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# Towards a sustainable technology for production of extra-pure Ti metal: Electrolysis of sulfurized Ti(C,N) in molten $CaCl_2$

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**Abstract:** A new concept for producing highly pure Ti metal powder from ilmenite ($FeTiO_3$) is proposed in this article. Titanium nitride (TiN) or titanium oxycarbonitride ($TiO_xC_yN_z$) could be synthesized in the first step via the simultaneous carbothermal reduction and nitridation (CTRN) of $FeTiO_3$ to remove oxygen roughly. To separate oxygen completely, high-quality $TiS_2$ samples were then synthesized from TiN and TiC using $S_2$ gas, and the clean sulfides were finally reduced to α-Ti powders with spherical morphology using electrolysis in molten $CaCl_2$. X-ray diffraction (XRD), scanning electron microscopy (SEM) in conjunction with energy-dispersive X-ray spectroscopy (EDS), and elemental LECO analysis were used to study the phases and microstructures of the sulfides and the electrochemically reduced powders. The Ti powder showed no carbon contamination and consisted of high-purity foil-like Ti sheets with very low oxygen, carbon, and nitrogen contents of less than 0.15wt% O, 0.02wt% C, and 0.003wt% N, respectively. The quality of the Ti powder was much higher than that of the powder obtained using the conventional OS process (proposed by K. Ono and R.O. Suzuki) starting directly from the oxides.

**Keywords:** titanium; molten salt electrolysis; sulfidation; titanium oxycarbonitride; ilmenite

## 1. Introduction

The electrochemical reduction of metal oxides in molten salts has opened a pathway for direct extraction of metals, particularly Ti metal through direct electrolysis of $TiO_2$ in molten calcium chloride ($CaCl_2$) [1–2]. Reduction in molten salts has been expanded as an effective way to alleviate the high energy consumption in high-temperature synthesis of titanium tetrachloride ($TiCl_4$) and its conversion to sponge Ti by Mg in the Kroll process [3–5]. This approach also leads to replacing the energy intensive recycling of liquid Mg and gaseous $Cl_2$ in the electrolysis of $MgCl_2$. The $CaCl_2$-based molten salts, including $CaCl_2$–NaCl, $CaCl_2$–KCl, $CaCl_2$–LiCl, and $CaCl_2$–$MgCl_2$–NaCl, have been used as alternative electrolytes for reducing metal oxides or sulfides to metals or alloys [6] because of their high solubility for CaO [6–8], in which the dissolved Ca acts as a reductant of the oxides or sulfides. Nevertheless, the high solubility of oxygen of approximately 31.9at% O in α-Ti has limited the emerging and newly developed methods for obtaining high-quality Ti metal in molten salts [9–10]. It should also be noted that Mg and Ca, having strong affinities for oxygen and chlorine, have been mainly used for extracting reactive metals that cannot be readily produced via carbothermal reduction. The effects of operational factors and the choice of $CaCl_2$-based molten salts on the efficiency of the process have been widely investigated to produce Ti from $TiO_2$, but the electrochemical reduction of $TiO_2$ by liquid Li in molten LiCl–KCl, which is operable at lower temperatures [8], did not work with sufficient efficiency to produce highly pure Ti metal from Ti ore, ilmenite ($FeTiO_3$).

On the other hand, TiN or $TiO_xC_yN_z$ can be sustainably synthesized via carbon reduction in $N_2$ gas (carbothermal reduction and nitridation, CTRN) of $FeTiO_3$ [11–12]. The previous works on CTRN of $FeTiO_3$ were conducted using a mixture of waste polyethylene terephthalate (PET) and coal as a reducing agent in an $H_2$–$N_2$ gas atmosphere, for example, at 1250°C for 3 h. The possible reactions to form TiN from $FeTiO_3$ in $N_2$ and $H_2$–$N_2$ atmospheres can be described as reactions (1)–(2) [11]:

$$2FeTiO_3 + 6C + N_2(g) = 2Fe + 2TiN + 6CO(g), \quad \Delta G^{\ominus}(1250°C) = -437.6\ \text{kJ/mol} \tag{1}$$

$$2FeTiO_3 + 4C + 2H_2(g) + N_2(g) = 2Fe + 2TiN + 4CO(g) + 2H_2O(g), \quad \Delta G^{\ominus}(1250°C) = -272.8\ \text{kJ/mol} \tag{2}$$

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TiN is formed through a three-step mechanism in CTRN ($FeTiO_3 \xrightarrow{1} Fe + TiO_2 \xrightarrow{2} Fe + Ti_3O_5 \xrightarrow{3} Fe + TiN$). The product Fe is oxidized in the presence of $NH_4Cl$ at 70°C and leached out in the form of $Fe_2O_3{\cdot}H_2O$ from the nitrided sample by the Becher process. The $TiO_xC_yN_z$ synthesized via CTRN from $FeTiO_3$ (characteristically called TiN) could be then applied for production of Ti metal via sulfidation and electrochemical reduction in molten salt [12–13]. The reduction of iron oxide in $FeTiO_3$ and separation of Fe by oxidation and leaching consume energy, but they are useful for preparing high-quality TiN. This process may result in a better separation of Fe particles from the matrix (i.e., TiN) in comparison with the current practice in industry for production of synthetic rutile ($TiO_2$) [11,14–15] used in the Kroll process. In the synthesis of $TiO_2$, $FeTiO_3$ is also carbothermally reduced to a mixture of Fe and $TiO_2$ in the initial step. Then, the Fe content of the reduced product is removed by the oxidative leaching via the Becher process. The proposed concept enables us to remove Fe almost completely from TiN, which is impossible to achieve using the traditional methods. The iron oxide generated in this method may be used in the steel industries to avoid environmental contamination.

