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An innovative process for production of Ti metal powder via TiS_x from TiN

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Abstract

This work presents a new processing concept for production of Ti metal powder from $FeTiO_3$ via TiN and TiS_x. Because $FeTiO_3$ can be converted to TiN by carbothermal reduction and nitridation (CTRN) method, TiN was taken as the starting material. $Ti_{2.45}S_4$ and TiS_2 powders were completely formed from TiN at 1473 K (1200 °C) in 3.6 and 10.8 ks, respectively. Either CS_2 or S_2 gas could be utilized for the sulfurization process. The sulfides were then converted to α-Ti metal powders by Ono and Suzuki (OS) process in molten $CaCl_2$ with a small addition of CaS. Employing S_2 gas in sulfurization step remarkably reduced the carbon contamination to 0.01 and 0.1 wt% C after sulfurization and reduction processes, respectively. α-Ti powders with spherical morphology and foil-like Ti sheets containing less than 0.15 wt% O were obtained from the electrochemical reduction in molten $CaCl_2$-0.5 mol% CaS. The approach applied here offers a promising strategy to design an innovate process for production of commercial grade Ti powders via TiS_x and TiN from $FeTiO_3$ by nitridation, sulfurization and OS processes.

Keywords: Titanium, molten salt, titanium nitride, sulfurization, electrochemical reduction

I. Introduction

Processing of metallic Ti has been primarily performed through the discontinuous Kroll process which requires high carbo-chlorination temperature of about 1273 K (1000 °C) to synthesis $TiCl_4$, distill it at 473 K (200 °C), and convert it at 1273 K (1000 °C) to sponge Ti by Mg.[1] In addition, molten salt electrolysis of $MgCl_2$ takes a long time at 923 K (650 °C) for recycling of

reductant Mg.[2-4] Thus, Ti communities are persistently working to innovate feasible and economically viable pyro and/or hydro-metallurgical processes to remarkably drive down the cost of Ti metal powder processing. The environmental regulations have been also considered in the newly developed methods such as innovative electrochemical reduction methods and low-temperature chlorination process (LTCP).[2] For example, TiO_2 feedstocks have been used for production of metallic Ti in the electro-deoxidation and calciothermic reduction routes as called FFC Cambridge (Fray, Farthing and Chen) and OS (Ono and Suzuki) processes.[5, 6] On the other hand, ilmenite ($FeTiO_3$) can be converted to titanium oxycarbonitride ($TiO_xC_yN_z$) via carbothermal reduction and nitridation (CTRN) process and subsequent iron removal step in an ammonium chloride (NH_4Cl) solution.[7-9] The TiN and $TiO_xC_yN_z$ prepared from $FeTiO_3$ can be easily chlorinated at very low temperatures such as about 400 °C [2], which could be an alternative route to carbo-chlorination at high temperatures taken in Kroll process. Especially, this method has a merit of the less contamination of Fe derived from $FeTiO_3$ with low operating costs.[2, 7, 8, 10]

Figure 1 illustrates the main processing steps in the present concept in comparison with various methods developed for production of Ti metal from $FeTiO_3$. High quality TiN or $TiO_xC_yN_z$ can be processed from Ti ores and utilized in chlorination or sulfurization processes. It is worth noting that $TiCl_4$, synthesized by high-temperature carbo-chlorination of TiO_2, has been employed for production of Ti metal by CSIRO ($TiRO^{TM}$)[11, 12] and TiH_2 powders by ADMA non-Kroll process by Mg reduction.[13, 14] In addition, iron-free TiN may be refined and converted to Ti metal powder by electrochemical USTB method.[15] Moreover, it has been stated that titanium oxycarbides can be readily converted to Ti metal by electrochemical MER[16, 17] and Chinuka[18] processes. Ti(C,O) pellets in these processes were prepared by partial carbothermal reduction of TiO_2 under vacuum or in an inert atmosphere and used as anodes in the successive refining process.

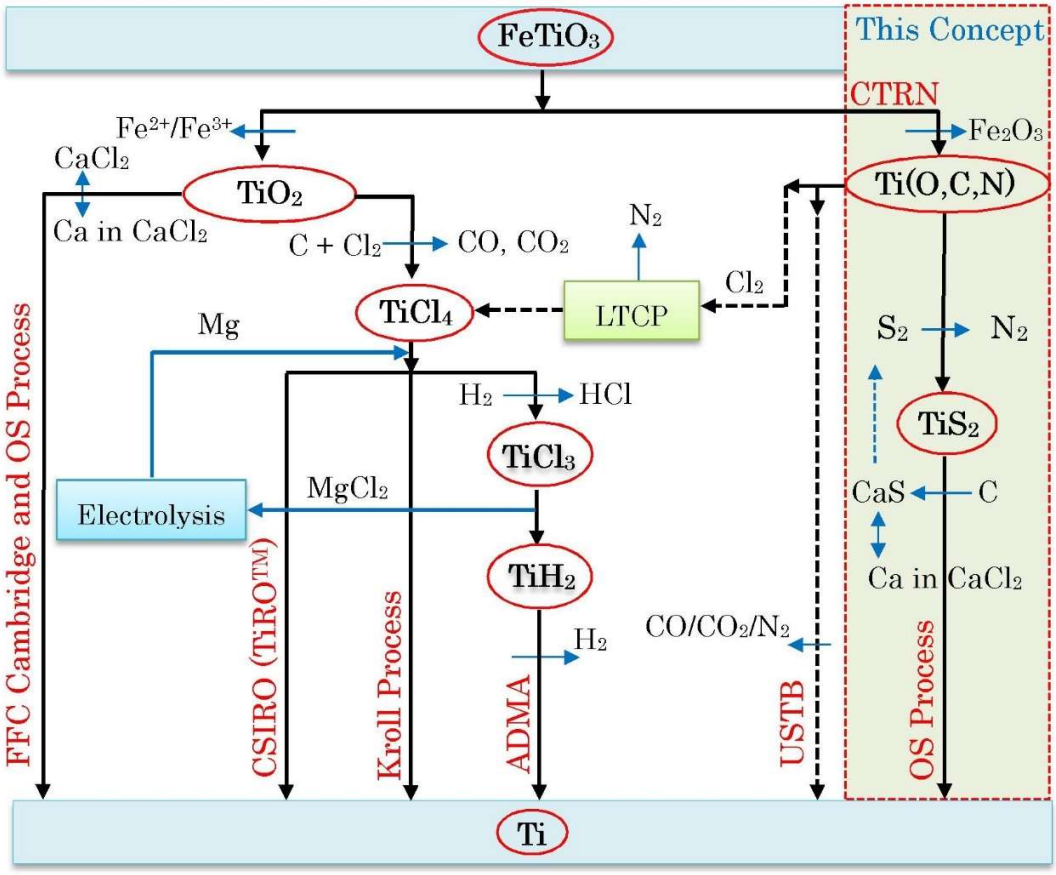


Fig. 1 — A flowchart of the concept for preparation of Ti metal powder via TiS_2 synthesized from TiN compared to the Kroll process[1], and newly developed CSIRO[11], FFC Cambridge[19], OS[6], ADMA non-Kroll[14] and USTB[15] processes.

