

Titanium Production via Titanium Sulfide

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Abstract

A new metallurgical process via titanium sulfide from ilmenite is proposed and experimentally approved: It consists of several stages; 1) The ilmenite ore is exposed to gaseous CS₂ to selectively sulfurize to FeS, which is wet-chemically removed. 2) The residual oxide is again exposed to CS₂ to form TiS₂. 3) TiS₂ is electrochemically reduced to metallic Ti using molten CaCl₂-CaS as an application of OS process.

TiFeO₃ was exposed to Ar-CS₂ mixed gas flow at 1173 K to form the mixture of FeS+TiO₂. FeS was easily separated by immersing in H₂SO₄ solution at 313 K. After recovery of TiO₂, it was converted completely to TiS₂ by the second sulfurization with CS₂. TiS₂ could be reduced to Ti powder by calciothermic reduction and simultaneous electrolysis in a CaS-CaCl₂ melt for about 6 hours at 1173 K and 3.0 V. The impurity decreased to a low level such as 0.021 mass%S due to very small solubility of S in a-Ti. However, 1.06 mass%O remained because of wide solubility of oxygen in a-Ti and water contamination in initial CaCl₂.

1. Introduction

Titanium dioxide converted from ilmenite (mainly FeTiO₃) has been normally taken as the starting material both for Kroll process [1] or for newly developing refining processes such as FFC Cambridge process [2] and OS process [3]. In case of direct reduction from the oxide, the complete removal of oxygen from the obtained metallic Ti has not yet achieved although many researchers have challenged. The reasons of this oxygen contamination are thermodynamically wide solubility of oxygen in a-Ti and the technically insufficient oxygen removal from the reactors. Once the oxide is taken as the starting material of reduction, a fairly amount of oxygen still remains in the obtained Ti particles, although many operating parameters were optimized such as reaction temperature, time, applying voltage, gas environment, crucible, salt constitutions and their compositions, particle size, oxide phases, electrode materials and cell arrangements [4].

Kroll process removes oxygen from TiO₂ once by conversion to TiCl₄ and CO/CO₂ gas, and highly pure titanium metal is formed, because Ti does not dissolve Mg and Cl, and because the distillation of TiCl₄ is available to get the higher purity [1]. In analogy with Kroll process, the authors proposed utilization of sulfur: Unfortunately there is no natural resource of Ti sulfides, but TiO₂ can be easily converted to TiS₂ and CO/CO₂ gas when CS₂ gas is used [5]. The reduction of TiS₂ is expected as an application of FFC Cambridge process or OS process; the molten salt electrolysis of TiS₂ in CaCl₂ melt is applied to remove sulfur from the cathode as CaS, which is exhausted out as S₂ gas from the carbon anode [6,7]. The extracted S₂ gas may be used to synthesis CS₂ for TiO₂-TiS₂ conversion, but the simple mixture of carbon and S₂ gas can be thermodynamically used for sulfurization of TiO₂ [8]. This may correspond to chlorination process in Kroll process. Fig.1 shows the combinations of various reactions on Ti refining.

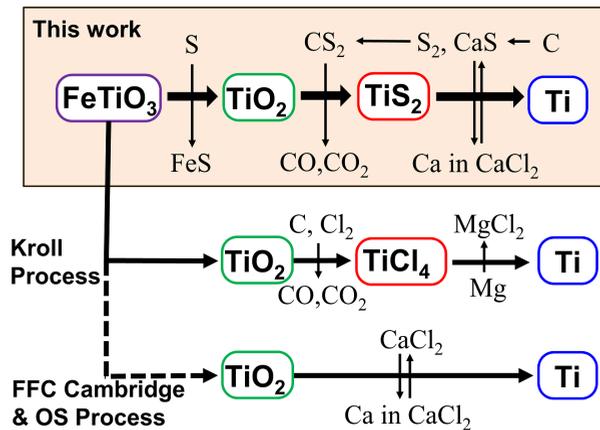


Fig. 1 Comparison of Ti preparation in Kroll process [1], oxide reduction processes such as FFC Cambridge process [2] and OS process [3] with this proposal using sulfur [6,7].

