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Calcium Reduction of TiS_2 in $CaCl_2$ Melt

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In this study, we reduce TiS_2 to Ti via both calciothermic reduction and electrolysis in a $CaCl_2$ melt. Upon calcium reduction at 1133 K in $CaCl_2$ melt, the concentration of sulfur decreases to 0.03 mass% S when an amount greater than twice the stoichiometric calcium amount is added. Upon electrolysis reduction at 1173 K in $CaCl_2$-CaS melt, the concentration of sulfur initially decreases significantly to 0.01 mass% S when a sufficiently large amount of electric charge is supplied. Our results indicate that it is possible to achieve sulfur removal via both calciothermic reduction and electrochemical reaction. [doi:10.2320/matertrans.MK201613]

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1. Introduction

The Kroll process forms the most prevalent approach to produce metallic titanium.[1)] This process consists of three steps: conversion from TiO_2 to $TiCl_4$, subsequent reduction of $TiCl_4$ to sponge Ti by Mg liquid, and electrolysis of the by-product $MgCl_2$ to Mg and Cl_2 for reuse in the former processes. It takes about a week for this reduction, and considerable thermal energy is lost during the manufacturing process.

The FFC electrochemical process and the OS process are well-known alternative titanium refining processes.[2–7)] The OS process, it was proposed by Ono and Suzuki, involves Ca reduction of TiO_2 and the electrolysis of CaO in $CaCl_2$ melt to produce Ca for further reduction. This process combines three effects: First, calcium reduces oxides directly. Second, molten $CaCl_2$ removes the by-product CaO immediately. Third, the electrolysis of CaO forms calcium continuously. The electrolysis reactions in the OS process are as follows:

$$CaO \rightarrow Ca^{2+} + O^{2-} \quad (1)$$

$$Ca^{2+} + 2e \rightarrow Ca\ (\text{in } CaCl_2) \quad (2)$$

$$2O^{2-} + C\ (\text{anode}) \rightarrow CO_2 + 4e \quad (3)$$

$$O^{2-} + C\ (\text{anode}) \rightarrow CO + 2e \quad (4)$$

The theoretical decomposition voltage for CaO to decompose to gaseous oxygen is 2.7 V at 1173 K. However, this voltage can decrease to about 1.6 V if a carbon anode is used[8)]. According to previous reports,[4,6,9)] this process can experimentally produce metallic titanium containing 2000 ppm of oxygen with long-time electrolysis.

However, long-time electrolysis leads to titanium being contaminated by large quantities of carbon. This is because carbon is formed by the following parasitic reactions:

$$2Ca + CO_2\ (\text{gas}) \rightarrow 2CaO + C \quad (5)$$

$$Ca + CO\ (\text{gas}) \rightarrow CaO + C \quad (6)$$

$$3Ca + {CO_3}^{2-} \rightarrow 3CaO + C + 2e \quad (7)$$

The reactions consume a large amount of Ca, and therefore, the current efficiency for reduction of TiO_2 becomes low[6,9)]. In this regard, dense yttria-stabilized zirconia (YSZ) has been experimentally examined for the elimination of carbon contamination via its use as a membrane between the carbon anode and Ca in salt because of its good oxygen-ion-conducting property.[10)] In such studies, the YSZ tube was used as oxygen ionic membrane to absorb oxygen, which looks like as the oxygen absorbing anode. The YSZ tube could prevent the reaction between Ca and CO_2/CO, and carbon content in the produced Ti was successfully lowered. However, because the anode was covered by YSZ, ionic transfer was delayed, which led to even longer electrolysis times. While the reduction of TiO_2 yields low-impurity metallic titanium, the process is complicated and time-consuming. In this context, in an attempt to reduce energy consumption in the preparation of metallic titanium, we examine the use of TiS_2 as a raw material to produce metallic Ti. Here, we remark that hydrogen and carbon are not apposite reductants for TiS_2,[11)] and therefore, in our study, we reduced TiS_2 by using the OS process. The use of TiS_2 for obtaining Ti is promising because the reduction of TiS_2 is easier than that of TiO_2, and the solubility of sulfur in solid titanium is negligible,[12)] which results in low residual sulfur content in the obtained titanium. Oxygen solubility in TiS_2 is unknown and neglected in binary phase diagram of Ti-S system.[12)]