Several methods have been proposed for production of Ti metal; however, the well-developed FFC and OS processes have been cited as economically viable routes for production of metallic Ti powders. The main limitations of electrochemical reduction of TiO_2 could be (a) formation of the intermediated phases, such as titanium suboxides or perovskite phase of calcium titanite ($CaTiO_3$) and (b) dissolution of CO/CO_2 gas from the surface of graphite anode in the molten salt.[20-22] The former phenomena are considered as kinds of kinetic barriers in hampering the diffusion of ionized oxygen from the cathode outward to the molten environment.[5, 23] The latter leads to the consumption of a significant amount of Ca and results in prolonged electrolysis. Use

of TiS_2 in the electrolysis hinders the formation of CO/CO_2 during electrolysis and carbon impurity of titanium can be remarkably reduced as stated by Suzuki et al. [22, 24-27] Therefore, developing a novel method for synthesis of TiS_2 from natural Ti resources could be a great interest in the Ti community.

As reported previously, both commercial TiN and $TiO_xC_yN_z$ synthesized from $FeTiO_3$ can be entirely sulfurized by CS_2 gas to TiS_x.[10] TiN can be fully transformed to the single phase of $Ti_{2.45}S_4$ by CS_2 sulfurization at (1473 K) 1200 °C in a short time, such as 3.6 ks, according to the following reaction:[10]

$$TiN + \frac{x}{2} CS_2(g) = TiS_x + \frac{x}{2} C + \frac{1}{2} N_2(g) \; ; (1 \leq x \leq 2) \quad (1)$$

where x is the molar ratio of S to Ti in the sulfide phases.

In sulfurization of TiN, apparent N^{3-} ions could be replaced by S^{2-} ions to have the balanced charge in the sulfide products.[10] Formation of non-stoichiometric $Ti_{2.45}S_4$ in the sulfides might be also explained by the crystalline defect of Ti_2S_3 and TiS_2 due to phase transformation as explored by Basu et al.[28] Formation of titanium oxysulfides prior to the electrolysis should be also avoided to obtain high-quality Ti powders, because the oxygen removal is more difficult than sulfur from the obtained Ti metal.

Recently, OS process has been applied to reduce the sulfides to the metallic Ti powders.[26, 27, 29] OS process originally involves: (a) calciothermic reduction of TiO_2 and (b) recovery of Ca from in situ electrolysis of CaO in molten $CaCl_2$ melt.[6, 30, 31] Suzuki et al.[26, 27] have expanded the applicability of OS process not only to the oxide but also to the sulfide. TiS_2 powder was also synthesized by CS_2 sulfurization from TiO_2[32], and the obtained sulfides were converted to Ti metal powder in molten salt.[26, 27] The reduction process of TiS_2 by Ca and formation of CS_2 / S_2 gases can be expressed according to the following reactions:[25, 27]

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

$$Ca^{2+} + 2e^{-} = Ca \quad (3)$$

$$TiS_x + x\ Ca = Ti + x\ CaS \quad (4)$$

$$S^{2-} = \frac{1}{2} S_2(g) + 2e^{-} \quad (5)$$

The amount of residual oxygen in the Ti powders, reduced from commercial TiS_2, was reported to be as high as 1.0 mass% O and the carbon contamination which is the main focus of the present work has not been discussed in details.[29] Hence, it is expected to prepare the sulfides with low oxygen contamination to increase the current efficiency of the process. Additionally, it is desired to design a process for the preparation of sulfides from natural resources such as $FeTiO_3$. In our previous studies, the commercial TiS_2 powder was contaminated by about 1.0 mass% O, and it was considered as high oxygen content after reduction of TiS_2. A high purity of TiS_2 is favorable to obtain the less residual oxygen, because the commercial purity of TiN is less than 0.01 mass% O. Thus, TiN can be taken as oxygen-free starting material.

In synthesis of sulfides from TiN by CS_2, samples may be contaminated to some extent by free carbon formed from decomposition of CS_2 gas in the reaction vessel. Indeed, the concern is raised on carbon contamination in case that gaseous CS_2 is applied in sulfurization step.[10, 26, 27] Applying naturally abundant S_2 gas in synthesis of TiS_2 is not only thermodynamically favorable, but also it can significantly reduce the carbon contamination and processing costs.

$$TiN + \frac{x}{2} S_2(g) = TiS_x + \frac{1}{2} N_2(g)\ ;\ (1 \le x \le 2) \quad (6)$$

Therefore, this work aims to present a new concept for production of industrial grade Ti metal powders by employing high quality TiS_2 in OS process. This paper presents that TiS_2 could be obtained by sulfurization of TiN using S_2 gas. In addition, carbon contamination which is a challenging and critical issue in production of high quality Ti metal powders is elaborated.

II. Experimental Procedure

A. Materials

TiN with the purity of about 99.5% and mean particle size of 50 μm (Wako Chemical Co., Japan), sulfur powder (≥ 98%, Wako Chemical Co.) and the volatile liquid carbon disulfide, CS_2 (99.99%, Wako Chemical Co.) were applied as starting materials in sulfurization experiments. Calcium chloride, $CaCl_2$ (99.1%, Hayashi Chemicals) and CaS (99%, Furuuchi Chemical Co., Japan) were also used as received without further purification in the electrochemical reduction step.

B. Synthesis of titanium sulfides

In this study, sulfurization of TiN was conducted at 1473 K (1200 °C) for either 3.6 or 10.8 ks using S_2 gas. Another sample was prepared by CS_2 sulfurization at 1473 K (1200 °C) for 3.6 ks. Details of the sulfurization process by using CS_2 gas were described elsewhere.[10] A dual-zone furnace was specifically designed and manufactured to evaporate the sulfur powder at relatively low temperatures of approximately 573 K (300 °C). It is noted that melting and boiling points of sulfur under standard atmospheric pressure are 385.95 K (112.8 °C) and 717.75 K (444.6 °C), respectively. S_2 gas was transferred into the hot zone of the reactor where 0.25 g of TiN was placed in an alumina boat. The dual-zone reactor is shown schematically in Figure 2(a). The temperature profile at experimental conditions is also plotted in Figure 2(b), which clearly shows the existence of two constant temperature zones. A high purity Ar gas (≥ 99.9998%) with the flow rate of 10 ml/min was used to transport S_2 gas to the reaction site. The carrier gas was passed through the silica gel columns to lose moisture. The mass changes of the samples were measured to quantify the progress of the sulfurization reaction.