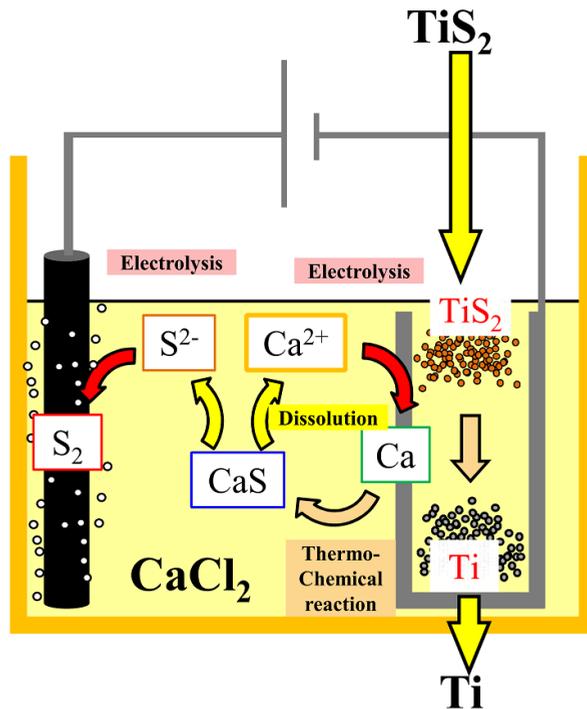


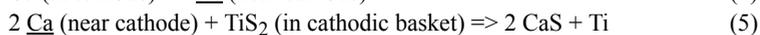
Fig. 2 Reactions of TiS_2 reduction in molten CaCl_2 [6,7].

Fig.2 illustrates the reactions in case of reduction of TiS_2 in the molten CaCl_2 - CaS mixture [6,7]. About 1.9 mol% CaS can dissolve in the CaCl_2 melt at 1173 K [9], and it decomposes to Ca^{2+} and S^{2-} as shown in eq.(1). By applying a higher cell voltage than the theoretical decomposition voltage (2.1-2.2V at 1173 K [8]), metallic Ca

and S₂ gas can be electrochemically precipitated on the cathode and anode surfaces, respectively, as expressed in eq.(2) and (3).



As considered in OS process [3,4], the deposited Ca from CaCl₂ melt again dissolves into the bulk due to the metallic solubility of Ca (about a few mol%). The dissolved Ca metal will be written here as Ca. It exists in the close vicinity of cathode, and thermochemically reacts with TiS₂ particles that were filled inside the cathode basket.



The product Ti precipitates as solid particles inside the cathodic basket. The another product, CaS, will dissolve by following eq.(1). In this sequence, Ca circulates in the melt and does not go out from the reaction vessel. The deposited S₂(g) in eq.(3) will leave from the anodic surface to the melt surface and diffuses to the gas phase over the melt. Finally it deposits on the wall of reaction vessel at the cooled parts, and it will be detected as amorphous sulfur or crystalline S₈(s).

For synthesis of TiCl₄ in Kroll process, chlorine gas should be safely circulated from the molten salt electrolysis without any leakage to the chlorination furnace. Because the melting point of TiS₂ is higher than 1273 K, the electrolysis and reduction can be operated as solid state of TiS₂. A stockyard of solid TiS₂ seems safer and more stable than a tank of liquid TiCl₄, and the circulation of solid sulfur seems not so serious in factory processing. It is also noted that a plenty amount of sulfur can be served from copper smelting industries. Once sulfur can be set in the material cycle, it is not necessary to charge the additional sulfur as the principle of this proposal. Although the reduction of Ti sulfide by the other alkaline earth metals such as Mg is applicable, the recycling of Mg may cause another issue, while Ca recycling is ready in OS process [3,4].