The reduction reaction of TiS_2 is shown below:

$$TiS_2 + 2Ca \rightarrow Ti + 2CaS \quad (8)$$

Here, Ca is generated by the electrolysis of CaS. Similarly, in the OS process, CaS can be theoretically recycled to obtain the reductant Ca. The theoretical decomposition voltage at which CaS decomposes to gaseous CS_2 and liquid Ca is 2.01 V at 1173 K with the use of a carbon anode.[8)] This value is lower than that for $CaCl_2$, 3.2 V.[8)] This result indicates that CaS is electrolyzed prior to decomposition of $CaCl_2$ salt. Further, S^{2-} reacts with carbon to form gaseous CS_2. This product CS_2 can be utilized for the conversion of TiO_2 to TiS_2. As reported by Ohta *et al.*,[13)] CS_2 gas is a powerful sulfurizing agent that can form TiS_2 through the following reaction:

$$TiO_2 + CS_2 \rightarrow TiS_2 + CO/CO_2 \quad (9)$$

Figure 1 illustrates the reaction mechanisms utilized in our approach. The conversion of TiO_2 to TiS_2 proceeds as per eq. (9). The operating temperature is about 1273 K, which is

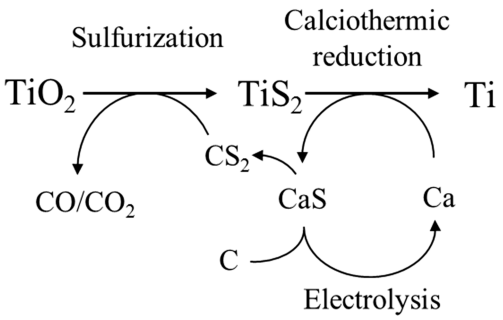


Fig. 1 Designed reaction mechanism of our study to yield titanium from titanium disulfide.

similar with chloridation of TiO_2 to $TiCl_4$.It is noted that 2 mol of Cl_2 is needed to form 1 mol Ti, but that 1 mol CS_2 gas is sufficient to produce 1 mol Ti. The less volume of gas handling is suitable for industrial application. Here, we clarify that the calciothermic reduction of TiS_2 and electrolysis of CaS can be conducted in molten $CaCl_2$ salt. The purpose of this study is to examine the reduction of TiS_2 by calciothermic reaction and by electrolysis in molten calcium chloride.

2. Experimental

Figure 2(a) depicts the furnace and reactor used for the calciothermic reduction. A stainless steel crucible (inner diameter of 70 mm and height of 100 mm) was filled with TiS_2 powder (1.77 mass% oxygen), lumps of calcium, and $CaCl_2$ powder and positioned in the setup shown in the figure. This sample mixture was dehydrated at 873 K overnight in vacuum and then continuously heated to 1133 K and allowed to react for 1.8 ks in an Ar atmosphere. Figure 2(b) shows the reactor used for the electrolysis reduction. A MgO crucible (99.5% purity, 90-mm inner diameter, 200-mm height) was set up as in the figure after being filled with precisely weighed $CaCl_2$-CaS mixed powder (~600 g). The salt was dehydrated at 873 K overnight in vacuum and then continuously heated to 1173 K for 18 ks in an Ar atmosphere. The anode was a carbon bar (10 mm in diameter), and the cathode was shaped in the form of a basket made of titanium net. About 1.5 g of TiS_2 powder was packed into the basket. Both electrodes were attached to Ti terminal rods. A constant voltage of 3.0 V was applied between the two electrodes at 1173 K. The applied voltage was continuously monitored and controlled. The electrolysis was terminated after a certain amount of electricity was supplied. At the end of both the calciothermic and electrolysis experiments, the solidified salt was removed by washing with water, dilute CH_3COOH aqueous solution, distilled water, and alcohol, and dried in vacuum. The sulfur and oxygen content in the two sets of samples were determined using LECO-CS600 and LECO-TC600 analyzers, and the existing phases were identified by means of X-ray diffraction (XRD). The structure of the particle surface was examined by scanning electron microscopy (SEM).