C. Electrochemical reduction of the sulfides

The sulfides synthesized at different conditions were used in OS process for production of Ti metal powder. 1.5 g of the sulfides was loaded into a basket cathode made of Ti net and reduced in molten $CaCl_2$ with addition of 0.1 or 0.5 mol% CaS. In addition to the sulfides, direct electrolysis of TiN was also conducted in molten $CaCl_2$-0.5 mol% CaS. A high-density carbon rod (10 mm in diameter) was used as an anode and it was attached to a Ti rod (6 mm diameter, 800 mm length). An MgO crucible with purity of 99.5% (90 mm in diameter and 200 mm in height) was filled with 600 g of mixed $CaCl_2$-CaS salt and gradually heated in vacuum (less than 10 Pa) up to 1173 K (900 °C). The supplied charge (Q/C), current density as well as electrolysis temperature and pressure were precisely monitored by a data acquisition unit (Agilent 34972A Data Acquisition Switch Unit). The molten salt was dehydrated overnight in vacuum at 1173 K (900 °C). $CaCl_2$-CaS melts were also purified by pre-electrolysis using an auxiliary carbon electrode at 2.0V and 1173 K (900 °C) in an Ar atmosphere with a continuous flow rate of 50 ml/min for 3.6 ks. Then, the electrolysis process was performed at 3.0V and Q/Q_0 = 400 % where Q_0 is stoichiometric electric charge. A schematic of the reactor in OS process used for the calciothermic reduction of TiS_2 is depicted in Figure 3.

D. Materials characterization

Characterization of the powders was performed by X-ray diffraction (XRD, Philips, PANalytical X'Pert Pro, Cu-K_α). The samples were coated with Au (JEOL, JFC-1200) and scanning electron microscopy (SEM; JEOL JSM 6510LA) equipped with energy dispersive X-ray spectrometer (EDS) was used to examine the chemical composition and morphologies of the products. LECO analyses (TC600 and CS600) were carried out to determine the residual O, C, N and S in the synthesized sulfides and Ti metal powders.

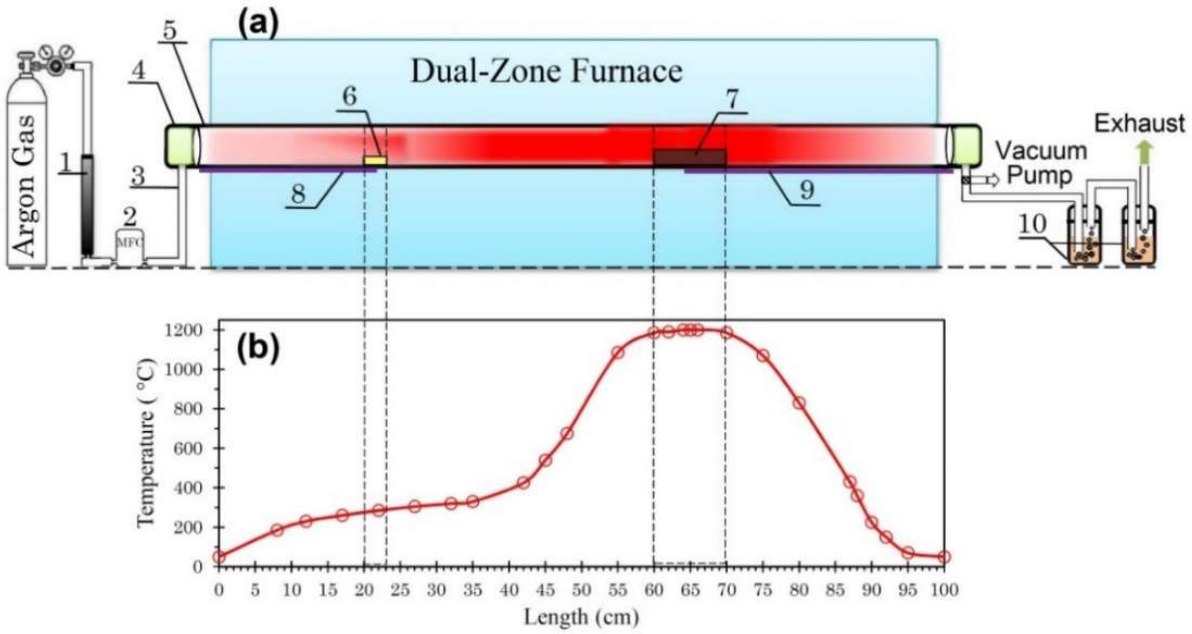


Fig. 2 — Experimental set-up for sulfurization process, (a) Schematic of the dual-zone furnace, (b) The temperature profile of the furnace set at 573 K (300 °C) and 1473 K (1200 °C), respectively for evaporation of sulfur and sulfurization of TiN. 1- silica gel, 2- mass flow controller (MFC), 3- Teflon tube, 4- glass cap, 5- reactor, 6-sulfur in an alumina boat, 7- sample in an alumina boat, 8, 9- thermocouples, 10- 1 M NaOH scrubber.

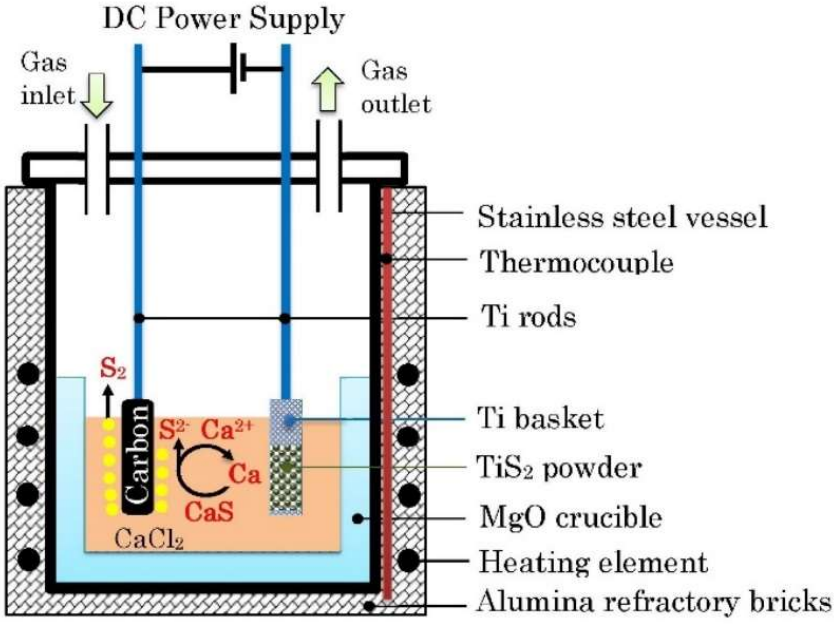


Fig. 3 — A schematic of the reactor used for electrolysis of TiS_2 powders.

III. Results and Discussion

A. Sulfurization of TiN by CS_2 and S_2 gases

In this study, titanium sulfides were synthesized from TiN using S_2 gas at 1473 K (1200 °C) in 3.6 ks or 10.8 ks, where the evaporation temperature of sulfur was set at 573 K (300 °C) in low-temperature zone of the furnace.