Notably, TiN and TiC were also easily converted to $TiCl_4$ at low temperatures of approximately 400°C [14], which is another attribute of the proposed process in the synthesis of $TiO_xC_yN_z$ from $FeTiO_3$. In terms of energy consumption, the low-temperature chlorination of TiN may be compared with the carbo-chlorination of $TiO_2$ at high temperatures of approximately 1000°C. In this process, $TiS_2$ was prepared and reduced to Ti metal in only approximately 2–3 h in molten salt, whereas the Kroll process via $TiCl_4$ may take 2–5 d for sponge Ti metal production and recycling of $MgCl_2$ [14,16]. The proposed process consumes less energy even when the sulfidation step is compared to the Kroll process consisting of Mg reduction of $TiCl_4$, $MgCl_2$ electrolysis, and the difficulties in handling the hazardous chlorine gas. More importantly, the electro-calciothermic reduction in molten salt has the potential for continuous processing in contrast to the batch-wise Kroll process. Hence, the energy consumption in the proposed method for reducing sulfides in molten salts can be remarkably reduced when TiN is used for low-temperature chlorination to synthesize $TiCl_4$ or for sulfidation.

TiN is easily converted to $TiS_x$ ($1 \le x \le 2$) because of its strong affinity for S [2–3], and the exhaust gas from this reaction is mainly $N_2$ gas, a non-greenhouse gas, demonstrating a merit of the present work. Needless to say, formation of a small amount of TiC in solid solution with TiN is inevitable because of the excess carbon used in CTRN. Thus, TiC should also be considered in sulfidation using $S_2$ gas, but this approach has not been addressed in the literature. Previously, we reported the synthesis of TiN or $TiO_xC_yN_z$ from ilmenite ($FeTiO_3$) [11–12,14] and sulfidation of individual TiO, TiC, TiN, and $TiO_{0.02}C_{0.13}N_{0.85}$ powders using $CS_2$ gas [12]. Hence, in the present work, the preparation of TiN or $TiO_xC_yN_z$ from $FeTiO_3$ was not examined. The sulfidation of pure TiN to $TiS_2$ and its conversion to Ti metal has also been recently disclosed [13]. $TiS_2$ can be also prepared from $TiO_2$ via $CS_2$ sulfidation [10] and was converted to Ti metal with a trace amount of sulfur because of the very slight solubility of sulfur (0.02at% S) in α-Ti [4–5]. Fig. 1 shows the various approaches for producing Ti metal from $TiO_2$, $TiS_2$, and TiN or $FeTiO_3$ via $TiS_2$.

The formation of the intermediate phases, such as calcium titanite ($CaTiO_3$), is one of the most important limitations of $TiO_2$ reduction, acting as kinetic barriers and reducing the diffusion of ionized oxygen from the sample to molten salt. It also increases the carbon contamination of the product because of a slow reaction rate. The use of $TiS_2$ can suppress the carbon contamination of the product, and $S_2$ can be re-

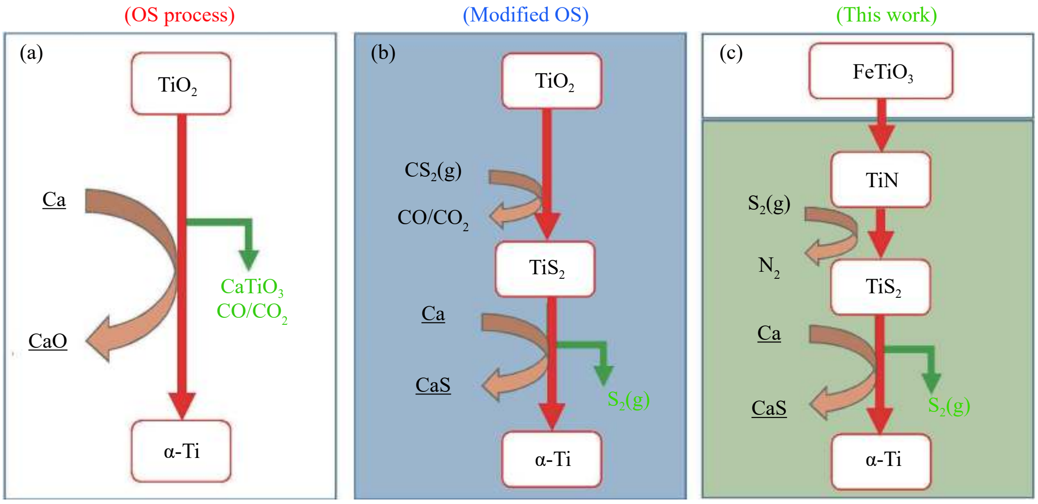

**Fig. 1. Schematics of the approaches for producing Ti metal by molten salt electrolysis via the OS process (a), modified OS process (b), and this work (c) using TiN or $FeTiO_3$.**

