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Citation	Metallurgical and materials transactions B-process metallurgy and materials processing science, 49(4), 1808-1821 https://doi.org/10.1007/s11663-018-1278-8
Issue Date	2018-08
Doc URL	https://hdl.handle.net/2115/75072
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Type	journal article
File Information	Revised Manuscript 24 .pdf



Formation of Titanium Sulfide from Titanium Oxycarbonitride by CS₂ Gas

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ABSTRACT

Previously this group reported that a good quality titanium metal powder can be produced from titanium sulfides by electrochemical OS process. In this study, the sulfurization procedure was examined to synthesize titanium sulfide from titanium oxycarbonitride by CS₂ gas. The experiments were carried out in the temperature range of 1173 - 1523 K (900 – 1250 °C) in a tube reactor with continuously flowing argon (Ar) as carrier gas of CS₂. The formation of titanium sulfide phases from the commercial TiN, TiC and TiO powders were studied as the initial step. Then, TiO_{0.02}C_{0.13}N_{0.85} coming from ilmenite was sulfurized to prepare single-phase of titanium sulfide. The products were characterized by X-ray diffraction (XRD), and the morphology of the sulfides was rigorously investigated, and the sulfur, oxygen and carbon contents in the products were analyzed. The process was remarkably dependent on the temperature and time. TiN and TiO_{0.02}C_{0.13}N_{0.85} powders could be fully converted to the single phase of Ti_{2.45}S₄ (Ti_{2+x}S₄) at 1473 K (1200 °C) in 3.6 ks. The maximum weight gain of TiN sample was ~ 55.3% indicating a full conversion of TiN to Ti₂S₃ phase. The carbon and oxygen contents in this sulfide prepared from the oxycarbonitride were about 1.8 wt.%C and 1.4 wt.%O, respectively. Therefore, the titanium sulfide could be a promising feedstock for the production of commercial grade titanium powder.

Keywords: Titanium sulfide; titanium nitride; sulfurization; oxycarbonitride

I. INTRODUCTION

The Ti-S system includes many compounds, namely, Ti_6S , Ti_3S , Ti_2S , TiS , Ti_{1+x}S , Ti_4S_5 , $\text{Ti}_{16}\text{S}_{21}$, $\text{Ti}_{2.67}\text{S}_4$, TiS_2 and TiS_3 .^[1,2] Among these compounds, TiS_2 , hexagonal layered structure (P3m1), is one of the most promising compounds reported for engineering applications. The excellent physical properties of TiS_2 are high electrical conductivity at room temperatures ($1.4 \times 10^3 \text{ ohm}^{-1}.\text{cm}^{-1}$)^[3] and low density (3.25 g.cm^{-3}) compared to commercial thermoelectric materials such as PbTe (8.24 g.cm^{-3}).^[4] In addition, sulfur (S) doping has been used for narrowing band gap energy of materials, for example, band gap energy of 1.4 eV reported for $\text{Ti}_{2-x}\text{S}_x$ compared to 2.3 eV for TiO_2 .^[5]

Two-dimensional (2D) layered materials have also exhibited exciting properties due to the distinct electronic and optical features.^[4,6] These properties make TiS_2 an attractive material for rechargeable lithium-ion batteries, hydrogen storage, photochemical energy conversion and catalytic hydrogen evolution.^[3-6] However, these sulfides do not exist as the natural product, and they are normally synthesized from the elemental sulfur and metallic titanium.

Synthesis of titanium sulfide from lower-grade Ti ores such as ilmenite, FeTiO_3 , and its subsequent conversion to metallic Ti could have considerable attentions as a new processing method of ilmenite. A variety of routes have been reported for the production of metallic Ti sponge/powder, which were mostly produced either from TiCl_4 or TiO_2 as the main precursors.^[7-14] Instead of the previous methods, Ti powder has been experimentally produced from titanium sulfide (TiS_2) as an alternative to TiO_2 by calciothermic reduction or electrolysis reduction.^[7]

The newly developed method for conversion of TiS_2 to metallic Ti powder is based on the electrochemical OS (Ono and Suzuki) process.^[11,15] In this process, carbon disulfide (CS_2) gas is formed from the decomposition of CaS in molten salt and from the reaction between S^{2-} and anodic carbon. This is fortunately able to be recycled.^[7] The gaseous CS_2 can be supplied for the preparation of the raw materials, for example, TiS_2 . It is expected that the prepared TiS_2 powder is used as starting material

50 instead of synthetic rutile (TiO_2) for reduction. Therefore, commercial grade titanium powder with low
51 oxygen and sulfur contaminations will be obtained from the OS process in the molten salt of CaCl_2 - CaS
52 at 1173 K (900 °C).^[7] Besides that, TiS_2 reduction to metallic Ti may be easier than TiO_2 reduction at
53 the similar conditions^[7] The calciothermic reduction of TiS_2 was illustrated according to the following
54 reaction.^[7]



56 Up-to-date, the preparation of TiS_2 with various morphologies has been investigated from various
57 materials and routes.^[4,16-19] For example, the work published by Oshima *et al.*^[16] showed that
58 stoichiometric TiS_2 can be merely prepared by a two-step process using a mixture of Ti metal and pure
59 sulfur powder under high pressures (10-200 MPa) at temperatures from 873 K to 1023 K (600 to 750 °C).
60 At the first stage, a mixture with the molar ratio of $\text{Ti/S} = 1.19$ was heated up to 673 K (400 °C) for 1 day
61 and subsequently at 1173 K (900 °C) for 4 days. At the second stage, the titanium sulfide product
62 obtained from the initial stage was remixed with the necessary quantity of sulfur powder (molar ratio of
63 $\text{Ti/S} = 1.3$) and then heated at the temperature range of 873 - 1023 K (600 – 750 °C) at 10-200 MPa to
64 produce stoichiometric TiS_2 . They could convert the initially prepared powder to stoichiometric TiS_2
65 phase successfully at 873 K (600 °C) under 15 MPa. Although the process yields stoichiometric TiS_2 , it
66 requires a long processing time for the preparation of the high-quality powder.^[16] It is noteworthy to
67 mention that other routes such as sol-gel process^[6] and vapor phase reactions^[17] have also been employed
68 for the synthesis of TiS_2 powder.^[6,17,18] One of the most common methods used for the production of
69 TiS_2 powder is based on the gas phase reaction ($\text{TiCl}_4 + 2\text{H}_2\text{S} \rightarrow \text{TiS}_2 + 4\text{HCl}$) in which titanium
70 tetrachloride (TiCl_4) is used as the main precursor.^[17] In addition, Ma *et al.*^[19] synthesized high purity
71 TiS_2 crystals with dendritic morphologies by thermal chemical vapor deposition (CVD) using titanium
72 and sulfur at 1073 K (800 °C). These methods are primarily applied for the synthesis of nano-sized

73 clusters and/or the powders of TiS_2 which are used as cathode material for lithium batteries, electrical
74 and electronic applications.

