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

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6 Abstract

7 This work presents a new processing concept for production of Ti metal powder from $FeTiO_3$
8 via TiN and TiS_x . Because $FeTiO_3$ can be converted to TiN by carbothermal reduction and
9 nitridation (CTRN) method, TiN was taken as the starting material. $Ti_{2.45}S_4$ and TiS_2 powders were
10 completely formed from TiN at 1473 K (1200 °C) in 3.6 and 10.8 ks, respectively. Either CS_2 or
11 S_2 gas could be utilized for the sulfurization process. The sulfides were then converted to α -Ti
12 metal powders by Ono and Suzuki (OS) process in molten $CaCl_2$ with a small addition of CaS.
13 Employing S_2 gas in sulfurization step remarkably reduced the carbon contamination to 0.01 and
14 0.1 wt% C after sulfurization and reduction processes, respectively. α -Ti powders with spherical
15 morphology and foil-like Ti sheets containing less than 0.15 wt% O were obtained from the
16 electrochemical reduction in molten $CaCl_2$ -0.5 mol% CaS. The approach applied here offers a
17 promising strategy to design an innovate process for production of commercial grade Ti powders
18 via TiS_x and TiN from $FeTiO_3$ by nitridation, sulfurization and OS processes.

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

20 I. Introduction

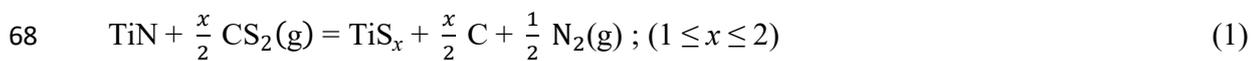
21 Processing of metallic Ti has been primarily performed through the discontinuous Kroll
22 process which requires high carbo-chlorination temperature of about 1273 K (1000 °C) to synthesis
23 $TiCl_4$, distill it at 473 K (200 °C), and convert it at 1273 K (1000 °C) to sponge Ti by Mg.^[1] In
24 addition, molten salt electrolysis of $MgCl_2$ takes a long time at 923 K (650 °C) for recycling of

25 reductant Mg.^[2-4] Thus, Ti communities are persistently working to innovate feasible and
26 economically viable pyro and/or hydro-metallurgical processes to remarkably drive down the cost
27 of Ti metal powder processing. The environmental regulations have been also considered in the
28 newly developed methods such as innovative electrochemical reduction methods and low-
29 temperature chlorination process (LTCP).^[2] For example, TiO₂ feedstocks have been used for
30 production of metallic Ti in the electro-deoxidation and calciothermic reduction routes as called
31 FFC Cambridge (Fray, Farthing and Chen) and OS (Ono and Suzuki) processes.^[5, 6] On the other
32 hand, ilmenite (FeTiO₃) can be converted to titanium oxycarbonitride (TiO_xC_yN_z) via carbothermal
33 reduction and nitridation (CTRN) process and subsequent iron removal step in an ammonium
34 chloride (NH₄Cl) solution.^[7-9] The TiN and TiO_xC_yN_z prepared from FeTiO₃ can be easily
35 chlorinated at very low temperatures such as about 400 °C^[2], which could be an alternative route
36 to carbo-chlorination at high temperatures taken in Kroll process. Especially, this method has a
37 merit of the less contamination of Fe derived from FeTiO₃ with low operating costs.^[2, 7, 8, 10]

38 Figure 1 illustrates the main processing steps in the present concept in comparison with various
39 methods developed for production of Ti metal from FeTiO₃. High quality TiN or TiO_xC_yN_z can be
40 processed from Ti ores and utilized in chlorination or sulfurization processes. It is worth noting
41 that TiCl₄, synthesized by high-temperature carbo-chlorination of TiO₂, has been employed for
42 production of Ti metal by CSIRO (TiROTM)^[11, 12] and TiH₂ powders by ADMA non-Kroll process
43 by Mg reduction.^[13, 14] In addition, iron-free TiN may be refined and converted to Ti metal powder
44 by electrochemical USTB method.^[15] Moreover, it has been stated that titanium oxycarbides can
45 be readily converted to Ti metal by electrochemical MER^[16, 17] and Chinuka^[18] processes. Ti(C,O)
46 pellets in these processes were prepared by partial carbothermal reduction of TiO₂ under vacuum
47 or in an inert atmosphere and used as anodes in the successive refining process.

60 of TiS₂ in the electrolysis hinders the formation of CO/CO₂ during electrolysis and carbon
61 impurity of titanium can be remarkably reduced as stated by Suzuki et al. [22, 24-27] Therefore,
62 developing a novel method for synthesis of TiS₂ from natural Ti resources could be a great interest
63 in the Ti community.