cycled from the electrolysis [13,17]. Nevertheless, sulfidation of $TiO_2$ using $CS_2$ may increase the carbon contamination of the product, and carbon has a detrimental effect on the mechanical properties of the Ti product [13,18]. TiN can be taken as an oxygen-free starting material, followed by sulfidation in a stream of $S_2$ gas to prepare a suitable material for Ti metal production in molten salt, as shown in Fig. 1. In the recently patented electrochemical reduction of $TiS_2$ to Ti metal, calcium sulfide or calcium oxide is added to the molten electrolyte to provide the calcium metal required for the reduction reaction [19]. This approach could be a great interest to the Ti community, especially when the feedstock is synthesized from TiN or $FeTiO_3$ because of the lack of $TiS_2$ natural resources. Suzuki *et al*. [9–10] reduced commercially available $TiS_2$ to Ti metal using the calciothermic reduction and electrolysis in $CaCl_2$–CaS melts. They showed that the sulfur concentration could be decreased to approximately 0.03wt% at the molar ratio of $Ca/TiS_2 = 2.0$. In addition, the sulfur content of Ti powder was reported to be as low as approximately 0.01wt% when the electric charge was four times larger than the stoichiometric amount for reduction of $TiS_2$ [10]. The Ti metal produced from the commercial grade $TiS_2$ was, however, contaminated by approximately 1.0wt% O because of the high oxygen contamination of the commercial $TiS_2$ powder.

The authors also reported the synthesis of $TiS_x$ from $FeTiO_3$ using the $CS_2$ sulfidation method and electrochemical reduction of the sulfurized TiN samples in molten $CaCl_2$ [12–13,20]. However, the effect of the supplied charge in the electrochemical reduction of the sulfide prepared from TiN has not been discussed. In addition, the synthesis of $TiS_2$ from TiC using $S_2$ gas has not been investigated, although it has a great potential for production of clean titanium sulfides. The total reaction for the sulfidation of Ti(O,C,N) using $S_2$ gas at 1200°C could then be expressed by the following reactions:

$$\mathrm{TiN} + \mathrm{S_2\,(g)} = \mathrm{TiS_2} + \frac{1}{2}\mathrm{N_2\,(g)},\quad \Delta G^{\ominus}(1200^{\circ}\mathrm{C}) = -85.4\ \mathrm{kJ/mol} \tag{3}$$

$$\mathrm{TiC} + \mathrm{S_2\,(g)} = \mathrm{TiS_2} + \mathrm{C},\ \Delta G^{\ominus}(1200^{\circ}\mathrm{C}) = -117.4\ \mathrm{kJ/mol} \tag{4}$$

The excess carbon formed from reaction (4) may act as a reductant in the sulfidation of TiO as written in reaction (5), or it can be simultaneously removed in the form of $CS_2$ gas by the excess sulfur through reaction (6).

$$\mathrm{TiO} + \mathrm{C} + \mathrm{S_2\,(g)} = \mathrm{TiS_2} + \mathrm{CO\,(g)},\quad \Delta G^{\ominus}(1200^{\circ}\mathrm{C}) = -122.2\ \mathrm{kJ/mol} \tag{5}$$

$$\mathrm{C} + \mathrm{S_2\,(g)} = \mathrm{CS_2\,(g)},\ \Delta G^{\ominus}(1200^{\circ}\mathrm{C}) = -20.4\ \mathrm{kJ/mol} \tag{6}$$

Hence, the sulfidation reaction of TiO in the presence of TiC can be written as reaction (7):

$$\mathrm{TiO} + \mathrm{TiC} + 2\mathrm{S_2\,(g)} = 2\mathrm{TiS_2} + \mathrm{CO\,(g)},\quad \Delta G^{\ominus}(1200^{\circ}\mathrm{C}) = -239.6\ \mathrm{kJ/mol} \tag{7}$$

In this work, we have initially sulfurized TiC and TiN powders to clean $TiS_x$ ($1 \le x \le 2$) using $S_2$ gas, and the intermediate sulfides were reduced to extra-pure Ti metal at the cathode. The electrochemical reduction of $TiS_x$ by the metallic Ca dissolved in the $CaCl_2$ melt is expressed as follows [10,13]:

$$\mathrm{CaS} = \mathrm{Ca^{2+}(in\ the\ melt)} + \mathrm{S^{2-}(in\ the\ melt)} \tag{8}$$

$$\mathrm{Ca^{2+}} + 2\mathrm{e^-} = \mathrm{Ca} \tag{9}$$

$$\mathrm{TiS}_x + x\mathrm{Ca} = \mathrm{Ti} + x\mathrm{CaS} \tag{10}$$

$$\mathrm{S^{2-}} = \frac{1}{2}\mathrm{S_2(g)} + 2\mathrm{e^-} \tag{11}$$

The reduction of $TiS_x$ synthesized from Ti(C,N) could be a promising scenario for establishing a new sustainable process for Ti metal production from $FeTiO_3$ via $TiO_xC_yN_z$ and $TiS_2$; however, the carbon contamination of the product has not been well clarified in the literature. On the other hand, electrolysis of the sulfides is more favorable than that of the oxides, and this approach significantly reduces the energy consumption. Furthermore, sulfur is also cheap, nontoxic, readily available globally, and it can be applied to the synthesis of intermediate clean sulfides, while $S_2$ gas plays an important role in reducing the oxygen content and particularly the carbon content of titanium metal obtained via the OS process (proposed by K. Ono and R.O. Suzuki). The purpose of this work is to prepare clean $TiS_2$ from Ti(C,N) via $CS_2$ and $S_2$ sulfidations and investigate the effects of the supplied charge and molar ratio of CaS in molten $CaCl_2$ on the production of industrial grades of Ti metal powders from TiN and TiC via $TiS_2$. This goal can be considered a noteworthy achievement toward sustainably processing Ti metal from $FeTiO_3$ via TiN and successive $TiS_2$ electrolysis in molten salt.