75 The conversion of TiO_2 to $\text{Ti}_{1+x}\text{S}_2$ phase by the sulfurization process using CS_2 gas was
76 experimentally evaluated by Ohta *et al.*^[4] in the temperature range of 973 to 1273 K (700 to 1000 °C) for
77 14.4ks. They succeeded to form a single phase of TiS_2 at 1073 K (800 °C) after 14.4ks sulfurization
78 process. Increasing the sulfurization temperature resulted in formation of non-stoichiometric Ti_2S_3 ,
79 $\text{Ti}_{6.9}\text{S}_9$ and $\text{Ti}_{8.2}\text{S}_{11}$ phases.^[4] It was also found that the process was incomplete and showed residual
80 rutile (TiO_2) at the lower sulfurization temperatures, for example at 973 K (700 °C). This could be
81 associated with the preparation of TiS_2 / $\text{Ti}_{1+x}\text{S}_2$ powder from high purity commercial rutile.^[4,7]
82 Nevertheless, the essential information on the conversion of FeTiO_3 to TiS_2 is lacking as industrially
83 applicable low-cost methods. No studies concentrated on the preparation of TiS_2 or $\text{Ti}_{1+x}\text{S}_2$ powder as
84 the main feedstock for Ti metal production from Ti minerals. In direct sulfurization process of ilmenite,
85 iron sulfide (FeS) could be preferentially formed, and its removal could be an insurmountable obstacle
86 for production of iron-free TiS_2 at atmospheric pressure. This is because a small amount of Fe in Ti
87 metal is harmful due to mechanical brittleness. Fortunately, ilmenite could be readily converted to iron
88 (Fe) free titanium oxycarbonitride ($\text{TiO}_x\text{C}_y\text{N}_z$) which is a solid solution of TiO , TiC and TiN phases^[20-22]
89 Iron free $\text{TiO}_x\text{C}_y\text{N}_z$ has been synthesized from ilmenite by carbothermal reduction and nitridation
90 simultaneously under an H_2 – N_2 atmosphere (CTRN process).^[20] In the second stage, $\text{TiO}_x\text{C}_y\text{N}_z$ might
91 be converted into $\text{Ti}_{1+x}\text{S}_2$ by sulfurization using CS_2 gas. The CTRN process has several advantages that
92 $\text{TiO}_x\text{C}_y\text{N}_z$ can be used as (i) a feedstock for low-temperature chlorination process in production of
93 titanium tetrachloride (TiCl_4)^[21] and as (ii) a consumable anode for cathodic titanium powder production
94 in high-temperature NaCl – KCl molten salts (USTB process).^[23] This article focuses on the preparation of
95 titanium sulfide from $\text{TiO}_x\text{C}_y\text{N}_z$ considering the industrial production of Ti metal by OS process.

96 In case of OS process using TiS_2 , a large amount of CS_2 gas can be exhausted out from the
97 electrochemical cells, and this CS_2 gas may become a heavy industrial waste if we cannot have any cycle
98 to use CS_2 in the proposed new method.^[7] Thus, the method to consume CS_2 gas is needed. The standard
99 Gibbs free energy changes (ΔG°) to form TiS and TiS_2 from TiO , TiC and TiN by sulfurization using
100 CS_2 and/or S_2 gases are evaluated by the thermodynamic database from Outokumpu HSC Chemistry,^[24]
101 and shown in Figure 1. The S_2 gas could be formed from the decomposition of CS_2 gas. It is noted that
102 TiS is only one of the intermediate phases compiled in Ref. [24], although many other sulfides can exist
103 in Ti-S binary system.^[1,2] As seen in Figure 1, TiN , TiC and TiO can be converted to TiS and/or TiS_2 by
104 using CS_2 and S_2 gases with precipitation of carbon or CO gas. Free energy changes for the conversion
105 of TiC to TiS phase are much higher than that of for the conversion of TiO and TiN to TiS phase. Apart
106 from TiS_2 , the reactions related to the formation of TiS by CS_2 and S_2 gases are shown in Figure 1. The
107 conversion to TiS depends on the temperature, particularly because the valence of Ti should be decreased
108 from 3+ to 2+ in TiN ; carbon does not work as the reductant of TiN , where the valency of Ti is reduced.
109 Figure 1 shows that CS_2 gas may contribute to convert TiO , TiN and TiC to TiS_2 , if a suitable
110 temperature is taken for the reactions. It should be also noted that the sulfurization can occur using a
111 powerful sulfurizing agent, CS_2 and S_2 gases, simultaneously.^[4] Thus, in this work, attempts were made
112 to synthesis TiS_2 / $\text{Ti}_{1+x}\text{S}_2$ powder from TiO , TiC and TiN as well as $\text{TiO}_x\text{C}_y\text{N}_z$ by sulfurization process
113 at high temperatures using CS_2 gas.

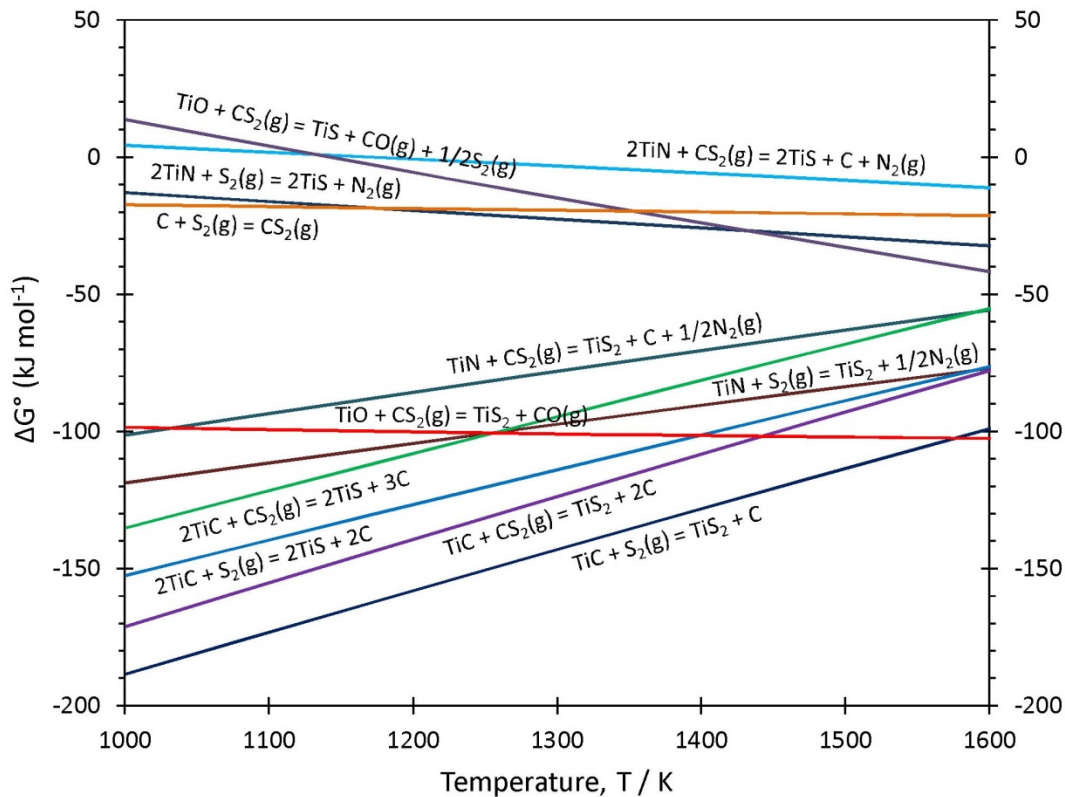


Fig. 1 — The Gibbs free energy change (ΔG°) for sulfurization reactions.