The purpose of this work is to confirm the experimental quality of Ti obtained by our proposed process when FeTiO₃ is taken as the starting material, although the fundamental reactions in molten salt electrolysis, (1)-(5), have already been studied by starting from the commercial TiS₂ powder [6,7]. Conversion from TiO₂ to TiS₂ was reported using CS₂ gas, and this study takes this idea, although the starting oxide is FeTiO₃.

2. Material and experiments

0.2 – 1.0 g FeTiO₃ (Furuuchi Chemicals, >99.9%) was placed on the alumina or mullite boats and heated at 573 – 1473 K in Ar-CS₂ gas flow, as illustrated in Fig. 3. Gas flow rate (20-100mL/min Ar) and reaction time (>1.8 ks) were chosen so that an excess amount of CS₂ (>99.0%) gas was carried into the furnace. The reduction experiments using 600 g CaCl₂ (Kanto Chemicals, >99.0%) - 0.5 mol%CaS mixed salt in MgO crucible were conducted at 1173 K, 3.0 V using graphite anode (10 mm in diameter) and Ti basket-like cathode, as reported separately [6,7]. The morphology, phases and metallic impurities were measured by SEM, XRD and XRF, respectively. The residual oxygen and sulfur were studied using LECO TC-600 and CS-600 analyzers, respectively.

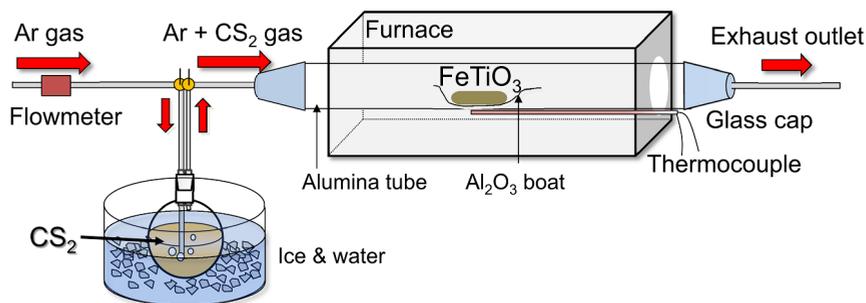


Fig. 3 Sulfurization in CS₂ gas flow.

3. Results and Discussion

3.1 Sulfurization of FeTiO₃

Powdery FeTiO₃ contained a small amount of TiO₂, as confirmed by XRD measurement (Fig.4). Volatile CS₂ in ice-water was carried by Ar gas bubbling into the furnace, where the FeTiO₃ powder was set on the ceramic boat. Fig. 4 shows also that the sample after sulfurization at 1073 K for 3.6 ks consisted of Fe_{1-x}S and TiO₂. Selectively Fe was sulfurized by CS₂ and no trace of Ti sulfides was found by XRD measurements.

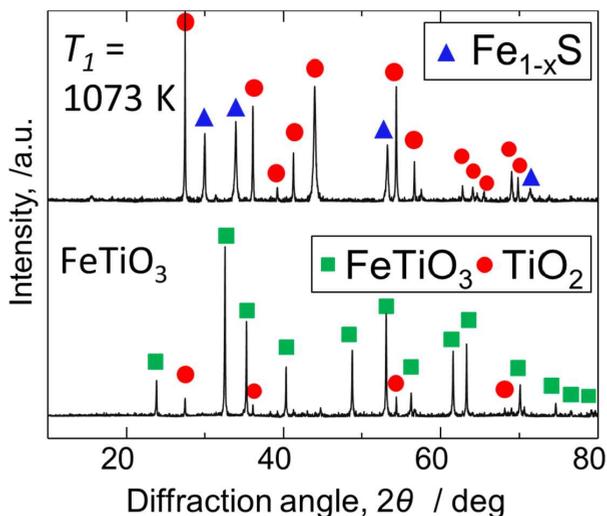


Fig. 4 XRD patterns of starting sample and the sample sulfurized in CS₂ gas flow at 1073 K.