## 2. Experimental

Commercial TiN and TiC powders (99.5%, 50 μm, Wako Chemical Co., Japan) were sulfurized in a dual-zone furnace. The sulfur powder was evaporated at 300°C and used for the sulfidation of Ti (C,N) at 1200°C for 3 h. A high-purity Ar gas with a flow rate of 10 mL/min was used to transport $S_2$ gas to the reaction site. In comparison, the sulfide samples were also prepared using $CS_2$ sulfidation at 1200°C for 3 h. Details on the preparation of the sulfides and the experimental setup have been provided elsewhere [13]. In the synthesis of sulfides from TiN and TiC, $CS_2$ or $S_2$ gas was used for synthesis of $TiS_x$. However, the samples prepared via $CS_2$ may be slightly contaminated by free carbon, which must be clarified. Hence, the two sulfur sources were used to evaluate the possibility of clean sulfide production.

The sulfides were electrochemically reduced at 900°C and 3.0 V via the OS process in 600 g of molten $CaCl_2$ with the addition of 0.5mol% CaS and various supplied charges ($Q/Q_0$) ranging from 200% to 600%, where $Q$ is the total supplied electricity (Coulomb) and $Q_0$ is the stoichiometric electric charge applied for the reduction of the samples. The experimental conditions were previously reported by the authors [13], and some outlines are briefly reported here. In addition to the supplied charge ($Q$), voltage, and current, the vacuum pressure and temperature of the electrolysis cell were precisely monitored using a data acquisition unit (Agilent 34972A Data Acquisition Switch Unit). The sulfide sample prepared from TiC was also reduced to Ti metal powder using this method at $Q/Q_0 = 400\%$. The molten salt was dehydrated at 900°C for 12 h in a vacuum (≤ 10 Pa). Then, the purification of the salt was conducted through pre-electrolysis at 2.0 V under an Ar atmosphere with a flow rate of 50 mL/min for 1 h using a supplementary carbon electrode prior to the electrolysis.

The Ti powders obtained from electrolysis of the sulfides were carefully separated from the Ti net used as the cathode and washed three times with distilled water and dilute acetic acid. Eventually, the products were washed with water, ethanol, and acetone and dried in vacuum for a day. The chemical analyses and morphologies of the final products were investigated using X-ray diffraction (XRD, Philips, X'Pert Pro, Cu $K_\alpha$) and scanning electron microscopy (SEM, JEOL JSM-6500F) in conjunction with energy-dispersive X-ray spectroscopy (EDS). The residual O, C, N, and S concentrations in the sulfides and the reduced samples were determined using LECO analyzers (TC600 and CS600).

## 3. Results and discussion

### 3.1. Synthesis of Ti sulfides

The previous results showed that the oxygen content of $TiO_xC_yN_z$ samples prepared from $FeTiO_3$ is negligible [11]. Additionally, the small amount of oxygen in the samples can be reduced in the molten salt. Hence, the oxycarbonitride obtained from CTRN could be considered TiCN. As a case in point, the $TiO_{0.02}C_{0.13}N_{0.85}$ intermediate was synthesized from $FeTiO_3$ and its sulfidation was also experimentally confirmed [12]. In this article, the sulfides were prepared through the sulfidation of TiN and TiC samples, and they were served for the electrochemical reduction to produce Ti metal. The $S_2$ gas in the present work was generated through the evaporation of sulfur at 300°C for 3 h in the low temperature region of the designed furnace. The details on the experimental set up have been presented elsewhere [12–13]. Notably, the sulfidation system may be modified on an industrial scale, and sulfur can be melted and purified in separate tanks to be continuously fed into the sulfidation furnace. The samples A, B, and C in Fig. 2(a) show the XRD patterns of the commercial TiN and the sulfides synthesized from TiN under the $CS_2$ and $S_2$ gases, respectively. TiN was transformed to the single phase of $Ti_{2.45}S_4$ (ICSD # 01-072-0820) at 1200°C for 3 h in a stream of $CS_2$ gas with a flow rate of 20 mL/min. Meanwhile, the samples synthesized in a $S_2$ gas atmosphere mainly contained the $TiS_2$ (ICSD # 01-088-2479) phase with a small amount of nonstoichiometric $Ti_{2.45}S_4$ phase. The synthesis of the low carbon samples is required for the present work; hence, samples with high sulfur contents (i.e., $TiS_2$) are more favorable for high-purity Ti metal production. The impurities concentration of these samples was determined using the LECO method, and the results are provided in Fig. 2(b). As shown, the sample prepared via $CS_2$ sulfidation was slightly contaminated with carbon, and the residual nitrogen content of the sample was as high as approximately 0.1wt%. However, a very clean $TiS_2$ sample was obtained using $S_2$ gas instead of $CS_2$. The carbon content of this sulfide prepared from TiN decreased to 0.01wt%, indicating a remarkable potential for preparation of clean sulfide from TiN.

Carbon removal is a crucial issue in the synthesis of clean sulfides, particularly from Ti(C,N) as a starting material.