It was known that fairly low oxygen content in titanium can be achieved in OS process even if TiO_2 is selected as starter.^[11,12] Therefore, it is desired that metallic Ti powder with low oxygen concentration using OS process can be realized if titanium sulfide does not contain oxygen so high content as oxide. The electrochemical method to produce a refined titanium powder starting from the natural ore of ilmenite can be established and developed based on the utilization of $\text{TiO}_x\text{C}_y\text{N}_z$ synthesized from ilmenite instead of TiO_2 . Thus, the preliminary stage is to prepare titanium sulfide through $\text{TiO}_x\text{C}_y\text{N}_z$ from ilmenite. No literature data is available on the preparation of TiS_2 / $\text{Ti}_{1+x}\text{S}_2$ from TiN and/or $\text{TiO}_x\text{C}_y\text{N}_z$ powders as far as the authors are aware. The purpose of this work is to study the production of TiS_2 / $\text{Ti}_{1+x}\text{S}_2$ from TiO, TiC, TiN and $\text{TiO}_x\text{C}_y\text{N}_z$. Therefore, the preparation of a single-phase of titanium sulfide from titanium oxycarbonitride was investigated by CS_2 sulfurization.

II. EXPERIMENTAL PROCEDURE

Titanium disulfide powder was prepared by isothermal sulfurization of the starting materials under CS_2 gas. Titanium nitride (TiN), titanium carbide (TiC), titanium mono-oxide (TiO) or titanium oxycarbonitride with the composition of $\text{TiO}_{0.02}\text{C}_{0.13}\text{N}_{0.85}$ was used as a starting material in the sulfurization experiments. The purity of the commercial powders was 99.5 %, and the mean particle sizes of the powders were $< 50\mu\text{m}$ for TiN and TiC and $< 150\mu\text{m}$ for TiO. The iron-free titanium oxycarbonitride powder with the mean particle size of $175\mu\text{m}$ was synthesized from ilmenite (FeTiO_3) in the following two steps. The first step was simultaneous carbothermal reduction and nitridation (CTRN) of FeTiO_3 under a $\text{H}_2\text{-N}_2$ gas atmosphere at 1523 K (1250 °C) for 10.8 ks with a mixture of coal and waste plastic as reductant. The detailed procedure was reported separately by the authors,^[20] and the same powder was served. The second step was iron removal via Becher process using an aeration leaching process in NH_4Cl solution at 343 K (70 °C).^[20, 21] The obtained particles were lined in distilled water, and dried.

The volatile liquid carbon disulfide, CS_2 (Wako Chemicals; $> 99.99\%$) was used for the sulfurization experiments. Argon gas with the flow rate of 20 mL min^{-1} was used to transport the CS_2 gas into the reactor through Teflon tubes. The flow rate of Ar gas was controlled by a digital mass flow controller (CMQ-V, Azbil Corporation, Japan).

In this work, the powder samples weighing about 0.25 g were placed in alumina boats and heated up to the required temperature under continuously flowing Ar gas. The isothermal experiments were performed in the temperature range of 1173 - 1523 K (900 - 1250 °C) for 1.8-10.8 ks in a tube reactor with continuously flowing Ar as carrier gas. The heating and cooling rates were 10 K min^{-1} . A schematic of the experimental apparatus for production of $\text{Ti}_{1+x}\text{S}_2$ / TiS_2 from $\text{Ti}(\text{O,C,N})$ is shown in Figure 2.

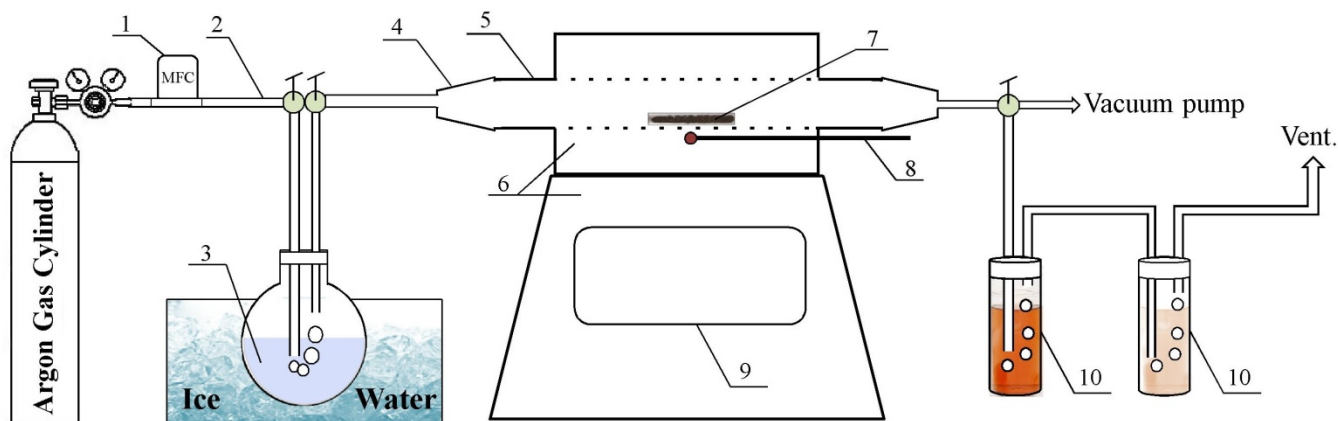


Fig. 2— Experimental set-up for sulfurization using CS_2 gas: 1- Mass flow controller (MFC), 2- Teflon tube, 3- Liquid CS_2 , 4- Glass cap, 5- Reactor, 6- Tube furnace, 7- Sample on alumina boat, 8- Thermocouple, 9- Furnace control unit, 10- 1 M NaOH scrubber

The sulfide phases, the compositions and morphology of the products were determined by X-ray diffraction (XRD, Philips, $\text{Cu-K}\alpha$) and Field Emission Scanning Electron Microscope (FE-SEM; JEOL JSM-6500F) equipped with energy dispersive X-ray spectrometer (EDS/EDX). The oxygen and carbon contents in the products were determined by LECO analyzers (TC600 and CS600). The nondestructive techniques of X-ray photoelectron spectroscopy (XPS, JEOL-JPS-9200) and energy-dispersive X-ray fluorescence spectrometer (EDXRF, JSX-3100RII) were also employed to analysis the final product.