64 As reported previously, both commercial TiN and TiO_xC_yN_z synthesized from FeTiO₃ can be
65 entirely sulfurized by CS₂ gas to TiS_x.^[10] TiN can be fully transformed to the single phase of
66 Ti_{2.45}S₄ by CS₂ sulfurization at (1473 K) 1200 °C in a short time, such as 3.6 ks, according to the
67 following reaction:^[10]



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

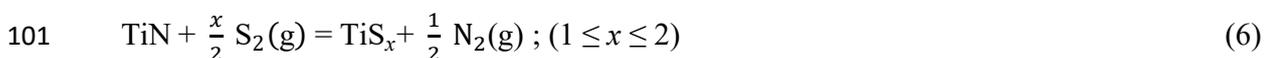
70 In sulfurization of TiN, apparent N³⁻ ions could be replaced by S²⁻ ions to have the balanced
71 charge in the sulfide products.^[10] Formation of non-stoichiometric Ti_{2.45}S₄ in the sulfides might
72 be also explained by the crystalline defect of Ti₂S₃ and TiS₂ due to phase transformation as
73 explored by Basu et al.^[28] Formation of titanium oxysulfides prior to the electrolysis should be
74 also avoided to obtain high-quality Ti powders, because the oxygen removal is more difficult than
75 sulfur from the obtained Ti metal.

76 Recently, OS process has been applied to reduce the sulfides to the metallic Ti powders.^{[26, 27,}
77 ^{29]} OS process originally involves: (a) calciothermic reduction of TiO₂ and (b) recovery of Ca from
78 in situ electrolysis of CaO in molten CaCl₂ melt.^[6, 30, 31] Suzuki et al.^[26, 27] have expanded the
79 applicability of OS process not only to the oxide but also to the sulfide. TiS₂ powder was also
80 synthesized by CS₂ sulfurization from TiO₂^[32], and the obtained sulfides were converted to Ti
81 metal powder in molten salt.^[26, 27] The reduction process of TiS₂ by Ca and formation of CS₂ /
82 S₂ gases can be expressed according to the following reactions:^[25, 27]



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

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



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

106 **II. Experimental Procedure**

107 **A. Materials**

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

114 **B. Synthesis of titanium sulfides**

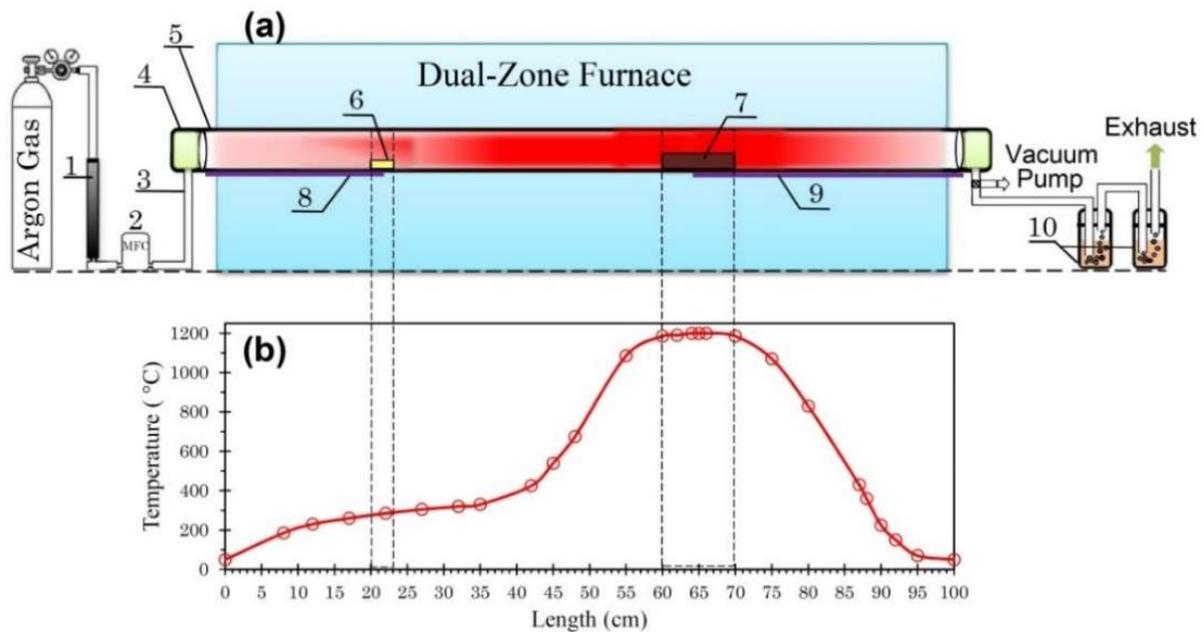
115 In this study, sulfurization of TiN was conducted at 1473 K (1200 $^\circ\text{C}$) for either 3.6 or 10.8 ks
116 using S_2 gas. Another sample was prepared by CS_2 sulfurization at 1473 K (1200 $^\circ\text{C}$) for 3.6 ks.
117 Details of the sulfurization process by using CS_2 gas were described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