The partial pressure of sulfur gas (P_{S_2}) was evaluated from the mass changes of sulfur powder in an alumina crucible. About 0.85 g sulfur was evaporated at 573 K (300 °C) for 3.6 ks under an Ar gas with the flow rate of 10 ml/min. This results in about 5 ml S_2 gas/min, and $P_{S_2}^{Exp}$ was experimentally approximated as 33 kPa.

The equilibrium pressure of sulfur ($P_{S_8}^0$) is 3.57 kPa at 573 K (300 °C) which was evaluated using thermodynamic database.[33]

$8S = S_8$ (g) $\Delta G°$ (at 573 K) = 15.937 kJ/mol (7)

In this way, we evaluated $P_{S_i}^0$ (i=2, 3, …, 8) and $P_S^{Total} = \sum P_{S_i}^0$ was obtained as 6.0 kPa which was lower than $P_{S_2}^{Exp}$ (33 kPa) in the reaction vessel. This apparent discrepancy could be because of the high Ar flow rate to transport sufficient sulfur to the reaction site and to prevent backflow and deposition of sulfur gas in inlet of the alumina tube.

The results were compared with the sample synthesized using CS_2 gas for 3.6 ks. Figure 4 shows the XRD diffraction patterns of a commercial grade TiN powder (ICSD# 01-087-0632)[34] and the obtained sulfides. The sulfurization process of TiN using CS_2 gas yielded the single phase of $Ti_{2.45}S_4$ (ICSD# 01-072-0820)[35] in 3.6 ks. However, the samples prepared in an S_2 gas atmosphere consisted mainly of TiS_2 (ICSD# 01-088-2479)[36] phase with small amount of non-stoichiometric phase of $Ti_{2.45}S_4$. TiS_3 phase was not observed in any of the samples. Carbon and S_8 were not also detected in the samples.

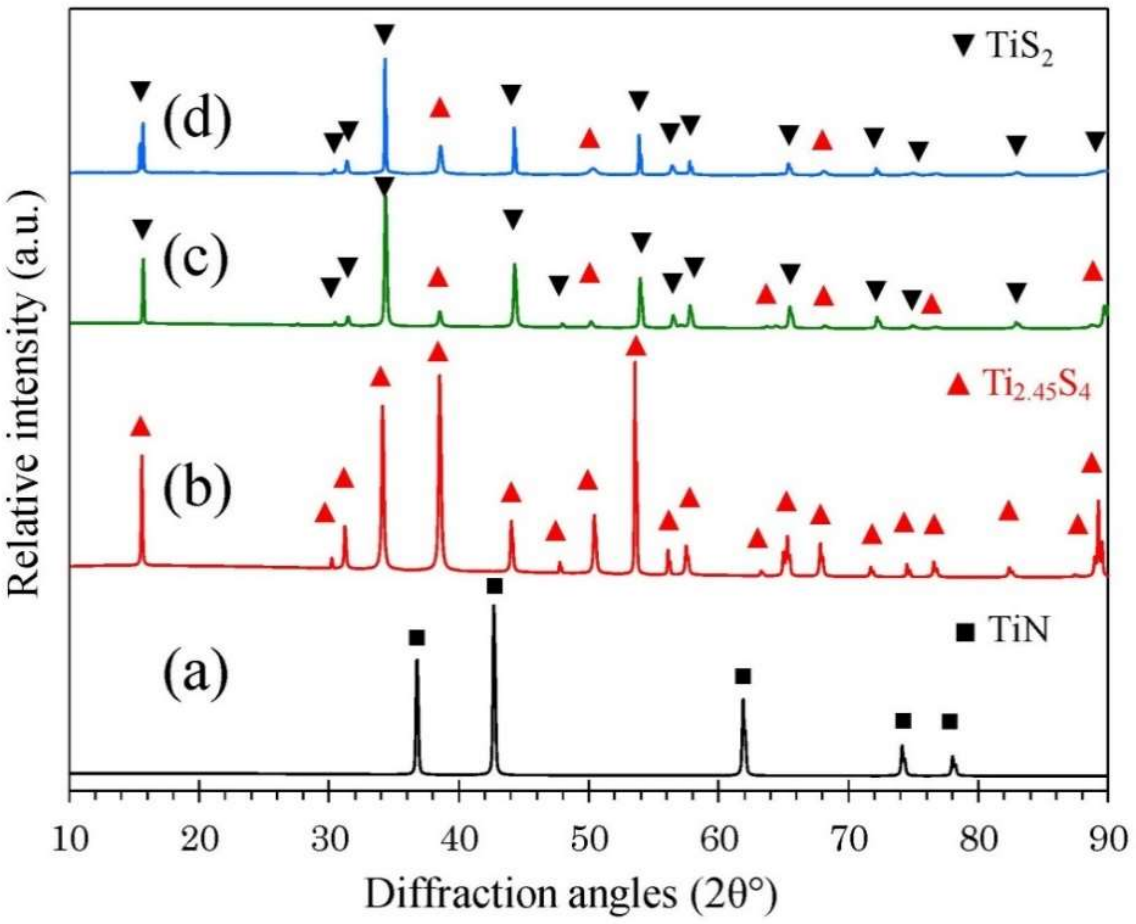


Fig. 4 — XRD patterns of (a) as-received TiN powder and the sulfurized TiN samples at 1473 K (1200 °C) using CS_2 gas for (b) 3.6 ks, S_2 gas for (c) 3.6 ks and (d) 10.8 ks.

The mass changes of TiN samples were measured after cooling in an Ar gas atmosphere to room temperature. The degree of sulfurization ($\Delta W/W_i$) of the samples was defined for the sulfurized samples, where ΔW and W_i represent the mass gain and initial weight of the samples, respectively. The degree of sulfurization, $\Delta W/W_i$, of the samples prepared in CS_2 and S_2 gases are listed in Table I. The degree of sulfurization of the sample prepared in an S_2 gas atmosphere in 10.8 ks was about 74 ± 0.6%, which is higher than 71 ± 0.8% and 55.3 ± 0.6% determined for the samples prepared in S_2 and CS_2 gases in 3.6 ks. The experimental data matched well with the theoretical values of 81.10% and 55.10% calculated for formation of Ti_2S_3 and TiS_2 phases,

192 respectively, from TiN. It is noted that the theoretical value for formation of $Ti_{2.45}S_4$ is 61.97%.
193 When CS_2 gas is applied as sulfurization agent, S_2 gas could be formed from the decomposition of
194 CS_2 gas [10]. Then, we may assume here that $Ti_{2.45}S_4$ and TiS_2 phases are formed by sulfur
195 enrichment from the stoichiometric Ti_2S_3.[37]