III. RESULTS AND DISCUSSION

A. Sulfurization of Pure TiN, TiC and TiO Powders

1. Sulfurization of TiN

In initial experiments, the effect of temperature on the sulfurization of pure TiN was examined at isothermal conditions in the temperature range from 1173 K to 1523 K (900 °C to 1250 °C). The weight gain of titanium nitride samples ($\Delta W/W_i$) was measured after cooling to room temperature. The results were compared as a function of sulfurization temperature using CS₂ gas mixed with Ar gas. The temperature of liquid CS₂ was kept at 273 K (0 °C) using ice water and the feeding rate of Ar gas was set constant at 20 mL min⁻¹, an average feeding rate of CS₂ was constantly 11.5 mLmin⁻¹ (8.6×10^{-6} mol s⁻¹) at any temperature. The average flow rate of CS₂ was calculated from the weight changes of liquid CS₂ recorded at different reaction times.

Figure 3 shows that the weight change of the sample increased depending on the sulfurization temperature and it reached a certain stable value at each specific temperature; the weight change was identical at 3.6 ks and 10.8 ks. The XRD patterns of the samples after 10.8 ks of sulfurization are shown in Figure 4. The diffraction peaks presented in Figure 4 indicate that sulfurization of TiN was remarkably dependent on the process temperature. The TiN with the inorganic crystal structure database number (ICSD# 01-087-0632) used as a starting material was completely converted to titanium sulfides at temperatures above 1373 K (1100 °C). The intense peaks of a phase of Ti_{2.45}S₄ (ICSD# 01-072-0820) appeared at 1173 K (900 °C), and the formation of single phase of Ti_{2.45}S₄ was confirmed at 1473 K (1200 °C). The sulfurization temperature above 1473 K (1200 °C) resulted in the formation of another titanium higher sulfide of TiS₂ (ICSD# 01-088-2479) and a faint amount of Ti_{0.685}S (ICSD# 01-071-1977). At low temperatures of 1373 K to 1423 K (1100 °C to 1150 °C), Ti_{2.45}S₄ phase was formed accompanying with TiS₂ and TiS_{1.748} (ICSD# 00-039-1020) phases. However, at 1173 K (900 °C) and 1273 K (1000 °C), the TiN phase was not entirely transformed to titanium sulfide, and the sulfurized

184 samples consisted of a large amounts of TiN, and small amounts of Ti_5S_8 (ICSD# 00-036-0532), $\text{Ti}_{2.45}\text{S}_4$,
 185 $\text{TiS}_{1.748}$ and TiS_2 phases.

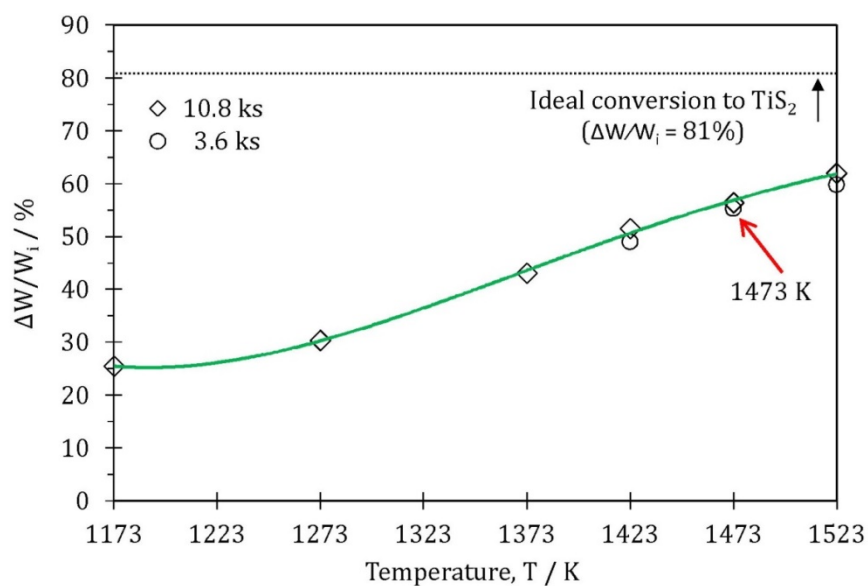


Fig. 3 — Weight gain versus sulfurization temperature for pure TiN samples.

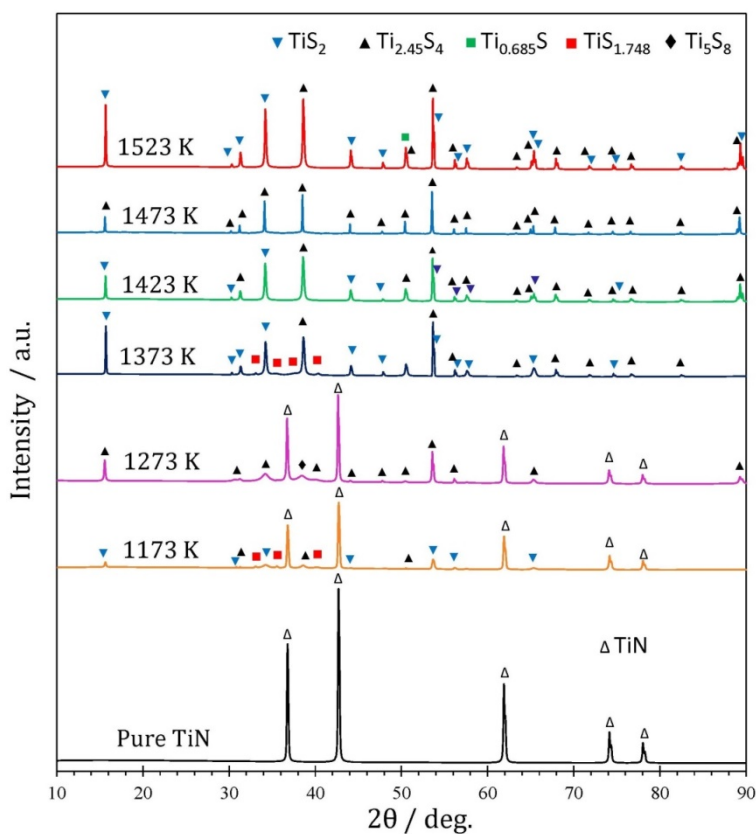
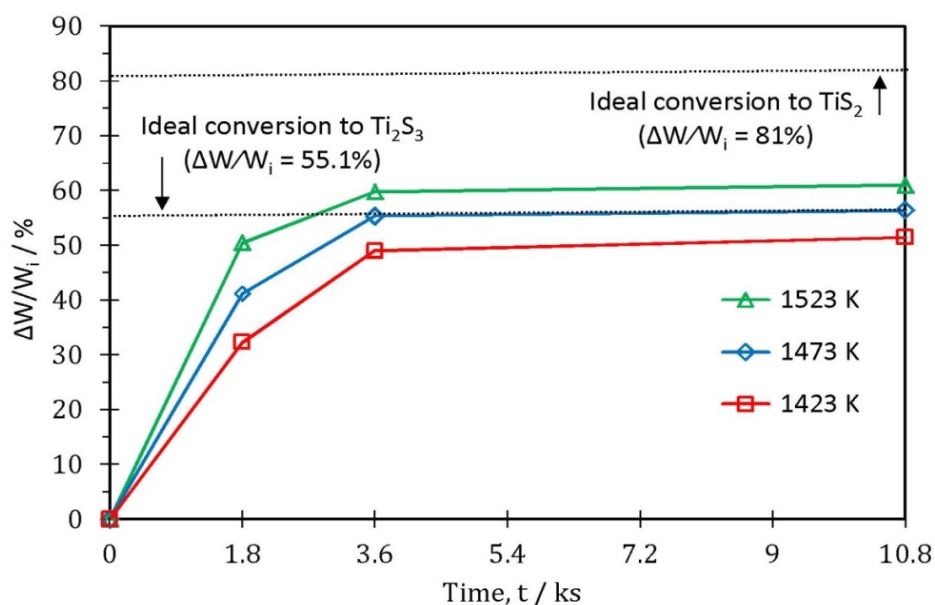