128 **C. Electrochemical reduction of the sulfides**

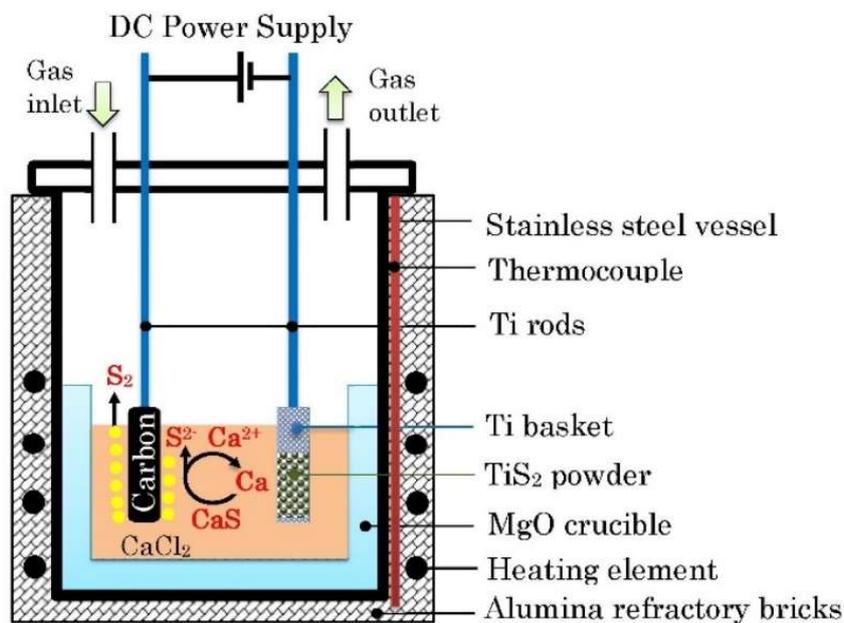
129 The sulfides synthesized at different conditions were used in OS process for production of Ti
130 metal powder. 1.5 g of the sulfides was loaded into a basket cathode made of Ti net and reduced
131 in molten CaCl₂ with addition of 0.1 or 0.5 mol% CaS. In addition to the sulfides, direct electrolysis
132 of TiN was also conducted in molten CaCl₂-0.5 mol% CaS. A high-density carbon rod (10 mm in
133 diameter) was used as an anode and it was attached to a Ti rod (6 mm diameter, 800 mm length).
134 An MgO crucible with purity of 99.5% (90 mm in diameter and 200 mm in height) was filled with
135 600 g of mixed CaCl₂-CaS salt and gradually heated in vacuum (less than 10 Pa) up to 1173 K
136 (900 °C). The supplied charge (Q/C), current density as well as electrolysis temperature and
137 pressure were precisely monitored by a data acquisition unit (Agilent 34972A Data Acquisition
138 Switch Unit). The molten salt was dehydrated overnight in vacuum at 1173 K (900 °C). CaCl₂-
139 CaS melts were also purified by pre-electrolysis using an auxiliary carbon electrode at 2.0V and
140 1173 K (900 °C) in an Ar atmosphere with a continuous flow rate of 50 ml/min for 3.6 ks. Then,
141 the electrolysis process was performed at 3.0V and $Q/Q_0 = 400\%$ where Q_0 is stoichiometric
142 electric charge. A schematic of the reactor in OS process used for the calciothermic reduction of
143 TiS₂ is depicted in Figure 3.

144 **D. Materials characterization**

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



151
 152 **Fig. 2** — Experimental set-up for sulfurization process, (a) Schematic of the dual-zone furnace, (b) The temperature
 153 profile of the furnace set at 573 K (300 °C) and 1473 K (1200 °C), respectively for evaporation of sulfur and
 154 sulfurization of TiN. 1- silica gel, 2- mass flow controller (MFC), 3- Teflon tube, 4- glass cap, 5- reactor, 6-sulfur in
 155 an alumina boat, 7- sample in an alumina boat, 8, 9- thermocouples, 10- 1 M NaOH scrubber.



156
 157 **Fig. 3** — A schematic of the reactor used for electrolysis of TiS₂ powders.

158 III. Results and Discussion

159 A. Sulfurization of TiN by CS₂ and S₂ gases

160 In this study, titanium sulfides were synthesized from TiN using S₂ gas at 1473 K (1200 °C)
161 in 3.6 ks or 10.8 ks, where the evaporation temperature of sulfur was set at 573 K (300 °C) in low-
162 temperature zone of the furnace.