196 SEM images taken from TiN and the prepared sulfides are shown in Figure 5. The well-
197 crystallized hexagonal plates of titanium sulfide can be clearly seen in the products. In addition,
198 homogeneous and entirely similar morphology of the sulfide particles with average size of about
199 5 μm were distinguished for both CS_2 and S_2 sulfurization. The energy dispersive X-ray
200 spectroscopy (EDS) analysis (Table II) also quantitatively proved the formation of higher sulfides.
201 The molar ratio of S to Ti in the hexagonal shape particles were 1.71 and 1.74 for the samples
202 synthesized by CS_2 and S_2 gases, respectively, for 3.6 ks. These values are close to $Ti_{2.45}S_4$ and
203 TiS_2 phases, respectively, as identified by XRD. The elemental analysis also showed that nitrogen
204 and particularly carbon contents of the sulfide prepared by CS_2 gas were fairly high, whereas they
205 were not detected in the sulfides prepared by S_2 gas, indicating that TiN was extremely transformed
206 to titanium sulfides under an S_2 atmosphere. The molar ratios of S to Ti (1.71 and 1.84) are also
207 in good agreement with the reported ratios of S/Ti = 1.74 for Ti_2S_3 and S/Ti = 1.97 for TiS_2
208 phases.[28]

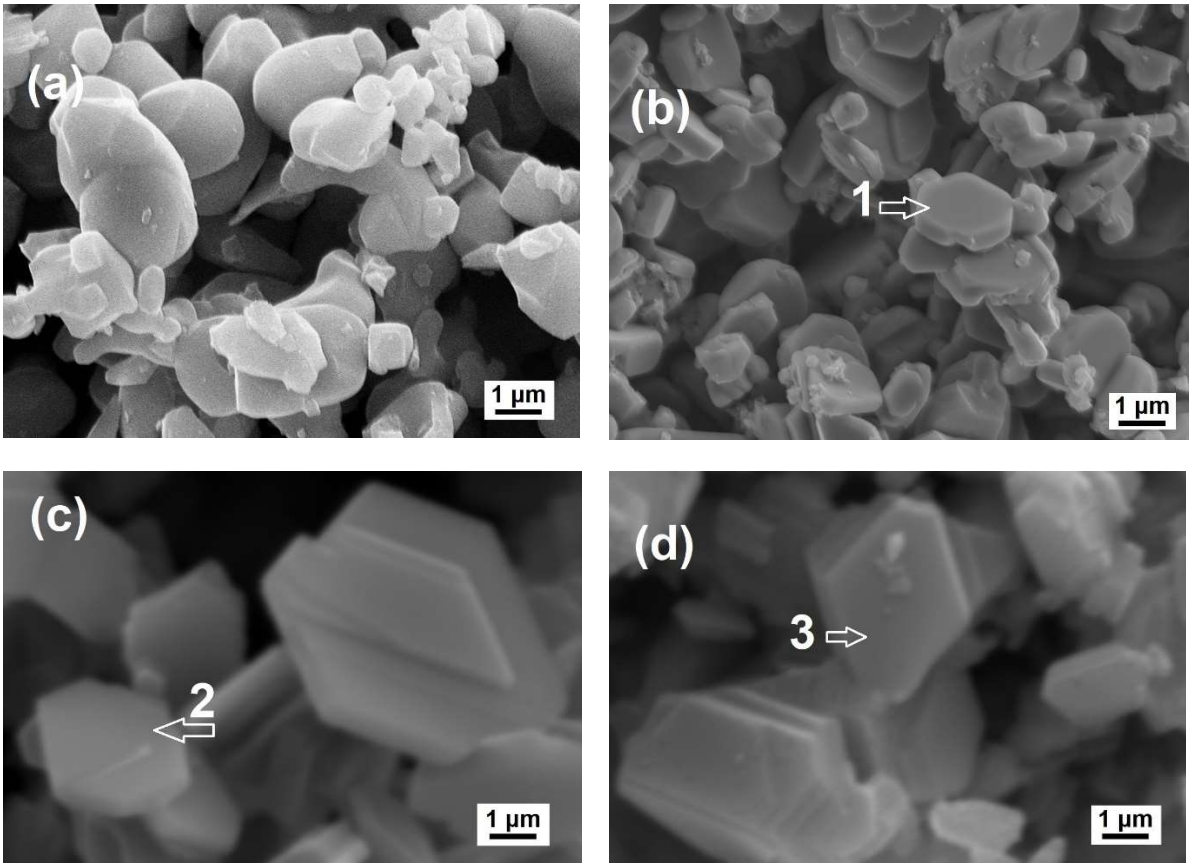


Fig. 5 — SEM morphology of (a) as-received TiN, (b) the single phase $Ti_{2.45}S_4$ synthesized from TiN at 1473 K (1200 °C) by CS_2, and the sulfides prepared from TiN at 1473 K (1200 °C) by S_2 gas for (c) 3.6 ks and (d) 10.8 ks.

The carbon, sulfur, oxygen and nitrogen contents in the sulfides prepared from TiN were determined by LECO analysis and summarized in Table III. About a few tens mg of the samples was analyzed, and at least three independent measurements were averaged. As is clearly presented, the sample sulfurized with CS_2 gas was contaminated with carbon by comparing to the sulfides prepared exclusively in S_2 gas at the same sulfurization temperature. The carbon contents of the sulfides were significantly reduced when CS_2 was replaced with S_2 gas in the sulfurization process. This is a great achievement in synthesizing low-carbon sulfides. The suppression of carbon contamination to less than 0.01 wt% can enable the synthesis of Ti powders coincident with the expectations and industrial regulations.

220 ***B. Electrochemical reduction of the titanium sulfides by Ca***

221 These sulfides were electrochemically reduced at 1173 K (900 °C) in molten $CaCl_2$-CaS salt
222 in which the concentration of CaS was set to 0.1 or 0.5 mol% CaS. Figure 6 illustrates the changes
223 of current (A/g of TiS_2) with respect to the supplied charge ($Q/Q_{0,}$%) during the electrolysis of the
224 sulfides by charging 3.0 V between two electrodes. The variation of the current recorded in the
225 process are in good agreement with the previous studies conducted the electrochemical reduction
226 of pure TiS_2 at various molar ratios of CaS in $CaCl_2$ molten salt.[24-27, 38] The graph for the direct
227 electrolysis of TiN (Run # 1) shows that the current recorded at 3.0 V in molten $CaCl_2$-0.5 mol%
228 CaS salt was very weak. The current was relatively constant at about 0.75 A/g for the whole
229 process time, and it was much lower than those of the sulfide samples. This indicates unsuccessful
230 calciothermic reduction of TiN in molten $CaCl_2$. In other words, the reaction between dissolved
231 Ca and TiN was thermodynamically unfavorable and Ca_3N_2 was not formed according to the
232 following reaction:

233 $$TiN + Ca = Ti + Ca_3N_2 \qquad \Delta G° \text{ (at 1173 K)} = + 253 \text{ kJ/mol} \qquad (8)$$

234 The high amount of current at the start of electrolysis could be also due to the presence of small
235 amount of water in the molten salt. However, the current for reduction of sulfide samples was
236 notably large particularly at the first stage of reduction which shows continues formation of CaS
237 and increasing the conductivity of the molten salts.