3. Result and Discussion

3.1 Calciothermic reduction

Figure 3 shows the correlations between the concentrations

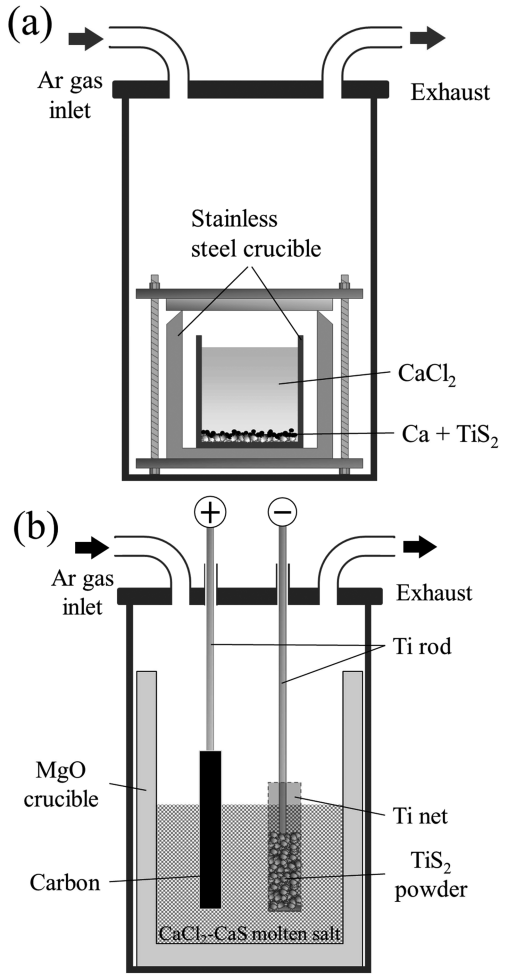


Fig. 2 Schematics of the reactor for (a) calciothermic reduction, (b) electrolysis reduction.

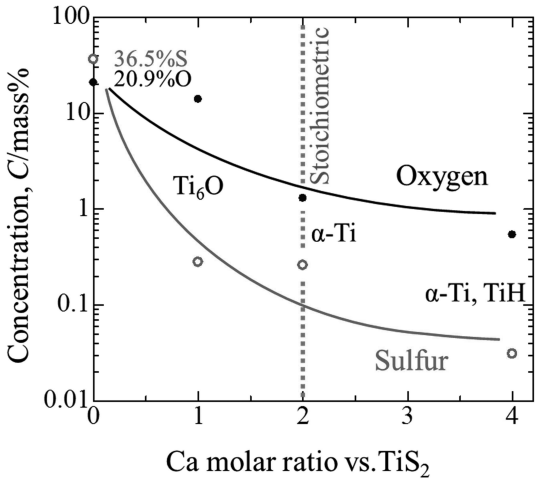


Fig. 3 Correlation between Ca, oxygen, and sulfur concentrations in the powder obtained by Ca reduction.

of sulfur, oxygen, and Ca. The stoichiometric Ca quantity was considered to be two in this reaction. Here, this ratio, r, is taken to express the molar quantity of Ca change. The concentration of sulfur decreased significantly in the Ca-poor region, and 0.03 mass% S was obtained when twice the amount of stoichiometric Ca was used. On the other hand,

residual oxygen was observed over the entire range of r, and the minimum mass% of O was 0.5. This residual oxygen may originate as a major impurity in raw materials or by contamination from air. Further, the washing process in water may have also contaminated the sample. The formation of α-Ti was identified at stoichiometric ratios of $r = 2$ and $r = 4$ by XRD. Further, the presence of titanium hydride was confirmed at $r = 4$; we speculate that the excess amount of Ca reacted with washing water and generated hydrogen gas to form TiH. Some amount of oxygen may also contaminate the surface of produced Ti particles due to water treatment. This is the reason why 0.54 mass% O was detected at $r = 4$. Further, Ti_6O was observed at $r = 1$. No lower sulfide could be found in any of the samples. This result indicates that titanium sulfide is not stable in washing solutions; we speculate that the lower sulfide transformed into lower oxide via reacting with the aqueous solution during washing. The residual oxygen level increased significantly for $r = 1$.

3.2 Reduction by OS process

Table 1 lists the concentrations of sulfur and oxygen along with their phases identified by XRD for the obtained samples. Here, Q represents the supplied charge in the experiment with Q_0 denoting the stoichiometric charge. At $Q > Q_0$, α-Ti was identified via XRD. Further, α-Ti and Ti_6O were observed at stoichiometric charge ($Q = Q_0$). For $Q < Q_0$, lower oxides were identified. No lower sulfide was identified, similar to the case of the calciothermic reduction mentioned in the previous section. The concentration of sulfur decreased significantly; we obtained 0.01 mass% S for $Q = 4Q_0$. However, the concentration of oxygen remained high, for example, we observed 16.78 mass% O at $Q = 0.5Q_0$ and 5.07 mass% O at $Q = Q_0$. The concentration of oxygen did not greatly change, and it did not decrease below 1 mass% O for $Q > Q_0$.

