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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. $\text{Ti}_{2.45}\text{S}_4$ 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 innovative 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, TiO₂ 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 (FeTiO₃) 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 (NH₄Cl) solution.^[7-9] The TiN and TiO_xC_yN_z prepared from FeTiO₃ 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 FeTiO₃ 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 FeTiO₃. 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 TiCl₄, synthesized by high-temperature carbo-chlorination of TiO₂, has been employed for production of Ti metal by CSIRO (TiROTM)^[11, 12] and TiH₂ 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 TiO₂ under vacuum or in an inert atmosphere and used as anodes in the successive refining process.

of TiS₂ in the electrolysis hinders the formation of CO/CO₂ 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 TiS₂ 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 FeTiO₃ can be entirely sulfurized by CS₂ gas to TiS_x.^[10] TiN can be fully transformed to the single phase of Ti_{2.45}S₄ by CS₂ sulfurization at (1473 K) 1200 °C in a short time, such as 3.6 ks, according to the following reaction:^[10]

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

In sulfurization of TiN, apparent N³⁻ ions could be replaced by S²⁻ ions to have the balanced charge in the sulfide products.^[10] Formation of non-stoichiometric Ti_{2.45}S₄ in the sulfides might be also explained by the crystalline defect of Ti₂S₃ and TiS₂ 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 TiO₂ and (b) recovery of Ca from in situ electrolysis of CaO in molten CaCl₂ 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. TiS₂ powder was also synthesized by CS₂ sulfurization from TiO₂^[32], and the obtained sulfides were converted to Ti metal powder in molten salt.^[26, 27] The reduction process of TiS₂ by Ca and formation of CS₂ / S₂ gases can be expressed according to the following reactions:^[25, 27]

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.

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 ($\geq 98\%$, 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 $^{\circ}\text{C}$) for either 3.6 or 10.8 ks using S_2 gas. Another sample was prepared by CS_2 sulfurization at 1473 K (1200 $^{\circ}\text{C}$) 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 $^{\circ}\text{C}$). It is noted that melting and boiling points of sulfur under standard atmospheric pressure are 385.95 K (112.8 $^{\circ}\text{C}$) and 717.75 K (444.6 $^{\circ}\text{C}$), 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 ($\geq 99.9998\%$) 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 TiS₂ powders.

III. Results and Discussion

A. Sulfurization of TiN by CS₂ and S₂ gases

In this study, titanium sulfides were synthesized from TiN using S₂ 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 S₂ 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]

In this way, we evaluated $P_{S_i}^0$ ($i=2, 3, \dots, 8$) 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 CS₂ 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 CS₂ gas yielded the single phase of Ti_{2.45}S₄ (ICSD# 01-072-0820)^[35] in 3.6 ks. However, the samples prepared in an S₂ gas atmosphere consisted mainly of TiS₂ (ICSD# 01-088-2479)^[36] phase with small amount of non-stoichiometric phase of Ti_{2.45}S₄. TiS₃ phase was not observed in any of the samples. Carbon and S₈ 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 CS₂ gas for (b) 3.6 ks, S₂ 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 CS₂ and S₂ gases are listed in Table I. The degree of sulfurization of the sample prepared in an S₂ gas atmosphere in 10.8 ks was about $74 \pm 0.6\%$, which is higher than $71 \pm 0.8\%$ and $55.3 \pm 0.6\%$ determined for the samples prepared in S₂ and CS₂ gases in 3.6 ks. The experimental data matched well with the theoretical values of 81.10% and 55.10% calculated for formation of Ti₂S₃ and TiS₂ phases,

respectively, from TiN. It is noted that the theoretical value for formation of $\text{Ti}_{2.45}\text{S}_4$ is 61.97%. When CS_2 gas is applied as sulfurization agent, S_2 gas could be formed from the decomposition of CS_2 gas [10]. Then, we may assume here that $\text{Ti}_{2.45}\text{S}_4$ and TiS_2 phases are formed by sulfur enrichment from the stoichiometric Ti_2S_3 .^[37]

SEM images taken from TiN and the prepared sulfides are shown in Figure 5. The well-crystallized hexagonal plates of titanium sulfide can be clearly seen in the products. In addition, homogeneous and entirely similar morphology of the sulfide particles with average size of about 5 μm were distinguished for both CS_2 and S_2 sulfurization. The energy dispersive X-ray spectroscopy (EDS) analysis (Table II) also quantitatively proved the formation of higher sulfides. The molar ratio of S to Ti in the hexagonal shape particles were 1.71 and 1.74 for the samples synthesized by CS_2 and S_2 gases, respectively, for 3.6 ks. These values are close to $\text{Ti}_{2.45}\text{S}_4$ and TiS_2 phases, respectively, as identified by XRD. The elemental analysis also showed that nitrogen and particularly carbon contents of the sulfide prepared by CS_2 gas were fairly high, whereas they were not detected in the sulfides prepared by S_2 gas, indicating that TiN was extremely transformed to titanium sulfides under an S_2 atmosphere. The molar ratios of S to Ti (1.71 and 1.84) are also in good agreement with the reported ratios of $\text{S/Ti} = 1.74$ for Ti_2S_3 and $\text{S/Ti} = 1.97$ for TiS_2 phases.^[28]

Fig. 5 — SEM morphology of (a) as-received TiN, (b) the single phase $\text{Ti}_{2.45}\text{S}_4$ 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.