238 The sulfide prepared by CS_2 gas in 3.6 ks was reduced to Ti metal by addition of 0.5 mol%
239 CaS into the melt (Run # 2). The samples prepared by S_2 gas in 3.6 and 10.8 ks were also,
240 respectively, reduced to Ti metal powders by addition of 0.1 and 0.5 mol% CaS in experimental
241 runs of # 3, 4 and 5, 6. Addition of higher mol% of CaS slightly increased the current density in
242 the electrolysis (Runs 5 and 6). The solubility limit of CaS in molten $CaCl_2$ was reported to be
243 1.77 ± 0.1 mol% CaS at 1173 K (900 °C).[25] At the initial stage of the electrolysis up to

approximately Q/Q_0 = 100%, the current densities were relatively high compared to the next step where the current decreased gradually. The current decreased with the progress of the electrolysis after some fluctuation and approached constant values of about 1.0 A/g at the end of electrolysis. This means that the reduction rate was relatively high in the beginning of the process when the decomposed Ca from CaS entered the cathode vicinity. The deposition of Ca at cathode may occur at higher rates particularly for the melts containing 0.5 mol% CaS (Runs 2, 5 and 6). This results in release of remarkable amounts of CS_2 and/or S_2 gases at carbon anode. Thus, the gas bubbling at the anode may lead to the fluctuation of the current density recorded in the first steps particularly up to about Q/Q_0 = 100% as is observed in Figure 6. When 0.1 mol% CaS was added into the melt, Ca metal could be steadily formed without current fluctuation and reacted with titanium sulfides.

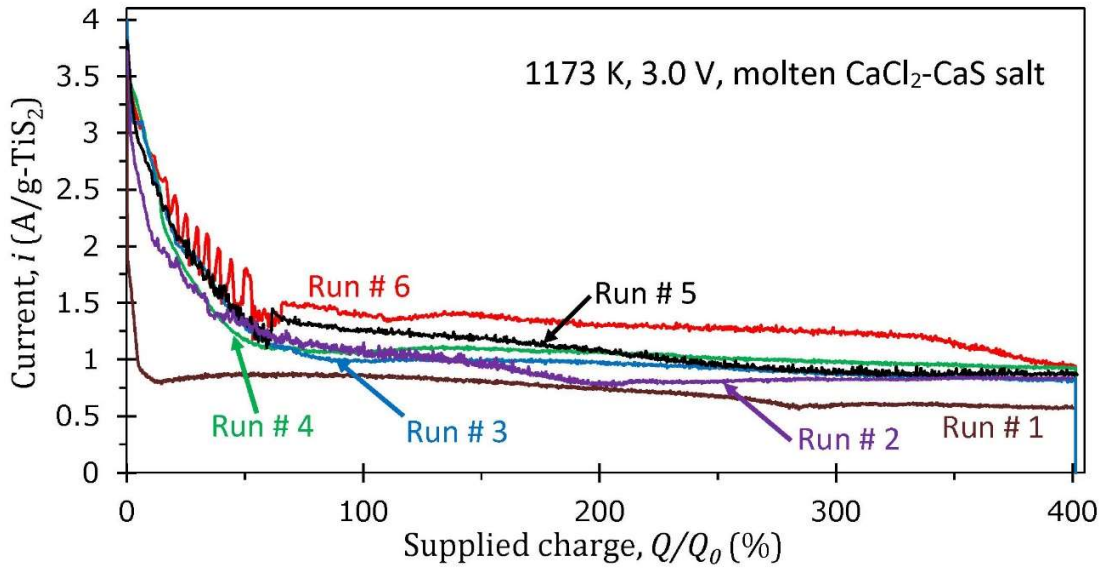


Fig. 6 — Cathodic current in ampere per gram (A/g) of TiS_2 as a function of supplied charge (%) in the electrolysis process at 1173 K (900 °C) and 3.0 V in $CaCl_2$-x mol% CaS (x = 0.1 and 0.5) for direct electrolysis of TiN and the sulfides prepared by CS_2 and S_2 gases in 3.6 ks and 10.8 ks at 1473 K (1200 °C).

The cathodes were taken out of the molten salt before cooling down under an Ar atmosphere. Then, Ti basket was separated from the solidified $CaCl_2$ salt in which Ti powder was formed. The

powders were carefully washed three times with distilled water and dilute acetic acid. Finally, the obtained Ti powders were washed with water, ethanol, acetone, and dried in vacuum for a day. The calciothermically reduced samples were analyzed by XRD and LECO methods.

It was impossible to obtain Ti metal by direct electrolysis of TiN in molten $CaCl_2$ by OS process. The final sample also contained merely unreacted TiN in agreement with time-dependency of current for reduction of TiN at cathode. However, electrochemical reduction of TiS_2 was attainable and the sulfide samples were easily reduced to Ti metal powders. The XRD and LECO results of the reduced sulfides are summarized in Table IV.

The samples reduced in $CaCl_2$ - 0.1 mol% CaS melts were not entirely transformed to α-Ti metal powder, and small amounts of titanium suboxides in the form of Ti_6O and/or Ti_3O appeared in XRD phase identifications (Runs 3 and 4). The existence of residual oxygen may be due to insufficient Ca supply. It is noted that liquid Ca can be formed from CaS, because its theoretical decomposition voltage is 2.01 V which is much lower than 3.2 V needed for theoretical decomposition of $CaCl_2$.[27] As is shown in Figure 6, the lower CaS molar ratios indicated the lower conductivity of the molten salts and resulted in prolonged electrolysis time. By increasing CaS addition, a higher amount of metallic Ca enters into the cathode vicinity increases the reduction rate of the samples particularly in the earlier stage. In contrast, the lower molar ratios of CaS in molten salts may require the longer electrolysis time to fully remove the residual oxygen due to slow diffusion of oxygen in α-Ti powder and low conductivity of the melts. The carbon contents of the samples reduced with 0.1 mol% CaS (Runs 3 and 4) were above 0.14 wt%, lower than that prepared by CS_2 (1.32 wt% C in Run 2). The carbon contents decreased further when 0.5 mol% CaS used in the reduction process (Runs 5 and 6), which might be due to high conductivity of the melts and faster electrolysis. The identified phases of the samples reduced in $CaCl_2$-0.5

283 mol% CaS melt were entirely metallic α-Ti powder. The residual S and N in its low-carbon sample
284 (Run 6) were also as low as 0.053 wt% S and 0.003 wt% N, respectively.