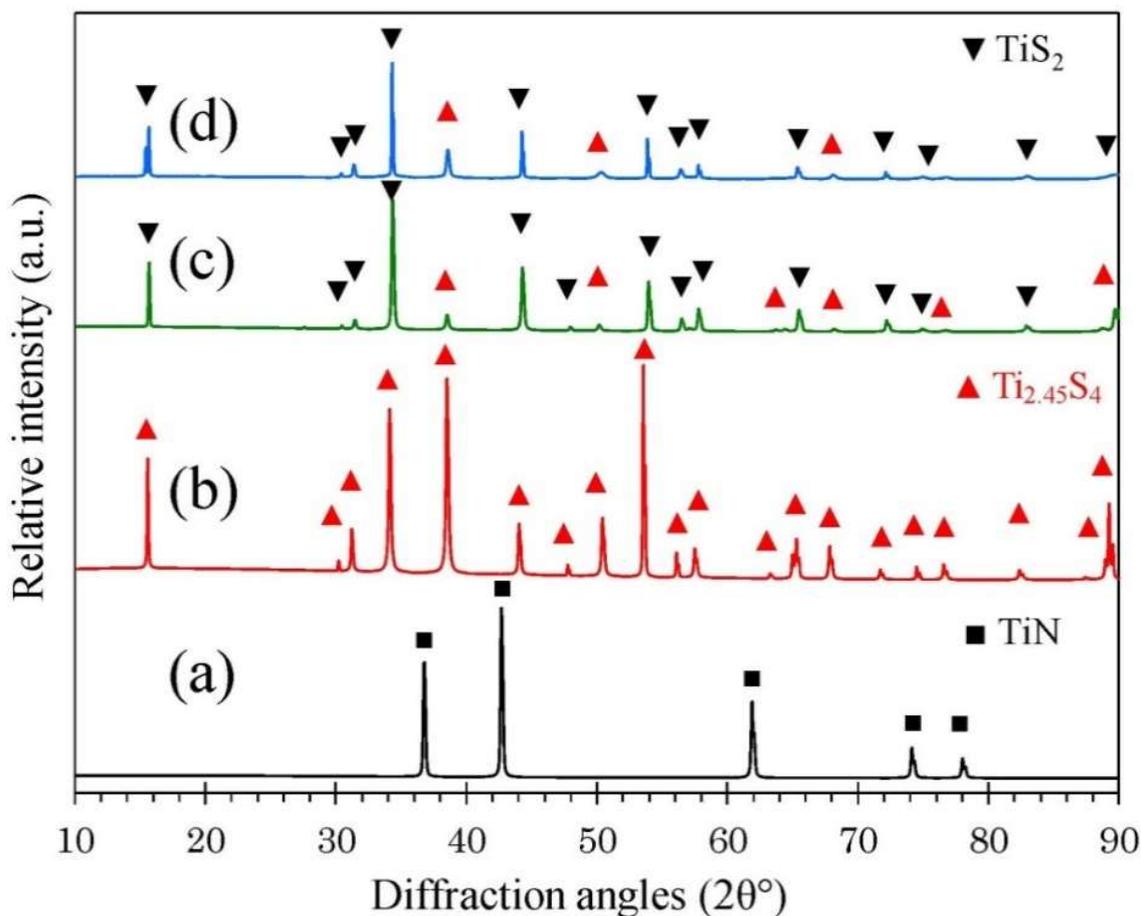
163 The partial pressure of sulfur gas (P_{S_2}) was evaluated from the mass changes of sulfur powder
164 in an alumina crucible. About 0.85 g sulfur was evaporated at 573 K (300 °C) for 3.6 ks under an
165 Ar gas with the flow rate of 10 ml/min. This results in about 5 ml S₂ gas/min, and $P_{S_2}^{Exp}$ was
166 experimentally approximated as 33 kPa.

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



170 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
171 was lower than $P_{S_2}^{Exp}$ (33 kPa) in the reaction vessel. This apparent discrepancy could be because
172 of the high Ar flow rate to transport sufficient sulfur to the reaction site and to prevent backflow
173 and deposition of sulfur gas in inlet of the alumina tube.

174 The results were compared with the sample synthesized using CS₂ gas for 3.6 ks. Figure 4
175 shows the XRD diffraction patterns of a commercial grade TiN powder (ICSD# 01-087-0632)^[34]
176 and the obtained sulfides. The sulfurization process of TiN using CS₂ gas yielded the single phase
177 of Ti_{2.45}S₄ (ICSD# 01-072-0820)^[35] in 3.6 ks. However, the samples prepared in an S₂ gas
178 atmosphere consisted mainly of TiS₂ (ICSD# 01-088-2479)^[36] phase with small amount of non-
179 stoichiometric phase of Ti_{2.45}S₄. TiS₃ phase was not observed in any of the samples. Carbon and
180 S₈ were not also detected in the samples.