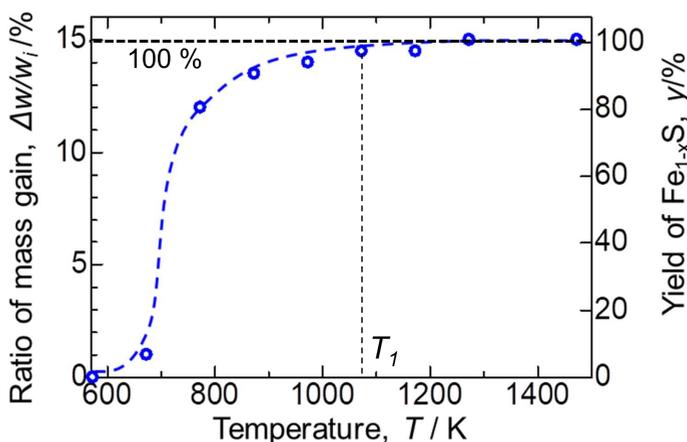
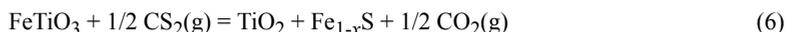
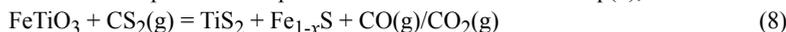


Fig.5 Mass change during sulfurization for 3.6 ks.

Fig. 5 shows the mass change during sulfurization by varying the holding temperature. When we assume that whole parts of initial sample consist of pure FeTiO₃ and that this sample is converted into the stoichiometric FeS and TiO₂, the conversion ratio of FeTiO₃ to FeS is defined as “yield of Fe_{1-x}S”, *y*, as shown in Fig. 5. *y* becomes 100% at $DW/W_i = 14.93\%$, where the non-stoichiometry of Fe_{1-x}S, *x* = 0.14. Note that *x* = 0 at $DW/W_i = 10.59\%$. The sulfurization started at the temperature as low as 773 K, and a steady value of 100% conversion was obtained above 1173 K. The sample at 1473 K was partially melted because the melting point of FeS is 1465 K [8]. By changing the Ar gas flow rate, the concentration of CS₂ in the mixed gas could be varied in the range of 25-34 vol%. However, DW/W_i was in a small variation of 11.5-15% for 3.6 ks at 1173 K and Ti sulfides were never found by XRD. Even after a long sulfurization such as 14.4 ks, no Ti sulfides were formed. The deposition of solid sulfur was found at the low temperature area of downstream. Therefore, the corresponding reaction of sulfurization can be shown as eq. (6) and/or (7).



Before this experiments, the authors had expected a complete sulfurization as shown in eq.(8),



and these reactions corresponds to $DW/W_i = 31.77\%$. Judging from these experimental results, CS₂(g) sulfurizes FeTiO₃ preferentially to form Fe_{1-x}S, and rutile-type TiO₂ remains as a by-product.

Thermodynamically these three reactions should proceed forward, although some data on the lower sulfides in Ti-S system are missing [8]. Therefore, the kinetic effect such as core-shell model is suspected that the converted FeS might cover the particle surface and prohibit further sulfurization.

3.2 Leaching of FeS in H₂SO₄ solution

In order to separate Fe from the metallic Ti in this proposal, it is necessary to remove Fe before electrolysis in the molten salt. Because the mixture of FeS and TiO₂ was obtained after CS₂ sulfurization, FeS

removal was conducted in an acidic solution. FeS can dissolve quickly either in 1M HCl or 1 M H₂SO₄ solutions, while FeTiO₃ was hardly dissolved in these solutions at room temperature. The sample sulfurized at 1073 K for 14.4 ks was leached in 1 M HCl solution for a day, and a fairly large amount of FeS remained. However, 1 M H₂SO₄ solution could remove most of FeS phase at the same conditions as identified by XRD measurement (Fig.6). In addition, the background intensity of XRD pattern was very high before leaching because of Fe fluorescence X-ray under Cu-K α radiation. The residual Fe in the leached samples in 1 M H₂SO₄ solution was therefore examined by XRF analysis as shown in Fig.7.