285 The reduction product obtained from the sample prepared by CS_2 contained a small amount of
286 TiC, which could be due to the following reasons: (a) high carbon content in the sulfide, (b)
287 formation of TiC from the reaction between Ti particles and partially generated CS_2 on the graphite
288 anode.[3, 22, 27] Interestingly, TiC was not detected by XRD in Ti powders obtained from the samples
289 sulfurized by S_2 gas. Furthermore, LECO analysis showed 0.84 and 0.76 wt% O in the samples
290 prepared by S_2 gas for 3.6 and 10.8 ks, respectively. Oxygen contamination might come from
291 insufficient drying process due to the strong hygroscopic properties of $CaCl_2$.[22, 39] The residual
292 oxygen may be reduced in a longer electrolysis time because of the slow diffusion of oxygen in
293 solid. Besides, Noguchi et al.[22] also investigated the effect of dehydration on the residual oxygen
294 contents of the samples, and they showed that Ti powder with 0.42 mass% O could be obtained
295 from $CaTiO_3$ at Q/Q_0 = 600%. Needless to note that the exposure of very fine Ti particles to water
296 taken for the present approach may also contaminate the sample surface. Thus, we believe that the
297 residual oxygen in the samples can be removed either by further improvement or longer refining
298 process.

299 In this process, half of the deposited Ca may be dissolved into molten $CaCl_2$ and the electrolysis
300 was mainly completed in two stages. The initial stage (Q/Q_0 < 100%) was quite efficient for
301 reduction of the sulfides and removing the residual oxygen. However, the late stage of deoxidation
302 was slower, and the excess supplied charge of $3Q_0$ was applied to remove the residual oxygen from
303 the sulfide. Therefore, the current efficiency of the electrolysis can be estimated to be roughly 25%
304 by considering a complete oxygen removal from the sulfurized sample.

XRD patterns and SEM micrographs of the electrochemically reduced samples obtained from Runs 5 and 6 are shown in Figures 7 and 8, respectively. The single phase of α-Ti in both specimens was identified by XRD patterns. The macro-structure of the analyzed powders consisted of foil-like Ti sheets as shown in Figures 7 (a) and (b).

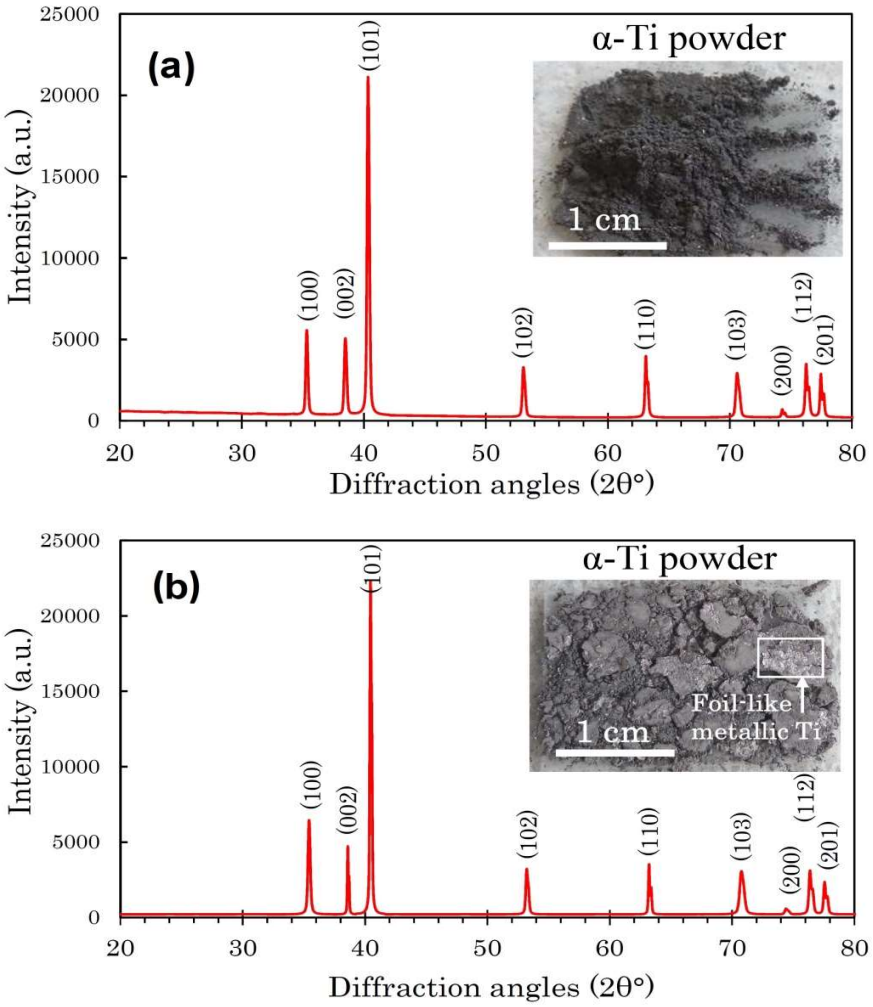


Fig. 7 —XRD patterns of α-Ti metal powders obtained from the sulfides prepared by sulfurization of TiN at 1473 K (1200 °C) using S_2 gas in (a) 3.6 ks and (b) 10.8 ks.

The concentration of oxygen in this work decreased to less than 1.0 mass% O which was reported for the samples obtained by electrolysis of commercial TiS_2.[26] The oxygen content may be lowered further by supplying higher charges and optimization of electrolysis cell. Nevertheless,

the residual carbon, sulfur and nitrogen contamination in the final powder (Run 6) were about 0.1 wt%, 530 ppm and 30 ppm, respectively. The foil-like metallic Ti sheets also showed a satisfying purity with low oxygen (≤ 0.15 wt% O) without carbon, nitrogen and sulfur contamination. As can be seen from Figures 8 (a) and (b), α-Ti powders are comprised of relatively spherical and interconnected round particles with particle sizes distribution ranged from 1 to 5 μm. The spherical shape Ti powders synthesized in the present work could have promising applications in additive manufacturing or 3D printing technology for manufacturing complicated, near-net-shape products.[40, 41] This work showed the feasibility of Ti metal powder production from TiN via TiS_x from the scientific viewpoint, but the exact evaluation of heat balance in the process was not yet evaluated deeply.

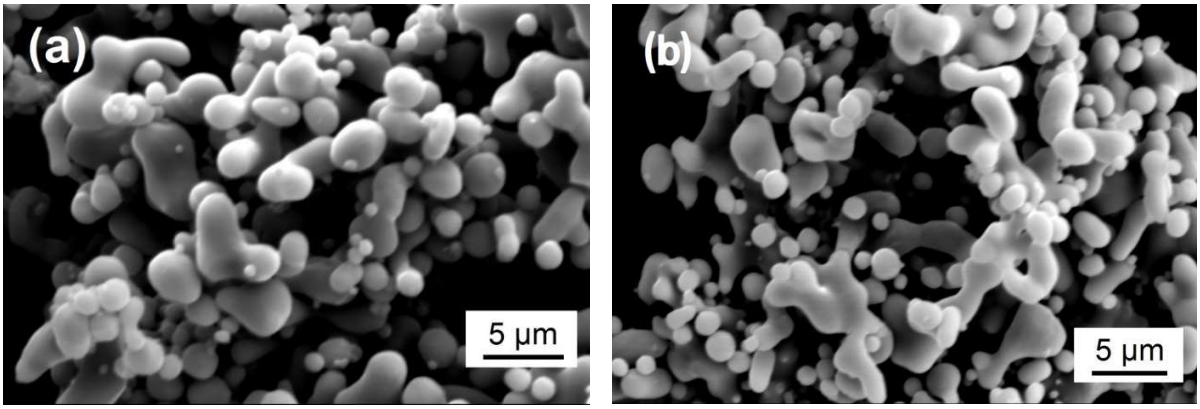


Fig. 8 — SEM micrographs of α-Ti metal powders produced in $CaCl_2$-0.5 mol% CaS melt by OS process from the sulfides synthesized at 1473 K (1200 °C) from TiN using S_2 gas in (a) 3.6 ks and (b) 10.8 ks.