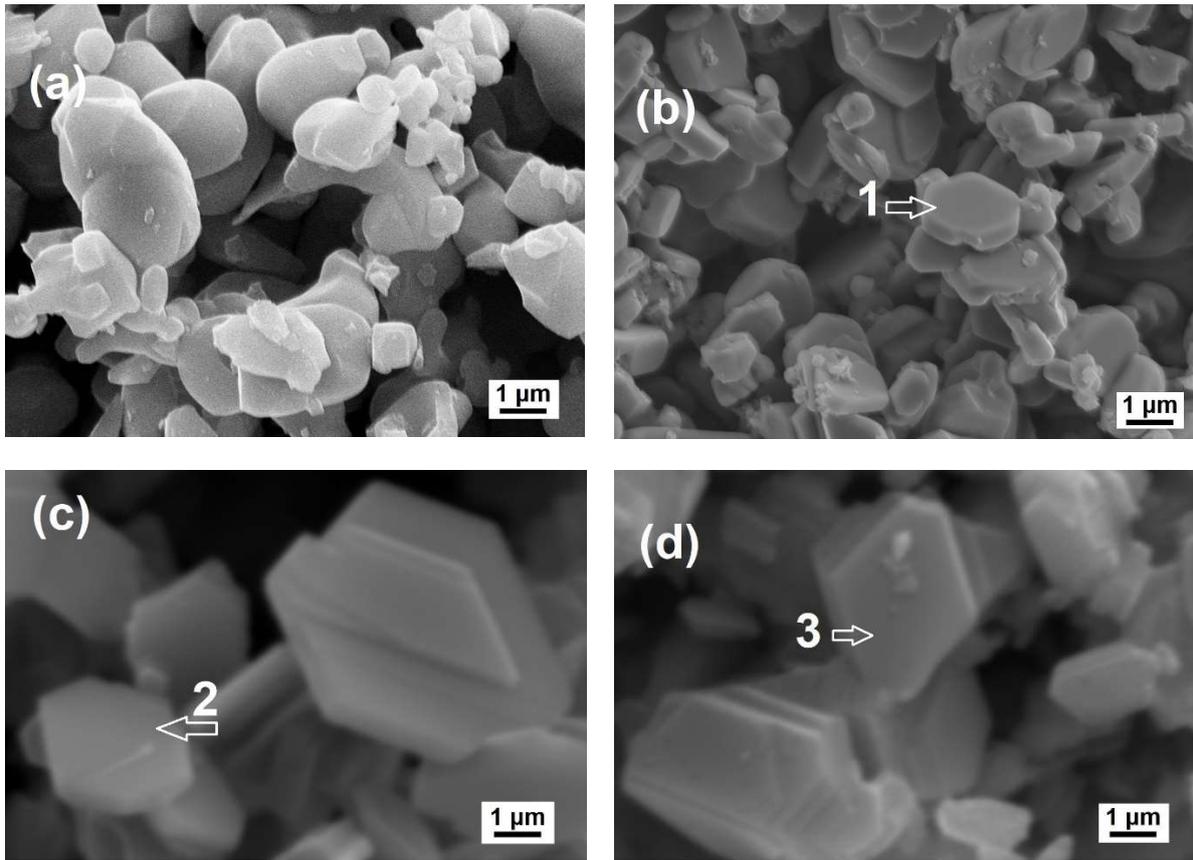


181
 182 **Fig. 4** — XRD patterns of (a) as-received TiN powder and the sulfurized TiN samples at 1473 K (1200 °C) using
 183 CS₂ gas for (b) 3.6 ks, S₂ gas for (c) 3.6 ks and (d) 10.8 ks.

184 The mass changes of TiN samples were measured after cooling in an Ar gas atmosphere to
 185 room temperature. The degree of sulfurization ($\Delta W/W_i$) of the samples was defined for the
 186 sulfurized samples, where ΔW and W_i represent the mass gain and initial weight of the samples,
 187 respectively. The degree of sulfurization, $\Delta W/W_i$, of the samples prepared in CS₂ and S₂ gases are
 188 listed in Table I. The degree of sulfurization of the sample prepared in an S₂ gas atmosphere in
 189 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
 190 samples prepared in S₂ and CS₂ gases in 3.6 ks. The experimental data matched well with the
 191 theoretical values of 81.10% and 55.10% calculated for formation of Ti₂S₃ and TiS₂ 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 $5\ \mu m$ 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]

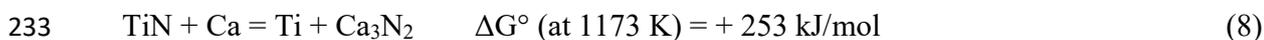


209 **Fig. 5** — SEM morphology of (a) as-received TiN, (b) the single phase $Ti_{2.45}S_4$ synthesized from TiN at 1473 K (1200
 210 °C) by CS_2 , and the sulfides prepared from TiN at 1473 K (1200 °C) by S_2 gas for (c) 3.6 ks and (d) 10.8 ks.