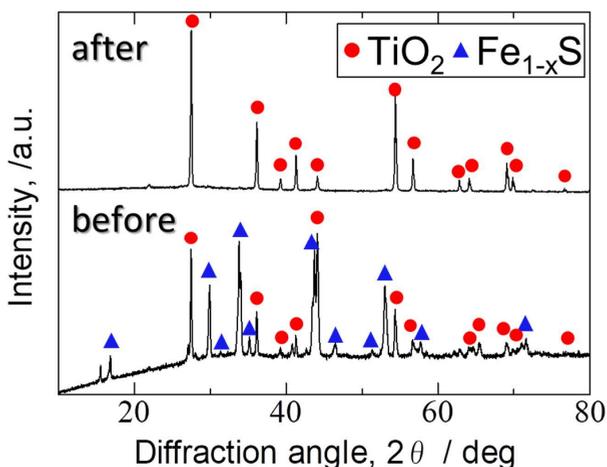


Fig. 6 Change of XRD patterns by 1 M H₂SO₄ leaching.

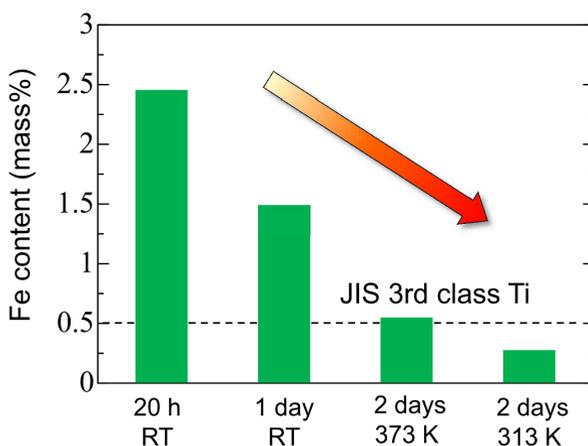


Fig. 7 Residual Fe after leaching in 1 M H₂SO₄.

Fe removal in 1 M H₂SO₄ solution could be conducted at room temperature and the heating did not enhance the Fe dissolution. It is noteworthy that a wet chemical process to remove Fe from FeTiO₃ is normally operated above 473 K in a conc. H₂SO₄ for a several days. FeS removal in this study was effectively quick to

promote Fe separation. As seen in Fig. 7, 0.28 mass%Fe leached for 172.8 ks at 313 K satisfied with the regulation for 3rd class of Japanese Industrial Standard (JIS) titanium. The residue in 1 M H₂SO₄ solution was coarse TiO₂ particles with about 10 μm in diameter, although its surface was rough suitable for successive gas reaction.

3.3 Secondary sulfurization by CS₂ gas

The FeTiO₃ samples sulfurized at a certain temperature by CS₂ gas flow for 14.4 ks were leached to form TiO₂, which were again sulfurized at the same temperature in CS₂ gas flow. Ti_{1.083}S₂, Ti_{2.45}S₄ and Ti₃S₄ were identified at 1073 K, 1173-1273 K and 1373-1473K, respectively, by XRD.

Fig. 8 shows the mass gain of the samples during sulfurization. At the higher temperatures, the lower sulfides in the Ti-S binary system appeared, and the mass change became the smaller. A small amount of SiO₂ and Al₂O₃ were detected at the high temperature samples, which may originate from the impurity in the initial FeTiO₃, or from the unexpected reaction with the boats.