Fig. 4 — XRD patterns of the sulfurized samples for 10.8 ks.

190 The weight gain during TiN sulfurization is shown in Figure 5 as a function of time. The XRD
 191 spectra of TiN samples sulfurized at 1473 K (1200 °C) for 1.8, 3.6 and 10.8 ks are shown in Figure 6.
 192 Based on the weight gain changes of the samples and the phase identification presented in Figures 4 and
 193 6, the lowest temperature and the shortest time to form a single phase of titanium sulfide ($\text{Ti}_{2.45}\text{S}_4$) were
 194 then approximately 1473 K (1200 °C) and 3.6 ks, respectively. At higher temperatures as shown in
 195 Figure 5, the degree of sulfurization, $\Delta W/W_i$, of the samples increased slightly. Although the degree of
 196 sulfurization obtained for the samples sulfurized at 1473 K (1200 °C) was slightly lower than that at
 197 1523 K (1250 °C), the product was the single phase of $\text{Ti}_{2.45}\text{S}_4$ after 3.6 ks of sulfurization and its
 198 weight-gain curve approached to the ideal conversion to Ti_2S_3 phase. It is noteworthy that the
 199 composition of $\text{Ti}_{2.45}\text{S}_4$ corresponds to $\text{Ti}_2\text{S}_{3.26}$. Because the valency state of Ti in TiN is also apparently
 200 3, and the valency state of Ti in Ti_2S_3 is apparently 3, there may be no valency change such as reduction.
 201 Although the crystalline structure of TiN and Ti_2S_3 are different, the simple replacement between
 202 nitrogen and sulfur can be seen apparently. Consequently, the main focus of this study was set on the
 203 conversion of TiN to Ti_2S_3 which is feasible at 1473 K (1200 °C) in 3.6 ks.



204 Fig. 5 — Weight gain versus sulfurization time for pure TiN samples at 1423 K (1150 °C), 1473 K (1200 °C) and 1523 K
 205 (1250 °C).
 206

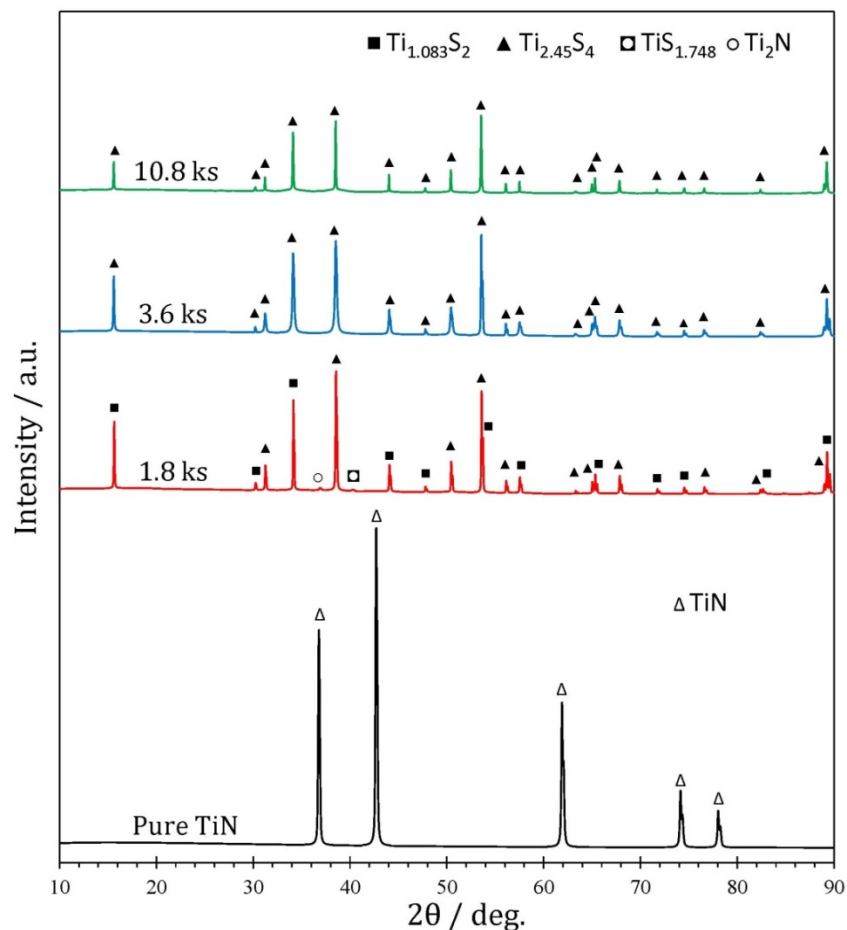


Fig. 6 — Sulfurization of TiN at 1473 K (1200 °C) for 1.8 ks, 3.6 ks and 10.8 ks.