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

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

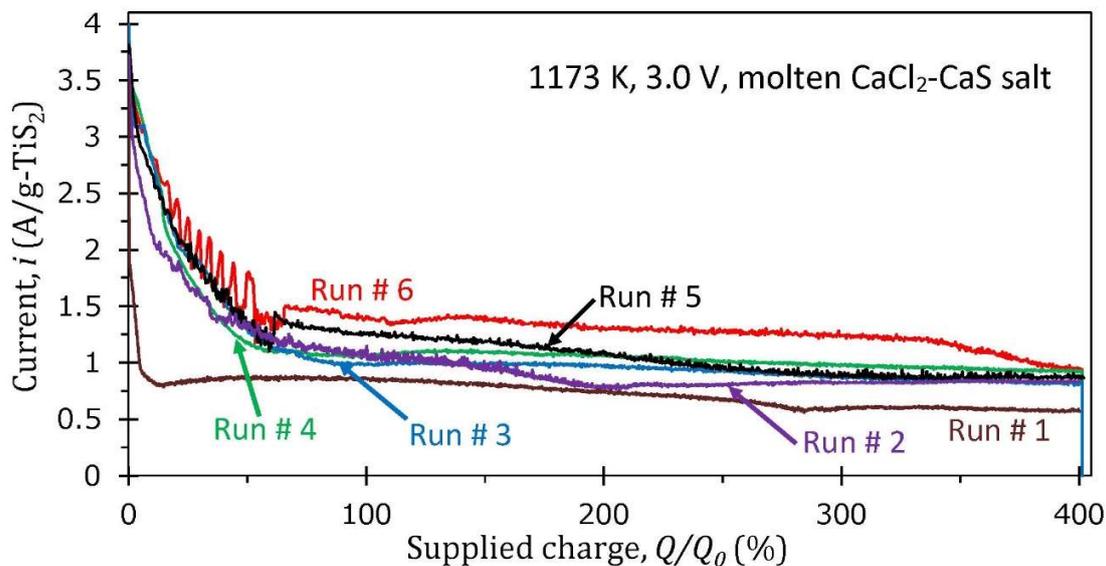
221 These sulfides were electrochemically reduced at 1173 K (900 °C) in molten CaCl₂-CaS salt
222 in which the concentration of CaS was set to 0.1 or 0.5 mol% CaS. Figure 6 illustrates the changes
223 of current (A/g of TiS₂) with respect to the supplied charge ($Q/Q_0, \%$) during the electrolysis of 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 TiS₂ at various molar ratios of CaS in CaCl₂ 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 CaCl₂-0.5 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 CaCl₂. In other words, the reaction between dissolved
231 Ca and TiN was thermodynamically unfavorable and Ca₃N₂ was not formed according to the
232 following reaction:



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 CS₂ 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 S₂ 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 CaCl₂ was reported to be
243 $1.77 \pm 0.1 \text{ mol\% CaS}$ at 1173 K (900 °C).^[25] At the initial stage of the electrolysis up to

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



254
 255 **Fig. 6** — Cathodic current in ampere per gram (A/g) of TiS_2 as a function of supplied charge (%) in the electrolysis
 256 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
 257 sulfides prepared by CS_2 and S_2 gases in 3.6 ks and 10.8 ks at 1473 K (1200 °C).