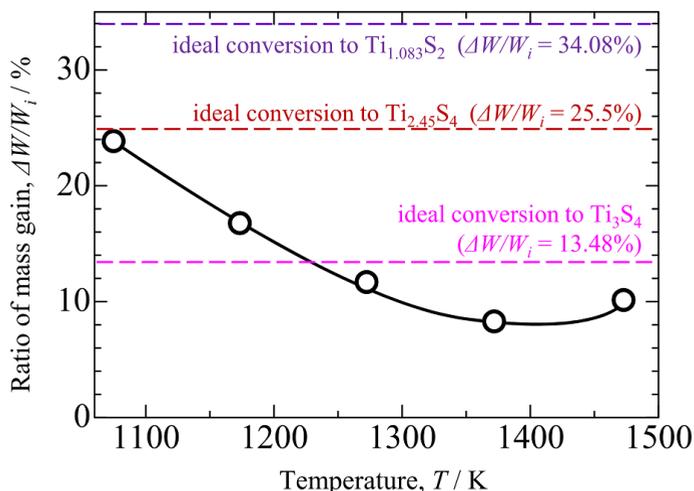


Fig. 8 Mass change during second sulfurization.

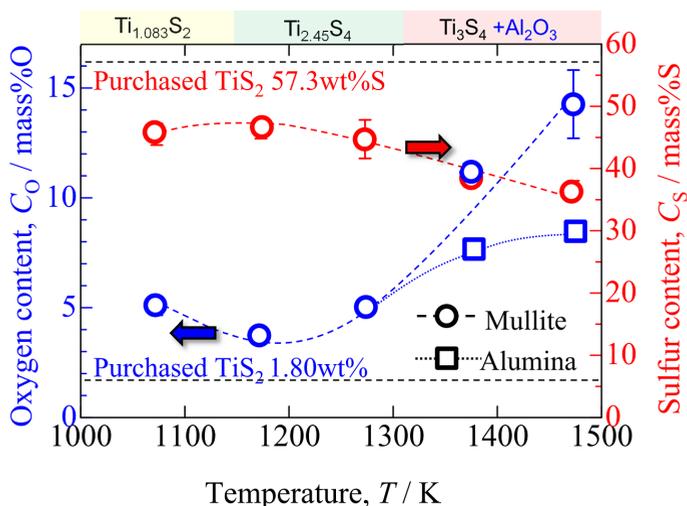


Fig. 9 Sulfur and oxygen analysis of secondary sulfurized samples on the ceramic boats.

Fig. 9 shows the analysis of oxygen and sulfur of the samples reacted for 14.4 ks. At the higher temperatures, the sulfur content decreased, and oxygen content increased significantly due to the reaction with the ceramic boats. Therefore, the conditions at 1173 K for 14.4 ks were taken as an optimal condition for the subsequent study. The sample at these conditions contained 3.58 mass%O and 46.3 mass%S, although the lowest oxygen content is desired. It is also noteworthy that the greater concentration of sulfur needs the larger amount of electricity in electrochemical reduction of molten salt.

After optimizing the other sulfurization parameters, two samples were prepared with about 1.5 g from FeTiO_3 at 1173 K for 43.2 ks by feeding CS_2 at 293 K in Ar 20mL/min flow. Their phase identification and impurity analysis are given in Table 1. They were used in the reduction experiments as described later. It is noted that the sulfurized powder from the commercial TiS_2 powder contained 0.43 mass%O and 58.4 mass%S in the same conditions [6,7]. The oxygen level below 0.4 mass%O were easily achieved at these conditions if TiO_2 powder was taken as the starting material.

Fig. 10 shows the SEM morphology of the sample obtained after second sulfurization at 1073 K for 14.4 ks. The secondary grain size was about 10 nm, and the primary particles were hexagonal plates of 100-200 nm size. This hexagonal thin plate-like character is common in transition metal chalcogenides (Ch) with formula of MCh_2 . The “polytype” of Ti sulfides exist in Ti-S binary system, and they consist of multi-stacking layers of closed hexagonal packing and fcc packing. Therefore, the sulfur concentration is varied in a wide range.