Figure 4 shows the time dependence of the current per g of TiS_2 during electrolysis when the added CaS amount was varied. The current was fairly large in the initial stage of the electrolysis for all the samples. Subsequently, the current decreased as the electrolysis progressed, and it approached constant values at a later stage. At 2.0 mol% CaS, the current reached its highest constant value at 2.3 A/g.

Table 2 lists the concentrations of sulfur and oxygen for various CaS concentrations. When the amount of added CaS increased, the sulfur concentration in the samples also increased. However, the concentration of oxygen remained as high as 1 mass% O, and it did not depend on the amount of CaS. The electrolysis time necessary for TiS_2 reduction decreased when CaS was added. This time can decrease to a quarter of that at 2.0 mol% CaS. The excess amount of CaS inhibited electrolysis in 5.0 mol% CaS because the current was less than that for 2.0 mol% CaS.

Figure 5 shows the image of the surface of the solidified salt in the MgO crucible after experiment Run #VIII and #IX. The gray regions comprised solidified $CaCl_2$, and a whitish substance was observed to be deposited on the salt, which deposition was identified by XRD to be CaS. These results indicate that the solubility of CaS in the $CaCl_2$ melt was not so high as 14 mass% O in CaO system and that the saturated solubility may be less than 5.0 mol% CaS at the experimental temperature of 1173 K. In previous reports of oxide reduction, TiC was sometimes detected in a part of sample after electrolysis, but in this work, TiC was never identified in all samples. CS_2 gas that is generated at anode did not influence to general metal titanium.

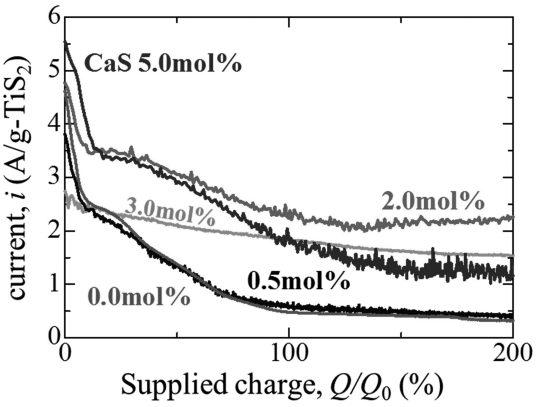


Fig. 4 Change in current per gram of TiS_2 during electrolysis Runs #IV, VI–IX under constant voltage 3.0 V at 1173 K in $CaCl_2$-0.5 mol% CaS.

Table 2 Experimental conditions and concentration of sulfur and oxygen in the obtained powder. The experiments were carried out at 1173 K under a constant voltage of 3.0 V with supplied $Q = 200\%Q_0$.

Run No.	CaS Concentration, (mol%)	Electrolysis time, t(s)	Sulfur Concentration, (mass%)	Oxygen Concentration, (mass%)
# VI	0.0	12000	0.011	1.01
# IV	0.5	10000	0.025	1.13
# VII	2.0	2800	0.147	1.3
# VIII	3.0	3700	0.133	1.85
# IX	5.0	3800	0.224	1.22

Table 1 Experimental conditions, phase identification by X-ray diffraction (XRD), and analyzed concentration of sulfur and oxygen in the obtained powder. The experiments were carried out at 1173 K under a constant voltage of 3.0 V. $CaCl_2$-0.5 mol% CaS was used as the molten salt.

Run No.	Supplied Electricity, Q(C)	Electrolysis time, t(s)	Q, ($\%Q_0$)	Phases Identified by XRD	Sulfur Concentration, (mass%)	Oxygen Concentration, (mass%)
# I	2612	850	50	Ti_2O	0.56	16.78
# II	4285	1970	80	Ti_3O	0.661	6.65
# III	5152	2800	100	Ti_6O,Ti	0.043	5.07
# IV	10425	10000	200	Ti	0.025	1.13
# V	20692	24000	400	Ti	0.01	0.96