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

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

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

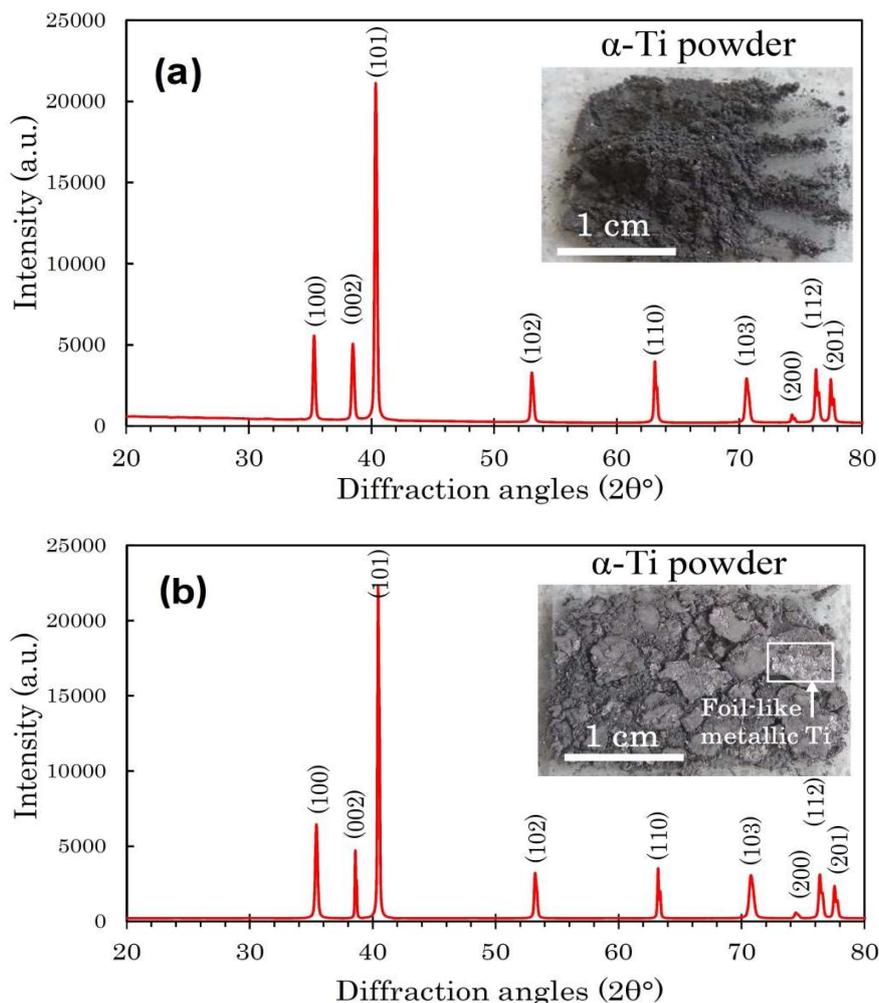
268 The samples reduced in CaCl_2 - 0.1 mol% CaS melts were not entirely transformed to α -Ti
269 metal powder, and small amounts of titanium suboxides in the form of Ti_6O and/or Ti_3O appeared
270 in XRD phase identifications (Runs 3 and 4). The existence of residual oxygen may be due to
271 insufficient Ca supply. It is noted that liquid Ca can be formed from CaS, because its theoretical
272 decomposition voltage is 2.01 V which is much lower than 3.2 V needed for theoretical
273 decomposition of CaCl_2 .^[27] As is shown in Figure 6, the lower CaS molar ratios indicated the
274 lower conductivity of the molten salts and resulted in prolonged electrolysis time. By increasing
275 CaS addition, a higher amount of metallic Ca enters into the cathode vicinity increases the
276 reduction rate of the samples particularly in the earlier stage. In contrast, the lower molar ratios of
277 CaS in molten salts may require the longer electrolysis time to fully remove the residual oxygen
278 due to slow diffusion of oxygen in α -Ti powder and low conductivity of the melts. The carbon
279 contents of the samples reduced with 0.1 mol% CaS (Runs 3 and 4) were above 0.14 wt%, lower
280 than that prepared by CS_2 (1.32 wt% C in Run 2). The carbon contents decreased further when 0.5
281 mol% CaS used in the reduction process (Runs 5 and 6), which might be due to high conductivity
282 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 CS₂ 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 CS₂ 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 S₂ gas. Furthermore, LECO analysis showed 0.84 and 0.76 wt% O in the samples
290 prepared by S₂ 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 CaCl₂.^[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 CaTiO₃ 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 CaCl₂ 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.

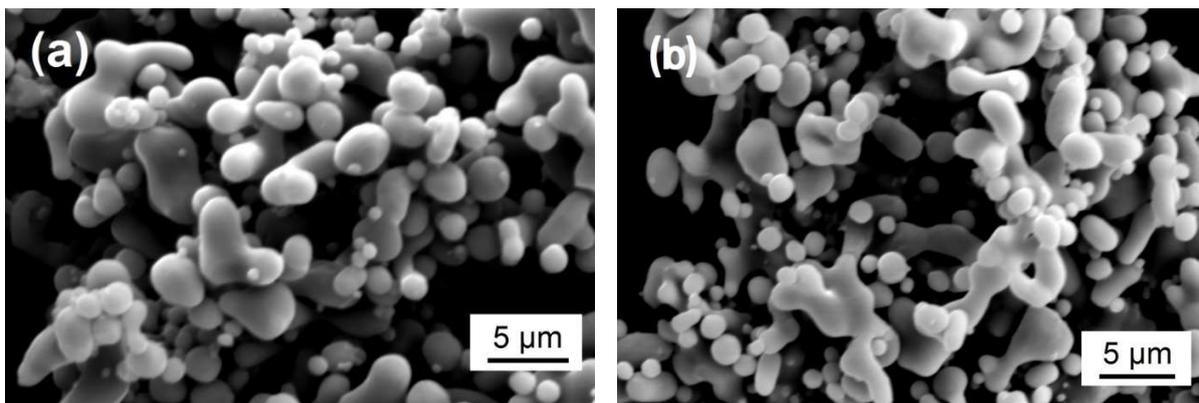
305 XRD patterns and SEM micrographs of the electrochemically reduced samples obtained from
306 Runs 5 and 6 are shown in Figures 7 and 8, respectively. The single phase of α -Ti in both specimens
307 was identified by XRD patterns. The macro-structure of the analyzed powders consisted of foil-
308 like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



309 **Fig. 7** —XRD patterns of α -Ti metal powders obtained from the sulfides prepared by sulfurization of TiN at 1473 K
310 (1200 °C) using S_2 gas in (a) 3.6 ks and (b) 10.8 ks.

