solid solubility of sulfur in any metal is generally much smaller than that of oxygen.<sup>22)</sup> It is expected that the concentration of residual sulfur in the metals reduced from their sulfides is very low.<sup>13-15)</sup> For example, our previous study on vanadium sulfide reduction examined V<sub>3</sub>S<sub>4</sub> as a starting material.<sup>15)</sup> Using CaCl<sub>2</sub>-CaS, a very low concentration of residual sulfur such as 210 ppm sulfur could be achieved starting from 45.6 mass%S in V<sub>3</sub>S<sub>4</sub>.<sup>15)</sup> For material balance and electric neutrality in the melt, the effect of CaS should be examined more precisely. The dissolution rate and solubility of S<sup>2-</sup> in the CaCl<sub>2</sub> melt are needed to design an industrial application.

\*Corresponding author, E-mail: rsuzuki@eng.hokudai.ac.jp

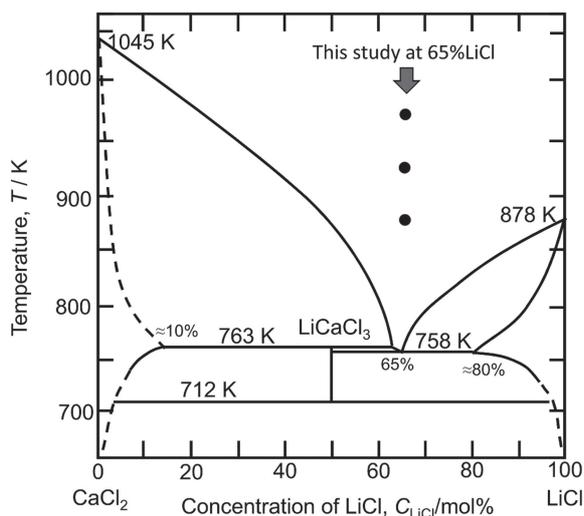


Fig. 1 Phase diagram of  $\text{CaCl}_2$ - $\text{LiCl}$  binary system<sup>31)</sup> and studied conditions.

The authors previously observed that solid particles of  $\text{CaS}$  floated on the top surface of  $\text{CaCl}_2$  when 3 mol%  $\text{CaS}$  was added to pure  $\text{CaCl}_2$  melt at 1173 K.<sup>14)</sup> Successive study showed the solubility of  $\text{CaS}$  to  $\text{CaCl}_2$  melt was only  $1.77 \pm 0.1$  mol%  $\text{CaS}$ <sup>21)</sup> in contrast with 20 mol%  $\text{CaO}$ .<sup>23-29)</sup> This small solubility of  $\text{S}^{2-}$ , however, seems enough to remove  $\text{S}^{2-}$  electrochemically from the sulfides.<sup>6,11,13,14)</sup> The operating temperature was normally set as high as 1173 K when pure  $\text{CaCl}_2$  was used as the media.<sup>1-5,11,13-15)</sup> This was because the melting point of  $\text{CaCl}_2$  is as high as 1048 K.<sup>22,30)</sup> The working at the lower temperature is desired for energy saving. As shown in Fig. 1, the eutectic temperature of 758 K in  $\text{CaCl}_2$ -65 mol%  $\text{LiCl}$  binary system<sup>31,32)</sup> is one of the targets. The electrochemical stability of  $\text{LiCl}$  is stronger than  $\text{CaCl}_2$  and it is expected that  $\text{LiCl}$  does not decompose prior to  $\text{CaCl}_2$  at the electrode voltage as low as 3.0 V.<sup>30)</sup>  $\text{Ca}$  is more favorable than  $\text{Li}$  as the reductant because of stronger stability of  $\text{Ca}$  even in sulfide systems.<sup>30)</sup> Additionally both  $\text{CaCl}_2$  and  $\text{LiCl}$  can dissolve  $\text{O}^{2-}$  in the melt, which may be favorable for possible contamination due to oxygen. The studied conditions are illustrated in the phase diagram<sup>31)</sup> (Fig. 1), and it is noted that these temperatures are lower than the melting temperature of pure  $\text{Ca}$ , but slightly higher than that of pure  $\text{Li}$ .<sup>30)</sup>