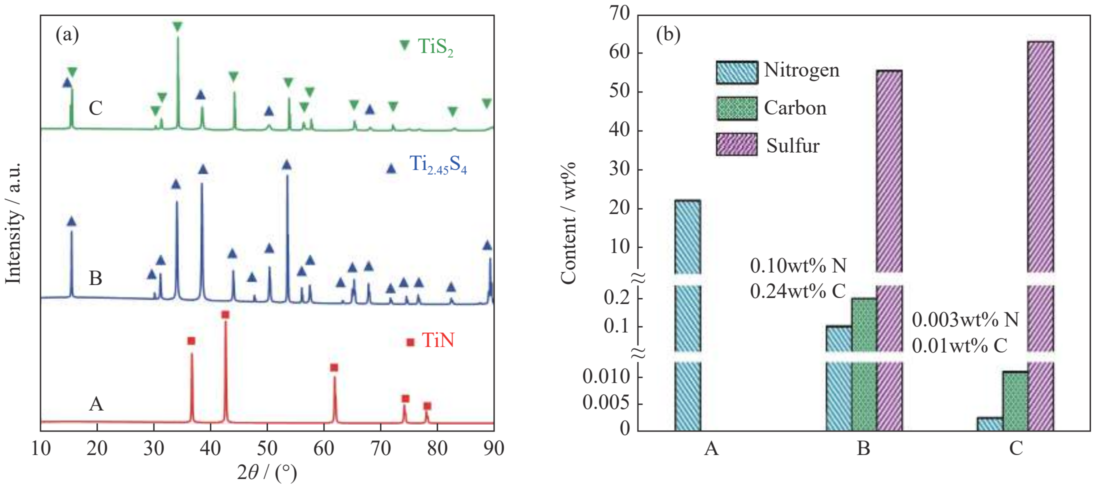

**Fig. 2. XRD patterns (a) and LECO analyses (b) of pure TiN (A) and the sulfides prepared from TiN using $CS_2$ (B) or $S_2$ (C) gas.**

Therefore, the sulfidation of TiC samples was also investigated separately, and the XRD and LECO analyses are shown in Fig. 3, where A, B, and C represent pure TiC, and the sulfides are prepared from TiC using $CS_2$ or $S_2$ gas, respectively. We found that the single phase of $Ti_{2.45}S_4$ could also be formed through sulfidation of TiC samples using $CS_2$ gas at 1200°C for 3 h. However, the carbon content of the sulfide sample was remarkably high compared to that of the sample obtained from TiN in $CS_2$ gas. The carbon impurity is derived from $CS_2$ decomposition, or the product of the reaction between TiC and $CS_2$ increased the carbon contamination of the sulfurized sample. The use of $S_2$ instead of $CS_2$ suppressed the carbon content of the sulfurized samples, which leads to a new approach for the synthesis of the sulfide. The XRD spectra also indicated the formation of mainly $TiS_2$ containing a tiny amount of $Ti_{2.45}S_4$. Interestingly, the residual carbon in the sulfide was entirely removed as $CS_2$ gas by the excess $S_2$ gas, which was detected via the $CS_2$ colorimetric tubes. In addition, $TiS_3$, TiC, and free carbon were not observed in the XRD patterns.

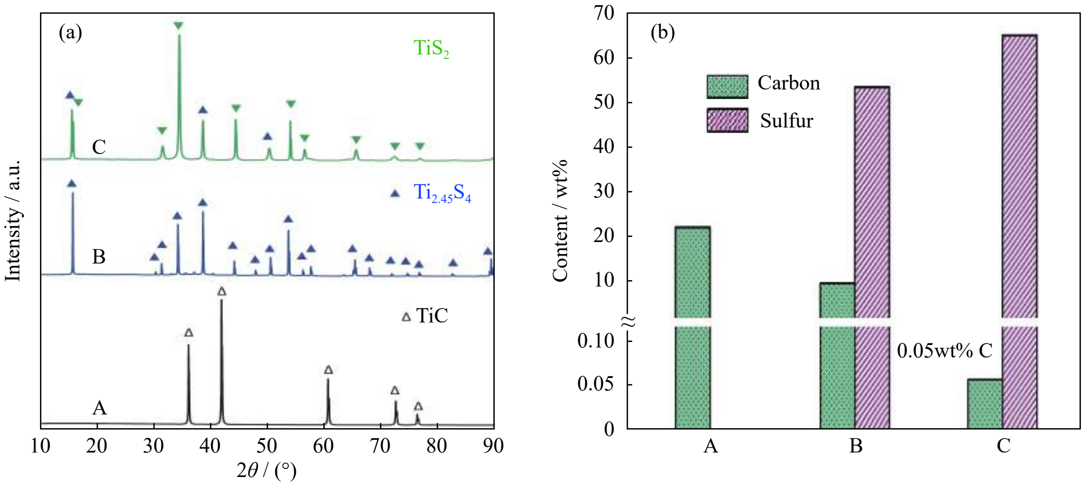

**Fig. 3. XRD patterns (a) and LECO analyses (b) of pure TiC (A) and the sulfides prepared from TiC using $CS_2$ (B) or $S_2$ (C) gas.**

The excess amount of carbon was reduced to a very low concentration when TiC samples were sulfurized using $S_2$ gas. As a result, the carbon contamination decreased to approximately 0.05wt% for the sample prepared at 1200°C for 3 h. It can be further decreased to approximately 0.024wt% by increasing the sulfidation time of the carbide sample to 5 h. It has been demonstrated that carbon removal in $CS_2$ sulfidation of TiC is barely possible. In practical processes, TiCN or $TiO_xC_yN_z$ should be converted to clean $TiS_2$ samples through sulfidation in a stream of $S_2$ gas. The stoichiometry of the sulfide products synthesized from TiN or TiC using $S_2$ gas is consistent with that of $TiS_2$.