2. Sulfurization of TiC and TiO

The sulfurization of TiC and TiO powders by CS₂ gas was evaluated at 1473 K (1200 °C). The XRD patterns of TiC and TiO samples in progress of sulfurization at 1473 K (1200 °C) are presented in Figures 7 and 8, respectively. After 7.2 ks of sulfurization under CS₂ gas, no residual TiC was detectable and TiC powder was totally converted to Ti_{2.45}S₄, TiS_{1.748} and TiS₂ phases. By increasing the sulfurization time to 10.8 ks, TiC intensively transformed into a mixture of TiS₂, TiS_{1.748} and Ti_{2.45}S₄ phases, which indicate the higher degree of sulfurization. The observed phases at 7.2 and 10.8 ks were the same; however the weight gain of the sample synthesized at 10.8 ks was about 1% higher than that calculated for the prepared sample at 7.2 ks. In addition, the intensity of the XRD peaks particularly for TiS₂ phase in the product obtained at 10.8 ks was much higher as presented in Figure 7. Thus it can be

219 inferred that the degree of sulfurization of TiC was slightly higher at 10.8 ks compared to the sample
220 prepared at 7.2 ks. In the samples sulfurized for a period shorter than 5.4 ks, Ti_8C_5 phase (ICSD# 01-
221 072-2496) was observed. For the sulfide phase, $\text{Ti}_{7.5}\text{S}_{12}$ (ICSD# 01-072-0242) and $\text{Ti}_{1.083}\text{S}_2$ (ICSD# 01-
222 084-0372) phases were also detected in the sample sulfurized at 1473 K (1200 °C) for 5.4 ks. The
223 appearance of these intermediate phases indicates that complicated sulfurization mechanisms occur
224 locally in the same sample.

225 In the case of TiO powder, a sulfurization time of 7.2 ks was not sufficient to convert TiO powder
226 fully to titanium sulfide due to the presence of titanium sub-oxides, $\text{Ti}_n\text{O}_{2n-1}$ ($n= 3, 7, 8$). Ti_3O_5 , Ti_7O_{13}
227 and Ti_8O_{15} Magneli phases that were readily identified by X-ray diffraction analysis in the samples
228 sulfurized for 1.8 ks to 7.2 ks. These Magneli phases formation was due the presence of very small
229 amounts of TiO_2 (ICSD# 01-076-0325) in initial TiO powder. However, with increasing the time to 10.8
230 ks, most of TiO powder was converted to $\text{Ti}_{2.45}\text{S}_4$, $\text{Ti}_{1.083}\text{S}_2$ and small amounts of $\text{Ti}_{9.2}\text{S}_{16}$ (ICSD# 01-
231 072-0005), $\text{Ti}_{5.36}\text{S}_8$ (ICSD# 01-072-0006) and TiS (ICSD# 00-012-0534) phases coexisted with the
232 dominated phases. With TiC and TiO powders, longer times were required for sulfurization compared to
233 TiN powder at the same temperature. The sulfurization time of TiO powder might be shortened either by
234 increasing temperature or by mixing vaporized sulfur to increase the partial pressure of sulfur during CS_2
235 sulfurization process. It is expected that the presence of small amounts of titanium sub-oxides does not
236 have significant effect on the feasibility of OS process for metallic Ti production, because OS process
237 can remove oxygen even from the sub-oxides such as Ti_3O .^[7]

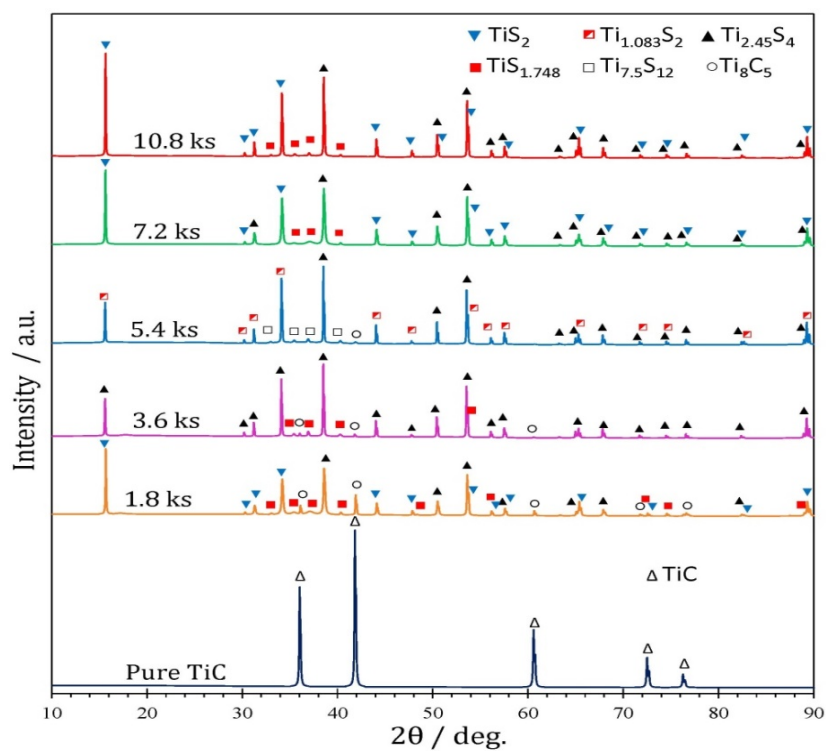


Fig. 7 — XRD patterns of TiC samples in progress of sulfurization at 1473 K (1200 °C).

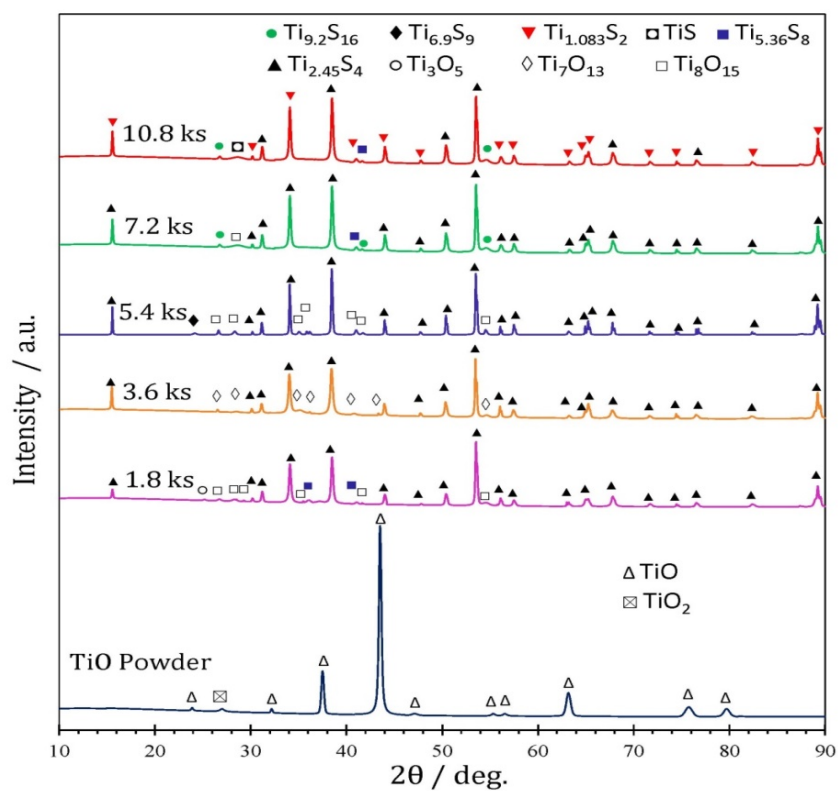


Fig. 8 — XRD patterns of TiO samples in progress of sulfurization at 1473 K (1200 °C).