The purpose of this work is to observe the dissolution behavior of  $\text{CaS}$  in liquid mixture of  $\text{CaCl}_2$  and  $\text{LiCl}$  when a small amount of  $\text{CaS}$  is added in the melt. The saturation value of  $\text{CaS}$  is determined at 923 K using the molten  $\text{CaCl}_2$ -65 mol%  $\text{LiCl}$ . (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  $\text{CaCl}_2$ - $\text{LiCl}$  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<sup>21)</sup> and the experimental procedure was also similar with the previous one.<sup>21)</sup> High

purity of anhydrous  $\text{CaCl}_2$  and  $\text{LiCl}$  powders (Wako-Chemicals Co., Japan), and  $\text{CaS}$  (99%, Furuuchi Chemical Co., Japan) were used. The samples with various composition of  $\text{CaCl}_2$ -65 mol%  $\text{LiCl}$ - $X$  mol%  $\text{CaS}$  mixture (about 150 g or 300 g,  $X = 0.2$ -1.0) were filled in an  $\text{Al}_2\text{O}_3$  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 intermitted stirring by inserting a K-type thermocouple. The stainless steel vessel was evacuated and heated to 723 K. Then 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  $\text{H}_2\text{O}$ ) for fixing sulfuric ions in water.<sup>33-35)</sup> The sulfur concentration was measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) as reported previously.<sup>21)</sup> The analytical values of ionic sulfur concentration in aqueous solution,  $C_{\text{S}^{2-}}$  (g/mL), was converted to the sulfur concentration in the solidified sample,  $C_{\text{CaS}}$  (in mass ratio) using

$$C_{\text{CaS}} = C_{\text{S}^{2-}} \frac{M_{\text{CaS}} V_{\text{solvent}}}{M_{\text{S}^{2-}} W_{\text{sample}}} \quad (7)$$

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

## 3. Results and Discussion

### 3.1 Dissolution of $\text{CaS}$

When the excess amount of  $\text{CaS}$  was added to the melt over the saturation limit, the residual  $\text{CaS}$  particles precipitated and floated to the top surface of melt due to density difference. The position for sampling by the quartz tube was carefully selected not to include these  $\text{CaS}$  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  $\text{CaCl}_2$ -65 mol%  $\text{LiCl}$ -0.2 mol%  $\text{CaS}$  and 0.5 mol%  $\text{CaS}$ , 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

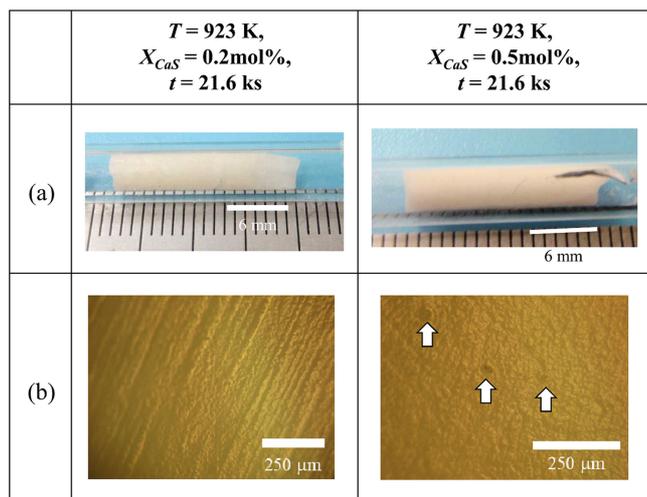


Fig. 2 (a) Samples in transparent quartz tube and (b) optical microscopic images. The samples were extracted from eutectic melt at 923 K after holding for 21.6 ks. White arrows show the precipitates.

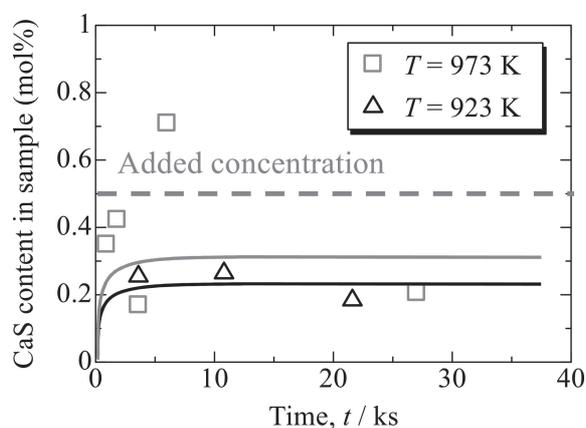


Fig. 3 Variation of CaS content in samples at 923 and 973 K from the molten CaCl<sub>2</sub>-65 mol%LiCl-0.5 mol%CaS. ( $W_{\text{salt}} = 300 \text{ g}$ )

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<sub>2</sub>-65 mol%LiCl-0.2 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.