The excess carbon in $CS_2$ sulfidation of TiC samples is an important issue. In previous studies, we reported the formation of nanosized carbon fibers in the sulfide product obtained in a $CS_2$ gas stream. However, we have shown that the sulfides prepared in the present work from TiN and TiC samples via $S_2$ gas were extremely clean and without carbon contamination. The free carbon generated from the sulfidation reaction of the TiC sample was *in situ* reacted with excess sulfur and was removed as $CS_2$ gas. Nevertheless, the off-gas in this approach mainly consists of $N_2$ gas, which is a good feature of the designed process. In the case of TiC sulfidation or carbides recycling, the off-gas may contain $CS_2$, which can be used for sulfidation of $FeTiO_3$ to remove Fe as FeS [13,20]. Therefore, all the sulfide products in our designed process can be recycled in several steps without generation of sulfur waste. Apparently, CO gas is the main waste generated in CTRN, and Fe is recycled as a $Fe_2O_3{\cdot}H_2O$ by-product [15]. The sulfide obtained from TiN is converted to extra-pure Ti metal, and $S_2$ gas is recycled and used for synthesis of the sulfides. The total reaction can be summarized as

$$FeTiO_3 + 3C = Ti + Fe + 3CO(g) \qquad (12)$$

where the reductant required for reaction (12) could be mainly supplied by recycling the waste PET plastic of the CTRN process.

The SEM images of the sulfurized TiN and TiC are shown in Fig. 4. The well-crystallized hexagonal plates of titanium sulfides are obviously apparent in the products obtained from TiN or TiC powder using $S_2$ gas. The sulfide products were entirely homogeneous plates with a mean size of approximately 5 μm. The EDS analysis showed that the S to Ti molar ratios were approximately 1.84 and 1.78 for the samples synthesized from TiN and TiC, respectively. These S/Ti ratios are inconsistent with the reported molar ratio of S/Ti = 1.97 for the $TiS_2$ phase [21]. The slightly lower analytical values are probably due to the coexistence of $Ti_{2.45}S_4$ and $TiS_2$ phases, although they could not be classified in the SEM images. The LECO analyses indicated that the sulfur contents of the samples synthesized using $S_2$ gas were higher than those

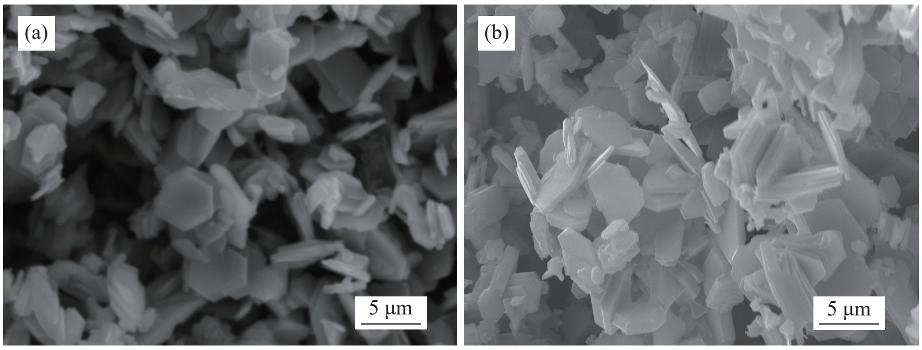

**Fig. 4. SEM images of the sulfides synthesized from (a) TiN and (b) TiC using $S_2$ gas.**

prepared using $CS_2$ gas, which is consistent with the EDS analysis. For instance, the hexagonal-shaped particles obtained from TiN via $CS_2$ gas at 1200°C for 3 h had an S to Ti molar ratio of approximately 1.71, which is lower than those determined for the samples synthesized using $S_2$ gas.

### 3.2. Electrolysis of the sulfides

The thermodynamic data (from HSC Ver. 8.08) predict that the calciothermic reduction of TiN and TiC in molten $CaCl_2$ is barely possible. Hence, the high-purity titanium sulfides were initially prepared from TiN as an alternative to $TiO_xC_yN_z$ using $S_2$ sulfidation at 1200°C for 3 h. The sulfide samples consisting of ≤0.003wt% N, 0.48wt% O, and ≤ 0.01wt% C were served as starting materials in the electrolysis. Fig. 5 shows the current per 1 g of the sulfide sample ($TiS_2$) with respect to the supplied charge ($Q/Q_0$). The current at the constant voltage of 3.0 V was substantial (3.5 A/g) in the initial stage of the electrolysis. Notably, the surface area of the anode immersed in the melt is estimated to be approximately 1020 mm$^2$. The currents decreased moderately with some fluctuations up to approximately $Q/Q_0$ = 100%, and approached constant values of approximately 1.0 A/g. Thereafter, the currents were constant during the electrolysis up to $Q/Q_0$ = 600% in the second step. The applied voltages in the experiments were much higher than the theoretical decomposition voltage of CaS (2.01 V), where liquid Ca can be formed from CaS [10]. Hence, the calcium is dissolved in the molten $CaCl_2$ and acts as a reducing agent. Notably, to avoid chlorine gas generation, the electrolysis voltage should not exceed 3.21 V, where the theoretical decomposition of $CaCl_2$ occurs at 900°C.