The yellow-colored sulfur was also deposited as a ring on the inner walls of the electrolysis cell. The deposited sulfur can be, therefore, recycled back for formation of sulfides from TiO-TiC-TiN and $FeTiO_3$.[10, 29] Because of sulfur distillation, the purified deposits can be taken, and this recycling method offers a promising strategy to produce industrial grades Ti metal powder from TiN by OS process.

IV. Concluding Remarks

TiN was successfully sulfurized to $Ti_{2.45}S_4$ and TiS_2 micro-sized powders by CS_2 and S_2 gases at 1473 K (1200 °C) in 3.6 ks. Then, electrochemical reduction of obtained TiS_2 samples were performed to produce Ti metal powder in molten $CaCl_2$-x mol% CaS (x = 0.1 and 0.5). Interestingly, Neither TiC nor TiN phases were observed in the samples prepared by S_2 gas sulfurization. The resulting spherical α-Ti powder with interconnected round particles consisted of high purity foil-like sheets of Ti that contained less than 0.02 wt% C, 0.15 wt% O, 0.002wt% S and 0.003wt% N. These values pass the chemical regulation of titanium powder specified by JIS 2nd grade. The sulfide with ≤ 0.01 wt% C and ≤ 0.05 wt% S was synthesized by abundant S_2 gas generated at 573 K (300 °C) in a short time (3.6 ks), followed by electrochemical reduction in $CaCl_2$-0.5 mol% CaS at 1173 K (900 °C). These findings confirm a promising method for production of industrial grade titanium powder.

Acknowledgments

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Fig. 1 — A flowchart of the concept for preparation of Ti metal powder via TiS_2 synthesized from TiN compared to Kroll process[1], and newly developed CSIRO[11], FFC Cambridge[19], OS[6], ADMA non-Kroll[14] and USTB[15] processes.

Fig. 2 — Experimental set-up for sulfurization process, (a) Schematic of the dual-zone furnace, (b) The temperature profile of the furnace set at 573 K (300 °C) and 1473 K (1200 °C), respectively for evaporation of sulfur and sulfurization of TiN. 1- silica gel, 2- mass flow controller (MFC), 3- Teflon tube, 4- glass cap, 5- reactor, 6-sulfur in an alumina boat, 7-sample in an alumina boat, 8, 9- thermocouples, 10- 1 M NaOH scrubber.

Fig. 3 — A schematic of the reactor used for electrolysis of TiS_2 powders.

Fig. 4 — XRD patterns of (a) as-received TiN powder and the sulfurized TiN samples at 1473 K (1200 °C) using CS_2 gas for (b) 3.6 ks, S_2 gas for (c) 3.6 ks and (d) 10.8 ks.

Fig. 5 — SEM morphology of (a) as-received TiN, (b) the single phase $Ti_{2.45}S_4$ synthesized from TiN at 1473 K (1200 °C) by CS_2, and the sulfides prepared from TiN at 1473 K (1200 °C) by S_2 gas for (c) 3.6 ks and (d) 10.8 ks.

Fig. 6 — Cathodic current density in ampere per gram (A/g) of TiS_2 as a function of supplied charge (%) in the electrolysis process at 1173 K (900 °C) and 3.0 V in $CaCl_2$-*x* mol% CaS

(x = 0.1 and 0.5) for direct electrolysis of TiN and the sulfides prepared by CS_2 and S_2 gases in 3.6 ks and 10.8 ks at 1473 K (1200 °C).

Fig. 7 — XRD patterns of α-Ti metal powders obtained from the sulfides prepared by sulfurization of TiN at 1473 K (1200 °C) using S_2 gas in (a) 3.6 ks and (b) 10.8 ks.

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Table I. Degrees of Sulfurization (%) of the Samples Synthesized by CS_2 or S_2 Gases at 1473 K (1200 °C).

Time (ks)	Degree of sulfurization, $\Delta W/W_i$ (%)	
	CS_2 gas	S_2 gas
3.6	55.3 ± 0.6	71 ± 0.8
10.8	—	74 ± 0.6

Table II. Compositional EDS Analyses of the Sulfurized Samples Presented in Figures 5(b)-(d).

Point	Elements (Weight Percent, wt%)					S/Ti (molar ratio)
	Ti	S	O	C	N	
1	45.6	52.2	—	1.3	0.9	1.71
2	46.3	53.7	—	—	—	1.74
3	44.8	55.2	—	—	—	1.84

Table III. Carbon, Sulfur, Oxygen and Nitrogen Contents of the Samples Sulfurized by CS_2 or S_2 Gases at 1473 K (1200 °C).

Time (ks)	Elements (Weight Percent, wt %)							
	CS_2 gas				S_2 gas			
	C	S	O	N	C	S	O	N
3.6	0.14	53.5 ± 0.6	0.58	0.17	< 0.01	59.4 ± 0.5	0.49	0.05
10.8	-	-	-	-	< 0.01	62.8 ± 0.4	0.48	0.003

Table IV. Experimental Conditions Used for the Preparation and Electrolysis of the Sulfides in $CaCl_2$-CaS Molten Salt at 1173 K (900 °C), 3.0 V and Q/Q_0 = 400%, and Chemical Analyses of Titanium Powders Produced by OS Process.

Run #	Sulfurization		Electrolysis and chemical analysis of titanium powders					
	Time (ks)	Agent	CaS mol%	Identified phases by XRD	Impurities			
					C	O	S	N
2	3.6	CS_2	0.5	α-Ti, Ti_3O, Ti_6O, TiC	1.32	1.76	0.17	0.178
3	3.6	S_2	0.1	α-Ti, Ti_3O, Ti_6O	0.24	2.45	0.5	0.067
4	10.8			α-Ti, Ti_6O	0.14	2.36	2.2	0.019
5	3.6		0.5	α-Ti	0.12	0.84	0.064	0.006
6	10.8			α-Ti	≤ 0.10	0.76	0.053	0.003
				α-Ti, Foil-like metallic sheets	≤ 0.02	≤ 0.15	0.002	0.003