Figure 3 shows the time dependency of analytical concentration of sulfur in the samples quenched from CaCl<sub>2</sub>-65 mol%LiCl-0.5 mol%CaS. The values at 923 K existed at a certain value close to 0.2 mol%CaS, although

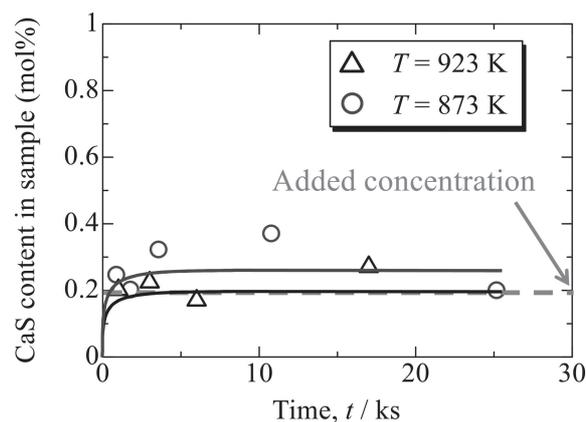


Fig. 4 Variation of CaS content in samples at 873 and 923 K from the molten CaCl<sub>2</sub>-65 mol%LiCl-0.2 mol%CaS. ( $W_{\text{salt}} = 300 \text{ g}$ )

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<sub>2</sub> 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 globe 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.

### 3.2 Scattering of analyzed values

Figure 4 shows the time dependency of analytical concentration of sulfur in the samples quenched from CaCl<sub>2</sub>-65 mol%LiCl-0.2 mol%CaS. The data scatter was well suppressed at 923 K. The amount of dissolved CaS approached to  $0.20 \pm 0.05 \text{ mol\%}$ , 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  $0.27 \pm 0.10 \text{ mol\%}$ , 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<sup>2-</sup> in the melt because of slow diffusion at the lower temperature. The light nature of CaS may float S<sup>2-</sup> 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

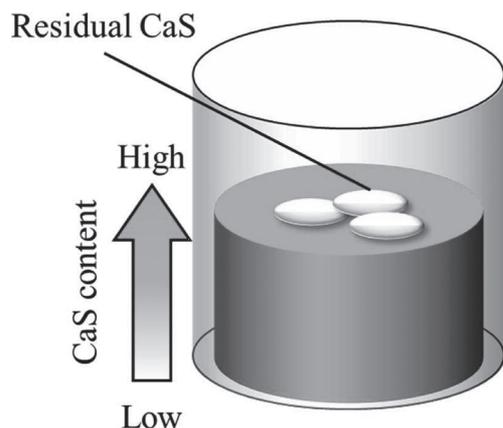


Fig. 5 Schematic of CaS distribution in molten salt.

solid CaS particles should be minimized but the distribution of  $S^{2-}$  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 0.4 mol%. The analyzed concentrations from the quenched samples did not arrive at the added concentration, and they converged to  $0.31 \pm 0.05$  mol%CaS at 973 K, and  $0.22 \pm 0.05$  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<sup>21)</sup> reported that pure  $CaCl_2$  could dissolve  $1.77 \pm 0.1$  mol%CaS in at 1173 K. At the higher temperature, the saturation value of CaS may increase in eutectic salt as those in  $CaCl_2$ –CaS system.<sup>21)</sup> However, at those temperature region, the evaporation of LiCl becomes significant<sup>30)</sup> 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  $CaCl_2$ –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

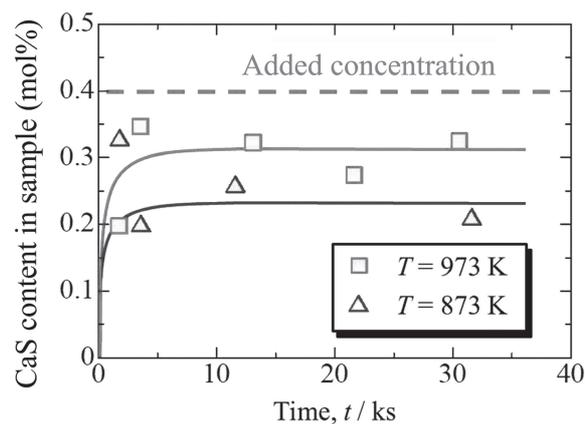


Fig. 6 Variation of CaS content in samples at 873 and 973 K from the molten  $CaCl_2$ –65 mol%LiCl–0.4 mol%CaS. ( $W_{salt} = 150$  g)

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  $0.31 \pm 0.05$  mol%CaS at 973 K, and  $0.22 \pm 0.05$  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.

## Acknowledgements

This work was financially supported in part by the Grant-in-Aid for Scientific Research (KAKENHI, #17H03434), and Japan Mining Industry Association (JMIA).