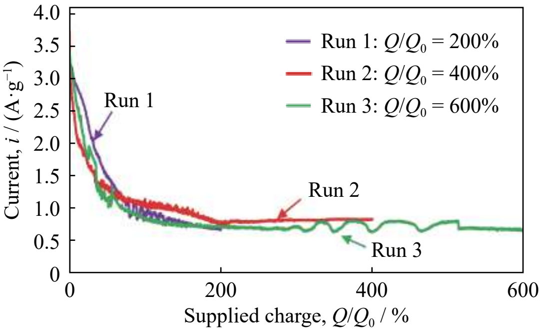

**Fig. 5. Cathodic current per 1 g of the $TiS_2$ vs. supplied charge during electrolysis of the sulfurized TiN samples.**

The influence of the CaS molar fraction in the molten $CaCl_2$ salt on the current efficiency of the reduction was examined. Slightly increasing the molar fraction of CaS in $CaCl_2$ from 0.1mol% to 0.5mol% substantially improved the sulfur removal because of the increased uptake of Ca. The higher CaS concentration in $CaCl_2$ melt as solvent results in a faster reduction. The oscillation of current can also be explained in terms of an excessive release of gaseous $S_2$ or $CS_2$ as bubbles on the carbon anode. The $S_2$ gas is formed from decomposition of CaS at the carbon anode, and it can be used in the sulfidation of Ti(O,C,N) or $FeTiO_3$.

The samples reduced at $2Q_0$ (Run 1) showed α-Ti, $Ti_3O$, and $Ti_6O$. However, the products prepared at $4Q_0$ (Run 2) and $6Q_0$ (Run 3) were composed entirely of the single phase of α-Ti, and neither TiC nor $Ti_6O$ was identified in the products. Fig. 6 presents the XRD patterns of α-Ti metal obtained from $TiS_2$ (Run 2). No oxides or carbides of titanium were observed in the products. A photograph (insert) of the α-Ti product consisting of high-purity Ti sheets is also shown in Fig. 6. The oxygen, carbon, nitrogen and sulfur contents of the Ti sheets, formed from sulfurized TiN, were respectively less than 0.15wt% O, 0.02wt% C, 0.003wt% N, and 0.005wt% S as determined by the LECO measurements.

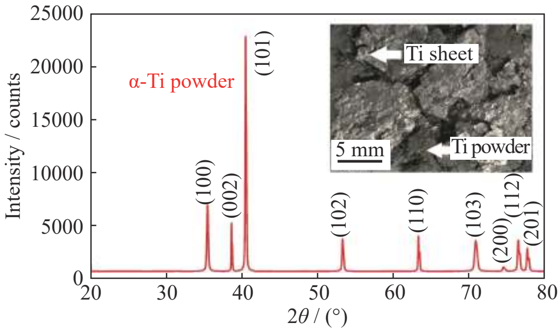

**Fig. 6. XRD pattern and the product photograph (insert) of the α-Ti powder and Ti sheets obtained from the sulfurized TiN by $S_2$ gas and electrochemical reduction in $CaCl_2$–0.5mol% CaS.**

The residual concentrations of O, C, N, and S in the α-Ti products plotted against the supplied charge ($Q/Q_0$) during electrolysis are presented in Fig. 7. The results demonstrate that the sulfide is mainly reduced by calcium in the first stage, whereas the residual oxygen is removed from the sample in the second step, particularly by increasing the supplied charge from 200% to 600%. This result is due to the relatively high concentration of Ca in the cathode vicinity, producing a rapid reduction of $TiS_2$ at the beginning of electrolysis. The sample reduced for 200% of the supplied charged contained approximately 2.2wt% of unreacted sulfur and a large amount of the oxygen impurity. No carbon impurity was detected in the Ti metals, which could be due to the low contamination with oxygen of the sulfide samples and the carbon anode acting as a non-consumable electrode in the electrolysis. In addition, α-Ti metal consisting of 0.32 ± 0.3wt% O, ≤0.07wt% C, and ≤0.05wt% S was successfully produced from the sulfurized TiC in conditions similar to those applied for TiN. As a result, $TiS_2$ was fully transformed to the single phase of α-Ti metal at $Q \geq 4Q_0$ without contamination in molten $CaCl_2$–0.5mol%CaS, as confirmed via the XRD spectra and LECO analysis. In this process, half of the deposited Ca may be dissolved into molten $CaCl_2$ because of the use of a basket-type cathode. The presence of a small amount of water impurity in $CaCl_2$ is also inevitable and results in formation of CaO and finally decomposition to calcium in the molten bath. The generated calcium from decomposition of CaO in $CaCl_2$ may also partially reduce the sulfide near the cathode. The electrolysis was mainly completed in two stages, as shown in Fig. 5. The initial stage ($Q/Q_0 < 100\%$) was quite efficient for reduction of the sulfides. However, the later stage of deoxidation from the residual oxygen in $TiS_x$ was slower, and an excess supplied charge of $3Q_0$ was applied to remove oxygen completely. Therefore, the current efficiency of the electrolysis can be estimated to be roughly 25% by considering a complete oxygen removal from the sulfurized sample.