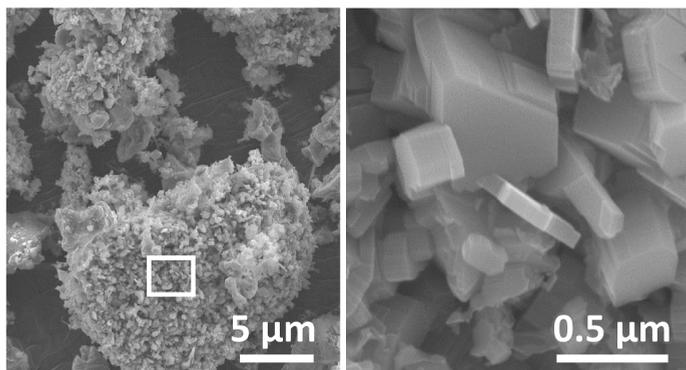


Fig. 10 SEM observation of the sample doubly sulfurized in CS₂ gas flow at 1073 K for 14.4 ks.

3.4 Electrolysis and Reduction in CaCl₂-CaS melt

The samples doubly sulfurized in CS₂ gas (#T and #U) were reduced at 1173 K, at 3.0 V in CaCl₂-0.5mol%CaS. The electric charge Q was served until $Q/Q_0 = 400\%$, where Q_0 is defined as the theoretical charge to form the necessary amount of Ca by considering the reduction of pure and stoichiometric TiS₂. As shown in Fig. 11, the current during the electrolysis with a constant voltage dropped at the initial stage, and approached to a constant value at $Q/Q_0 = 100\%$. The measured current vibrated a little probably because of the gas bubbling at the anode. After cooling, yellow sulfur was deposited on the inner surface of cooled parts of reaction vessel. The solidified salt and the sample were removed from the Ti basket in the dilute acetic acid with a slight smell of sulfur. After several rinsing with water, ethanol and acetone, the sample was dried and analyzed as listed in Table 1.

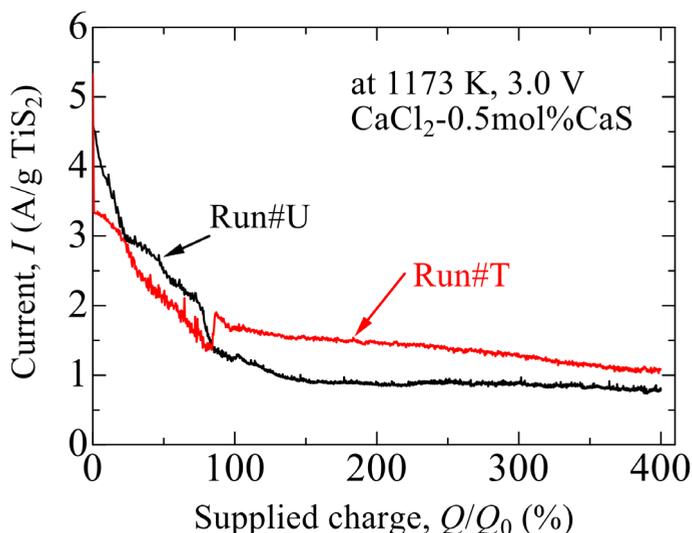


Fig. 11 Current behavior during electrolysis at 1073 K.

Table 1 Samples sulfurized from FeTiO₃ and subsequently reduced in molten salt.

Sample	#T	#R
Sulfurization by CS ₂ (g)	Temperature of CS ₂ (liq) = 293 K. Sulfurized at 1173 K for 43.2 ks.	
Phases after 2nd sulfurization	Ti _{2.45} S ₄ and Ti _{7.07} S ₁₂ with a small amount of TiO ₂	Ti _{2.45} S ₄ and Ti _{7.07} S ₁₂ with a small amount of TiO ₂
Impurity after 2nd sulfurization	2.95 mass%O 50.8 mass%S	1.16 mass%O 58.4 mass%S
Electrolysis	at 1173 K and 3.0 V in CaCl ₂ -0.5 mo%S, Q/Q ₀ = 400 %	
Phases after electrolysis	α-Ti and small amounts of TiO + Ti ₃ O ₅	α-Ti and a small amount of TiC
Impurity after electrolysis	1.38 mass%O, 0.053 mass%S, 0.34 mass%C	1.06 mass%O, 0.021 mass%S, 2.04 mass%C