## 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.O. Suzuki and S. Inoue: *Metall. Mater. Trans. B* **34** (2003) 277–285.
- 5) G.Z. Chen and D.J. Fray: *J. Appl. Electrochem.* **31** (2001) 155–164.
- 6) X. Ge, X. Wang and Seetharaman: *Electrochem. Acta* **54** (2009) 4397–4402.
- 7) M. Tan, R. He, Y. Yuan, Z. Wang and X. Jin: *Electrochim. Acta* **213** (2016) 148–154.
- 8) D. Wang, C. Lu, X. Zou, K. Zheng, Z. Zhou and X. Lu: *J. Mater. Sci. Chem. Eng.* **6** (2018) 82412.
- 9) T. Wang, H. Gao, X. Jin, H. Chen, J. Peng and G.Z. Chen: *Electrochem. Commun.* **13** (2011) 1492–1495.
- 10) H.P. Gao, L.B. Rong, M.S. Tan, Z.Y. Wang, X.B. Jin and G.Z. Chen: *Scientia Sinica Chimica* **44**(8) (2014) 1354–1361.
- 11) G. Li, D. Wang, X. Jin and G.Z. Chen: *Electrochem. Commun.* **9** (2007) 1951–1957.
- 12) H. Gao, M. Tan, L. Rong, Z. Wang, J. Peng, X. Jin and G.Z. Chen: *Phys. Chem. Chem. Phys.* **16** (2014) 19514–19521.
- 13) N. Suzuki, M. Tanaka, H. Noguchi, S. Natsui, T. Kikuchi and R.O. Suzuki: *ECS Trans.* **75**(15) (2016) 507–515.
- 14) N. Suzuki, M. Tanaka, H. Noguchi, S. Natsui, T. Kikuchi and R.O. Suzuki: *Mater. Trans.* **58** (2017) 367–370.
- 15) T. Matsuzaki, S. Natsui, T. Kikuchi and R.O. Suzuki: *Mater. Trans.* **58** (2017) 371–376.
- 16) R.A. Sharma: *J. Phys. Chem.* **74** (1970) 3896–3900.

- 17) A.I. Zaitsev and B.M. Mogutnov: *Metall. Mater. Trans. B* **32** (2001) 305–311.
- 18) L.-I. Staffansson and D. Sichen: *Scand. J. Metall.* **21** (1992) 165–171.
- 19) A.S. Dworkin, H.R. Bronstein and M.A. Bredrig: *Discuss. Faraday Soc.* **32** (1961) 188.
- 20) S. Shaw and R. Watson: *ECS Trans.* **16**(49) (2009) 301–308.
- 21) T. Matsuzaki, R.O. Suzuki, S. Natsui, T. Kikuchi and M. Ueda: *Mater. Trans.* **60** (2019) in this issue.
- 22) H. Okamoto: *Desk Handbook, Phase Diagrams for Binary Alloys*, (ASM International, Materials Park, OH, USA, 2000).
- 23) B. Neumann, C. Kröger and H. Jüttner: *Z. Elektrochem.* **41**(10) (1935) 725–736.
- 24) G.S. Perry and L.G. MacDonald: *J. Nucl. Mater.* **130** (1985) 234–241.
- 25) W.D. Threadgill: *J. Electrochem. Soc.* **112** (1965) 632–633.
- 26) D.A. Wenz, I. Johnson and R.D. Wolson: *J. Chem. Eng. Data* **14** (1969) 250–252.
- 27) V. Dosaj, C. Aksaranan and D.R. Morris: *J. Chem. Soc. Faraday Trans.* **71** (1975) 1083–1098.
- 28) S. Wang, F. Zhang, Z. Liu and L. Zhang: *Thermochim. Acta* **470**(1–2) (2008) 105–107.
- 29) V.L. Cherginets and T. Rebrova: *Thermochim. Acta* **654** (2017) 51–53.
- 30) A. Roine and P. Kobylin: HSC Chemistry, ver.8.0.8, (Outotec Research Center, Poli, Finland, 2014).
- 31) K.H. Mahendran, S. Nagaraj, R. Sridharan and T. Gnanasekaran: *J. Alloys Compd.* **325** (2001) 78–83.
- 32) G.A. Bukhalova and A.S. Arabadzhan: *Zh. Neorg. Khim.* **7** (1962) 2230.
- 33) R.A. Day *et al.*: *Quantitative Analytical Chemistry*, Revised Ed., (Fubaikan, Tokyo, 1999) (in Japanese).
- 34) M. Yano: “Quantitative analysis of hydrosulfide in hot spring water using methylene blue absorption method”, Research Report at Hyogo Prefectural Institute for Healthy Life Science, (Hyogo, Japan, 2002) (in Japanese).
- 35) Japan Industrial Standard, JIS K0108 9.1.2.7, “methylene blue absorption Method—Standard solution of sulfide ion”, (Tokyo, Japan, 2010).