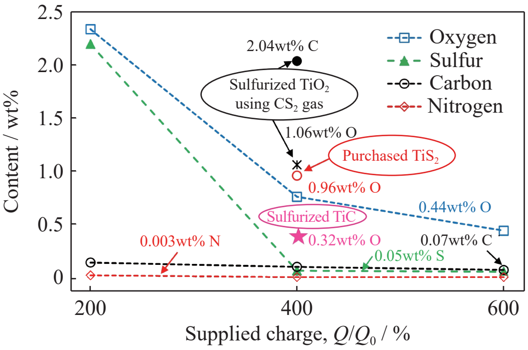

**Fig. 7. Residual concentration of O, C, N, and S in the α-Ti powders vs. the supplied charge ($Q/Q_0$) during electrolysis of the sulfurized TiN and TiC samples prepared using $S_2$ gas.**

Fig. 7 also indicates that the powder samples prepared from the sulfides prepared from TiN or TiC by $S_2$ sulfidation showed less oxygen and particularly carbon contamination (0.07wt% C) than the powder samples prepared from $TiO_2$ by $CS_2$ sulfurization or reduction of $TiO_2$ in molten $CaCl_2$ [9–10]. This result strongly indicates that the current efficiency is highly enhanced and CO/$CO_2$ does not form in this improved OS process. Furthermore, the oxygen and nitrogen contents of the sample reduced at the supplied charge of $6Q_0$ were much lower than those of the sample reduced at $4Q_0$. They were analytically determined to be as low as 0.44wt% O and 0.003wt% N in the reduction of the $TiS_x$ prepared from TiN using $S_2$ gas.

The SEM images of the α-Ti powders obtained from sulfurized TiN and TiC are shown in Fig. 8. The α-Ti powders consisting of relatively spherical or interconnected, round particles with diameters ranging from 1 to 5 μm were formed through the electro-calciothermic reaction between $TiS_2$ and dissolved calcium in molten salt. This result might be due to the higher diffusion rate of ions, strong dissolving capability of CaS in the molten salt, and the effect of the interfacial tension of the molten salt [22]. Powders obtained at $Q \geq 4Q_0$ also contained high-purity Ti foils (0.125wt% O). The low oxygen concentration in the product is well compatible with the defined international standards for high-purity Ti powder.

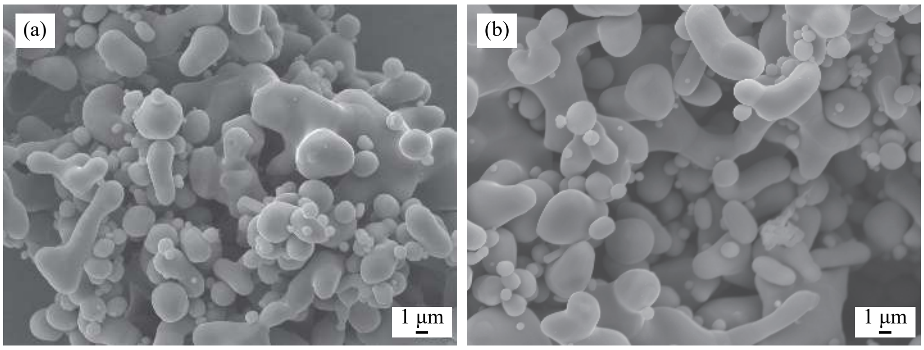

**Fig. 8. SEM image of the α-Ti powders obtained from electro-calciothermic reduction of (a) the sulfurized TiN at $Q/Q_0$ = 600% and (b) the sulfurized TiC at $Q/Q_0$ = 400% in molten $CaCl_2$–0.5mol% CaS salt.**

The spherically shaped Ti powders from this work could have promising applications in additive manufacturing or 3D printing technology for manufacturing complicated, near-net-shape products [23–24]. Therefore, TiN or $TiO_xC_yN_z$ has a great potential as a starting material for the production of commercial grade Ti metal powders using $TiS_2$ via sustainable sulfidation and calciothermic reduction in molten $CaCl_2$ salt.

## 4. Conclusion

In summary, a single phase of $Ti_{2.45}S_4$ was formed from TiC and TiN using $CS_2$ gas, whereas $TiS_2$ consisting of small amounts of $Ti_{2.45}S_4$ was obtained under a $S_2$ atmosphere at 1200°C for 3 h. The present process enables the synthesis of clean $TiS_2$ from Ti(C,N) samples without carbon contamination of the products. We found that production of α-Ti powders with trace amounts of oxygen and especially carbon is attainable not only from TiN but also from TiC via $TiS_2$ instead of $TiO_2$. The electro-calciothermic reduction of the sulfides for 400% of the supplied charge in molten $CaCl_2$ –0.5mol%CaS indicated the formation of spherical α-Ti powders containing the foil-like Ti sheets from the sulfurized TiN and TiC samples. The extra-pure Ti sheets obtained from the sulfurized TiN and TiC samples contained less than 0.15wt% O, 0.02wt% C, 0.002wt% S, and 0.003wt% N and less than 0.125wt% O, 0.02wt% C, and 0.005wt% S, respectively. This process has, therefore, a great potential for commercialization and sustainable production of low-cost Ti metal powders from $TiS_x$ via TiN and TiC, possibly synthesized from $FeTiO_3$.

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