242 The time dependence of the sulfurization process for three different initial powders, TiN, TiC and
243 TiO, in the preparation of titanium sulfide has been compared based on the weight changes. Figure 9
244 compares the weight gain of TiN, TiC and TiO powders at 1473 K (1200 °C). As is seen, the weight gain
245 of TiC was larger than that obtained for TiN and TiO powders. The weight gain indeed depends on
246 atomic weight of the elements bonded to Ti, and in the case of TiC the reaction produces solid carbon.
247 The XRD data presented in Figures 6, 7 and 8 show that some portion of larger weight gain could be due
248 to the formation of $\text{TiS}_{1.748}$, $\text{Ti}_{1.083}\text{S}_2$ ($\text{TiS}_{1.846}$) and/or TiS_2 phases at 1.8-5.4 ks from TiC. These phases
249 could be hardly seen in the samples prepared from TiN and TiO powders. The feasibility of conversion
250 of the investigated compounds has therefore been substantiated based on the XRD data and it was in the
251 order of $\text{TiC} > \text{TiN} > \text{TiO}$.

252 This is because the dissociation energy of Ti-C bonding is lower than that reported for Ti-O and Ti-
253 N.^[25] The dissociation energies per a bond of Ti-O, Ti-N, Ti-C and Ti-S are 667 ± 7 , 501 ± 13 , 395 ± 23
254 and $461.1 \pm 6.3 \text{ kJ mol}^{-1}$ at 298 K (25 °C), respectively. These energy data suggest the difficulties
255 involved in the conversion of above mentioned compounds, especially TiO which has the highest bond
256 energy to TiS and/or TiS_2 . Therefore, according to the bond dissociation energy, TiC could be readily
257 converted to TiS_2 which is in good agreement with the results obtained in the present study.

258 From the XRD patterns, it can be also concluded that the main peaks belong to $\text{Ti}_{2.45}\text{S}_4$ (close to
259 Ti_2S_3 phase), when TiN powder was used as an initial material in the sulfurization process. Furthermore,
260 titanium exhibits apparent valency states of +2, +3, and +4 in TiO, TiN and TiC compounds,
261 respectively.^[25] The weight gain ($\Delta W/W_i$) of TiC sample sulfurized at 1473 K (1200 °C) for 3.6 ks was
262 82.5% which is close to the ideal conversion of TiC to Ti_2S_3 with consideration of the solid carbon in the
263 reaction. However, with increasing the reaction time to 7.2 and 10.8 ks, the mass changes of the samples
264 were 100% and 101%, respectively. Therefore, in longer reaction times $\text{Ti}_{2.45}\text{S}_4$ and TiS_2 with the
265 relative conversions of about 103% and 107% in the order could be formed from TiC. In the calculation

266 of ideal mass changes for TiC, mass of the solid carbon was considered in the product, as well. Thus, it
 267 might be reasonable to assume the ideal conversion of TiN to pseudo-hexagonal Ti_2S_3 , and of both TiC
 268 and TiO powders to TiS_2 phases. In the formation of Ti_2S_3 or $\text{Ti}_{2.45}\text{S}_4$, the electronic charge must be
 269 balanced. Hence, the N^{3-} ions in TiN are replaced by S^{2-} ions to have the balanced charge. However,
 270 there might be some deviations from the stoichiometric composition due to the presence of small
 271 amounts of oxygen and carbon which may result in formation of nonstoichiometric phase of $\text{Ti}_{2.45}\text{S}_4$.

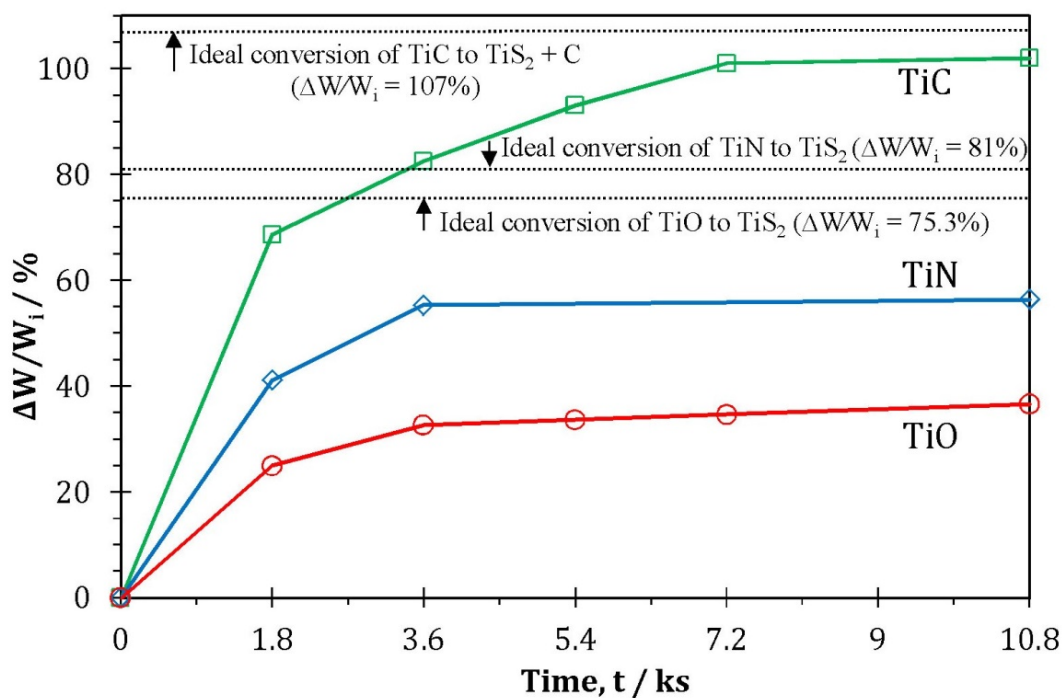


Fig. 9 — Weight gain versus sulfurization time for TiO, TiN and TiC samples at 1473 K (1200 °C).