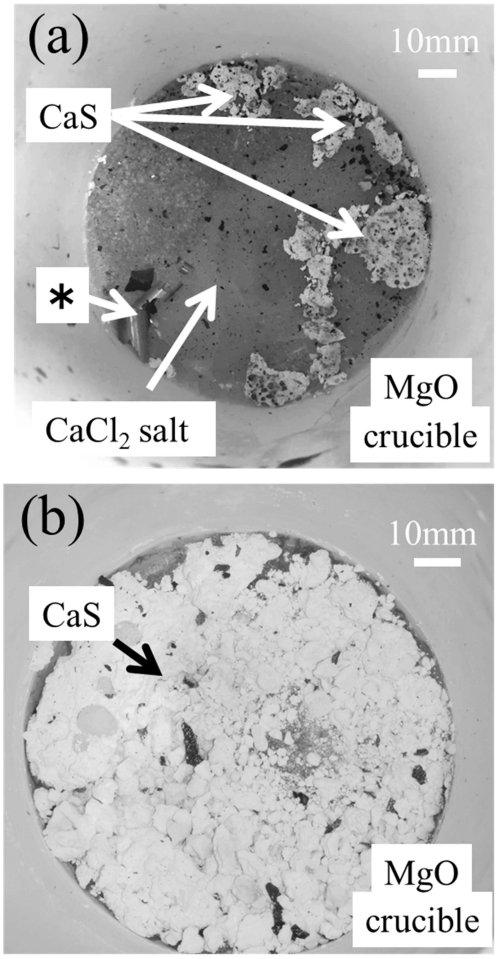


Fig. 5 Photo of MgO crucible after experiment (a) Run #VIII, and (b) Run #IX. *in(a): a broken piece of Ti rod. The inside diameter of crucible is 90 mm.

4. Conclusion

In this study, we performed the reduction of TiS_2 by calcium in molten $CaCl_2$ and by electrolysis in $CaCl_2$-CaS molten salt. The residual concentrations of sulfur and oxygen in the obtained samples were analyzed, and the sample compositions were identified by means of XRD. With the use of calciothermic reduction, a single phase of metallic titanium was obtained with 0.03 mass% S. With the use of electrolysis, 0.01 mass% S was obtained when the charge supplied was 4 times larger than stoichiometric charge (Q_0), $Q = 4Q_0$. A single phase of metallic titanium was obtained when the supplied Q was $>2Q_0$. The concentration of oxygen decreased to 0.5 mass% O with calciothermic reduction and to 1.0 mass% O with electrolysis. The further addition of CaS can decrease the electrolysis time for reduction.

We believe that our findings can significantly contribute further refining the processes used to obtain titanium.

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REFERENCES

1) W. Kroll: Trans. Electrochem. Soc. **78** (1940) 35–47.
2) G.Z. Chen, D.J. Fray and T.W. Farthing: Nature **407** (2000) 361–364.
3) R.O. Suzuki, K. Teranuma and K. Ono: Metall. Mater. Trans., B **34** (2003) 287–295.
4) K. Ono and R.O. Suzuki: JOM Mem. J. Miner. Met. Mater. Soc. **54** (2002) 59–61.
5) R. O. Suzuki and K. Ono, *Proc. 13th Int. Symp. on Molten Salt*, (The Electrochem. Soc. Penningston, NJ) (2002) pp.810–821.
6) R.O. Suzuki: J. Phys. Chem. Solids **66** (2005) 461–465.
7) R. O. Suzuki, *Proc. 10th World Conference on Titanium*, (Deutche Geselsch. Metalk. Germany, 2003).
8) A. Roine, HSC Chemistry, Ver.6.01, (Outokump Research Oy, Pori, Finnland, 2006).
9) R.O. Suzuki and S. Fukui: Mater. Trans. **45** (2004) 1665–1671.
10) R. O. Suzuki, *Proceedings of 11th World Conference on Titanium (Ti-2007)*, (Kyoto, Japan, June 3–7, 2007). "*Ti-2007 Science and Technology*", ed. by M.Niinomi, S.Akiyama, M.Ikeda, M.Hagiwara and K. Maruyama, The Japan Institute of Metals (JIM), Sendai, Japan, pp.99–102.
11) N. Suzuki, M. Tanaka, H. Noguchi, S. Natsui, T. Kikuchi, and R. O. Suzuki, *Proceeding of PRiME 2016* (Honolulu, Hawaii, October 2–7. 2016) in press.
12) J.L. Murray: Bulletin of Alloy Phase Diagrams **7** (1986) 156–163.
13) M. Ohta, S. Satoh, T. Kuzuya, S. Hirai, M. Kunii and A. Yamamoto: Acta Mater. **60** (2012) 7232–7240.