B. Electrochemical reduction of the titanium sulfides by Ca

These sulfides were electrochemically reduced at 1173 K (900 °C) in molten CaCl₂-CaS salt in which the concentration of CaS was set to 0.1 or 0.5 mol% CaS. Figure 6 illustrates the changes of current (A/g of TiS₂) with respect to the supplied charge (Q/Q_0 , %) during the electrolysis of the sulfides by charging 3.0 V between two electrodes. The variation of the current recorded in the process are in good agreement with the previous studies conducted the electrochemical reduction of pure TiS₂ at various molar ratios of CaS in CaCl₂ molten salt.^[24-27, 38] The graph for the direct electrolysis of TiN (Run # 1) shows that the current recorded at 3.0 V in molten CaCl₂-0.5 mol% CaS salt was very weak. The current was relatively constant at about 0.75 A/g for the whole process time, and it was much lower than those of the sulfide samples. This indicates unsuccessful calciothermic reduction of TiN in molten CaCl₂. In other words, the reaction between dissolved Ca and TiN was thermodynamically unfavorable and Ca₃N₂ was not formed according to the following reaction:

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

The sulfide prepared by CS₂ gas in 3.6 ks was reduced to Ti metal by addition of 0.5 mol% CaS into the melt (Run # 2). The samples prepared by S₂ gas in 3.6 and 10.8 ks were also, respectively, reduced to Ti metal powders by addition of 0.1 and 0.5 mol% CaS in experimental runs of # 3, 4 and 5, 6. Addition of higher mol% of CaS slightly increased the current density in the electrolysis (Runs 5 and 6). The solubility limit of CaS in molten CaCl₂ was reported to be 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

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

The reduction product obtained from the sample prepared by CS₂ contained a small amount of TiC, which could be due to the following reasons: (a) high carbon content in the sulfide, (b) formation of TiC from the reaction between Ti particles and partially generated CS₂ on the graphite anode.^[3, 22, 27] Interestingly, TiC was not detected by XRD in Ti powders obtained from the samples sulfurized by S₂ gas. Furthermore, LECO analysis showed 0.84 and 0.76 wt% O in the samples prepared by S₂ gas for 3.6 and 10.8 ks, respectively. Oxygen contamination might come from insufficient drying process due to the strong hygroscopic properties of CaCl₂.^[22, 39] The residual oxygen may be reduced in a longer electrolysis time because of the slow diffusion of oxygen in solid. Besides, Noguchi et al.^[22] also investigated the effect of dehydration on the residual oxygen contents of the samples, and they showed that Ti powder with 0.42 mass% O could be obtained from CaTiO₃ at $Q/Q_0 = 600\%$. Needless to note that the exposure of very fine Ti particles to water taken for the present approach may also contaminate the sample surface. Thus, we believe that the residual oxygen in the samples can be removed either by further improvement or longer refining process.

In this process, half of the deposited Ca may be dissolved into molten CaCl₂ and the electrolysis was mainly completed in two stages. The initial stage ($Q/Q_0 < 100\%$) was quite efficient for reduction of the sulfides and removing the residual oxygen. However, the late stage of deoxidation was slower, and the excess supplied charge of $3Q_0$ was applied to remove the residual oxygen from the sulfide. Therefore, the current efficiency of the electrolysis can be estimated to be roughly 25% 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 $\text{Ti}_{2.45}\text{S}_4$ 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.

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A List of Figures :

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 $\text{Ti}_{2.45}\text{S}_4$ 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 CS₂ and S₂ 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 S₂ gas in (a) 3.6 ks and (b) 10.8 ks.

Fig. 8 — SEM micrographs of α -Ti metal powders produced in CaCl₂-0.5 mol% CaS melt by OS process from the sulfides synthesized at 1473 K (1200 °C) from TiN using S₂ 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 CS₂ or S₂ 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 CS₂ or S₂ 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 CaCl₂-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 ₃ O, Ti ₆ O, TiC	1.32	1.76	0.17	0.178	
3	3.6	S ₂	0.1	α -Ti, Ti ₃ O, Ti ₆ O	0.24	2.45	0.5	0.067	
4	10.8			α -Ti, Ti ₆ O	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	