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

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



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

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

331 **IV. Concluding Remarks**

332 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
333 at 1473 K (1200 °C) in 3.6 ks. Then, electrochemical reduction of obtained TiS_2 samples were
334 performed to produce Ti metal powder in molten CaCl_2 -x mol% CaS (x = 0.1 and 0.5).
335 Interestingly, Neither TiC nor TiN phases were observed in the samples prepared by S_2 gas
336 sulfurization. The resulting spherical α -Ti powder with interconnected round particles consisted
337 of high purity foil-like sheets of Ti that contained less than 0.02 wt% C, 0.15 wt% O, 0.002wt% S
338 and 0.003wt% N. These values pass the chemical regulation of titanium powder specified by JIS
339 2nd grade. The sulfide with ≤ 0.01 wt% C and ≤ 0.05 wt% S was synthesized by abundant S_2 gas
340 generated at 573 K (300 °C) in a short time (3.6 ks), followed by electrochemical reduction in
341 CaCl_2 -0.5 mol% CaS at 1173 K (900 °C). These findings confirm a promising method for
342 production of industrial grade titanium powder.

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420 **A List of Figures :**

421 **Fig. 1** — A flowchart of the concept for preparation of Ti metal powder via TiS₂ synthesized from
 422 TiN compared to Kroll process^[1], and newly developed CSIRO^[11], FFC Cambridge^[19],
 423 OS^[6], ADMA non-Kroll^[14] and USTB^[15] processes.

424 **Fig. 2** — Experimental set-up for sulfurization process, (a) Schematic of the dual-zone furnace,
 425 (b) The temperature profile of the furnace set at 573 K (300 °C) and 1473 K (1200 °C),
 426 respectively for evaporation of sulfur and sulfurization of TiN. 1- silica gel, 2- mass flow
 427 controller (MFC), 3- Teflon tube, 4- glass cap, 5- reactor, 6-sulfur in an alumina boat, 7-
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429 **Fig. 3** — A schematic of the reactor used for electrolysis of TiS₂ powders.

430 **Fig. 4** — XRD patterns of (a) as-received TiN powder and the sulfurized TiN samples at 1473 K
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432 **Fig. 5** — SEM morphology of (a) as-received TiN, (b) the single phase Ti_{2.45}S₄ synthesized from
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 434 by S₂ gas for (c) 3.6 ks and (d) 10.8 ks.

435 **Fig. 6** — Cathodic current density in ampere per gram (A/g) of TiS₂ as a function of supplied
 436 charge (%) in the electrolysis process at 1173 K (900 °C) and 3.0 V in CaCl_{2-x} mol% CaS

437 (x = 0.1 and 0.5) for direct electrolysis of TiN and the sulfides prepared by CS₂ and S₂ gases
438 in 3.6 ks and 10.8 ks at 1473 K (1200 °C).

439 **Fig. 7** — XRD patterns of α-Ti metal powders obtained from the sulfides prepared by sulfurization
440 of TiN at 1473 K (1200 °C) using S₂ gas in (a) 3.6 ks and (b) 10.8 ks.

441 **Fig. 8** — SEM micrographs of α-Ti metal powders produced in CaCl₂-0.5 mol% CaS melt by OS
442 process from the sulfides synthesized at 1473 K (1200 °C) from TiN using S₂ gas in (a) 3.6
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444 **A List of Tables:**

445 **Table I.** Degrees of Sulfurization (%) of the Samples Synthesized by CS₂ or S₂ Gases at 1473 K
446 (1200 °C).

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

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451 CaCl₂-CaS Molten Salt at 1173 K (900 °C), 3.0 V and $Q/Q_0 = 400\%$, and Chemical Analyses
452 of Titanium Powders Produced by OS Process.

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467 **Table I. Degrees of Sulfurization (%) of the Samples Synthesized by CS₂ or S₂ Gases at**
 468 **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

469 **Table II. Compositional EDS Analyses of the Sulfurized Samples Presented in Figures 5(b)-**
 470 **(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

471 **Table III. Carbon, Sulfur, Oxygen and Nitrogen Contents of the Samples Sulfurized by CS₂**
 472 **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

473 **Table IV. Experimental Conditions Used for the Preparation and Electrolysis of the Sulfides**
 474 **in CaCl₂-CaS Molten Salt at 1173 K (900 °C), 3.0 V and $Q/Q_0 = 400\%$, and Chemical Analyses**
 475 **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		

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