Very low sulfur concentration reflects the non-soluble nature of sulfur in Ti. It proved that the present proposal can work from ilmenite, and that sulfur acts as the media to produce a high quality of metallic titanium with a very low sulfur concentration.

Carbon contamination might come from the graphite anode through the electrolysis of CO₃²⁻ [3,4]. It is also possible that CS₂ gas may be formed at the anode from the reaction of anodic graphite and S²⁻. In the used alignment for electrolysis, this CS₂ gas can react with the obtained Ti to form TiC. These carbon contaminations can be improved by the cell modification for electrolysis.

Oxygen contamination may come from the residual oxygen in sulfurization and partially from the water in CaCl₂ [4]. Thus some extra-tuning in operating conditions of sulfurization, iron removal and electrolysis is needed.

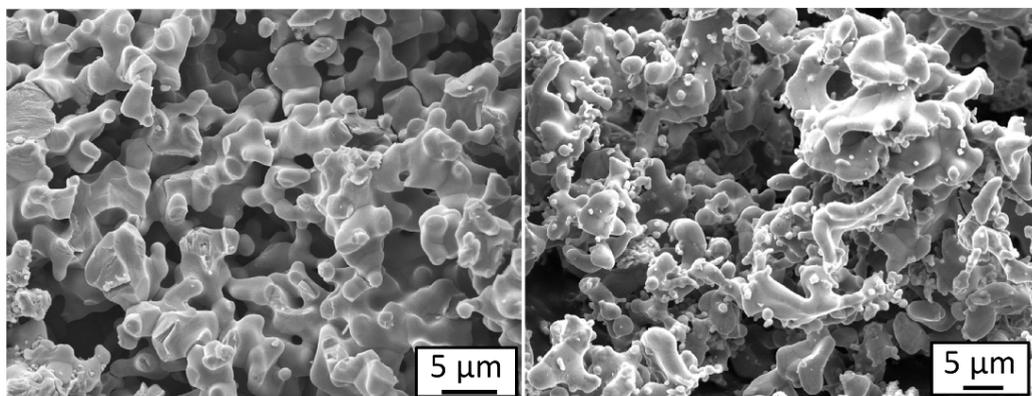


Fig. 12 SEM observation of the obtained titanium powder via TiS₂ (a) from TiO₂ and (b) from ilmenite.

Fig. 12 shows the comparison of titanium metallic particles obtained via TiS₂. Fig.12(a) and (b) show the powders starting from the commercial TiO₂ and from ilmenite, respectively, at the same electrochemical conditions. Reflecting the hexagonal plates of Ti sulfides, these Ti powders showed the porous morphology that some nodules jointed with a central spherical ball. This characteristic feature of Ti powder is expected suitable for 3D printer application.

4. Conclusion

Using CS₂ gas evaporated at room temperature, ilmenite was easily sulfurized to the mixture of Fe_{1-x}S and TiO₂ (rutile). Fe_{1-x}S was selectively removed by 1 M H₂SO₄ solution even at room temperature to the suitable level of 0.5 mass%Fe in Ti. Heating and violent stirring were not needed. After second sulfurization by CS₂ gas, Ti sulfides lower than TiS₂ were obtained and this mixture was electrochemically reduced in the molten CaCl₂-CaS at 1173 K. Successfully γ -Ti was obtained and the residual sulfur in Ti was as low as 0.021 mass%S. The by-product S₂(gas) in this work should be served to synthesis CS₂, which has already utilized in the chemical industry.

5. Acknowledgements

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6. References

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