274 Onoda and *et al.*^[26] reported the formation of nonstoichiometric compounds when synthesized in the
 275 compositional range between $\text{TiS}_{1.4}$ and $\text{TiS}_{1.6}$ at high temperatures of 1073 K (800 °C). The compounds
 276 which exist in the range of TiS - TiS_2 have been referred to by various formulas such as Ti_2S_3 , Ti_3S_4 and
 277 $\text{Ti}_{2+x}\text{S}_4$ phases.^[26] Their structures were analyzed to be based on close packing of sulfur; hexagonal close
 278 packing for TiS or TiS_2 , and more complex structures of the close packing layers for the intermediate
 279 phases. The identified phase as $\text{Ti}_{2.45}\text{S}_4$ from the XRD investigations could be therefore one of Ti_2S_3 ,
 280 Ti_3S_4 and $\text{Ti}_{2+x}\text{S}_4$ phases. The single crystal of $\text{Ti}_{2+x}\text{S}_4$ was successfully prepared in a vapor transport

281 reaction by Norrby and Franzen.^[27] However, they have used titanium monosulphide as initial material
282 and ammonium chloride was also used as additive to provide the chloride species for a vapor transport
283 reaction occurred in an enclosed silica tube. They reported that a single and sulphur-rich condensed
284 phase was prepared from the vapor transport reaction in a temperature gradient of 1173 K to 973 K
285 (900 °C to 700 °C) at the colder part of the reaction tube. The operating temperature was lower than our
286 temperature, but this is reasonable because our sulfurization pressure might be higher. Their reports
287 agreed well with our findings that showed the formation of multi-phase titanium sulfides from TiC and
288 TiO powders by the sulfurization using CS₂ gas at 1473 K (1200 °C) for 7.2 and 10.8 ks, respectively.

289 *B. Sulfurization of Iron-Free TiO_xC_yN_z*

290 Figure 10 demonstrates the XRD patterns of Fe-free titanium oxycarbonitride (TiO_xC_yN_z) sample
291 produced from ilmenite by carbothermal reduction and nitridation (CTRN) process.^[20,21] and the
292 subsequently sulfurized sample. The composition of starting material for the sulfurization process was
293 TiO_{0.02}C_{0.13}N_{0.85}. It was synthesized by a two-step process including CTRN process from ilmenite at
294 1523 K (1250 °C) for 10.8 ks under a H₂–N₂ gas mixture, and subsequent iron removal by using NH₄Cl
295 solution at temperature of about 343 K (70 °C). As can be seen from Figure 10(a), all phases containing
296 Fe have been successfully removed from the prepared sample. However, a small amounts of impurities
297 such as silica, SiO₂ (ICSD#01-081-1665), aluminum oxide, Al₂O₃ (ICSD# 01-075-0782) and alumina
298 silicate, Al_{5.65}O_{9.175}Si_{0.35} (ICSD# 01-082-1237) were detected in the iron-free titanium oxycarbonitride
299 with the composition of TiO_{0.02}C_{0.13}N_{0.85} (Figure 10 (a)). It is noted that TiN can form a solid-solution
300 having NaCl structure with TiO and TiC. The oxygen and carbon contents of our sample
301 TiO_{0.02}C_{0.13}N_{0.85} were, however, low enough to be considered as titanium nitride (TiN), thus, the CS₂
302 sulfurization of TiO_xC_yN_z was also conducted at 1473 K (1200 °C) for 3.6 ks for production of the
303 single phase of Ti_{2.45}S₄.

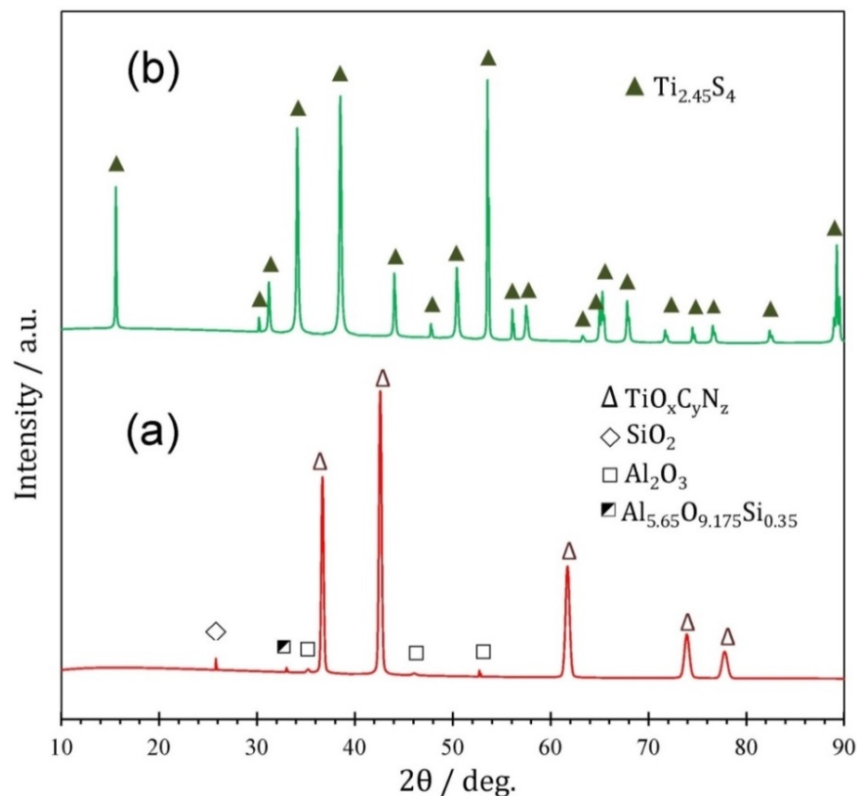


Fig. 10 — XRD patterns for (a) titanium oxycarbonitride and (b) sulfurized sample at 1473 K (1200 °C) for 3.6 ks.

The X-ray diffraction peaks associated with $\text{TiO}_x\text{C}_y\text{N}_z$ disappeared as shown in Figure 10(b), when the sample was sulfurized at the same experimental conditions applied for the sulfurization of pure TiN. The XRD peaks of the sulfurization product were very sharp reflecting a high degree of crystallinity and all the peaks were identified as $\text{Ti}_{2.45}\text{S}_4$. None of the TiO, TiC and TiN peaks was detected in the product, indicating a favorable sulfurization for the sample prepared from ilmenite. The ideal weight gain of TiN sample could be 55.1 % when we consider Ti_2S_3 phase as the main product of the process. The mass change for full conversion to $\text{Ti}_{2.45}\text{S}_4$ is calculated to be about 62%. The weight gain of $\text{TiO}_{0.02}\text{C}_{0.13}\text{N}_{0.85}$ sample was 55.3 %, showing that the extent of sulfurization approached close to 100% with the balance charges of Ti^{3+} in TiN and Ti_2S_3 . Therefore, it can be concluded that the CS_2 sulfurization of $\text{TiO}_{0.02}\text{C}_{0.13}\text{N}_{0.85}$ at 1473 K (1200 °C) provides the single phase of $\text{Ti}_{2.45}\text{S}_4$ (hexagonal, P63mc), which is consistent with the findings obtained for pure TiN powder at the similar experimental conditions. Both

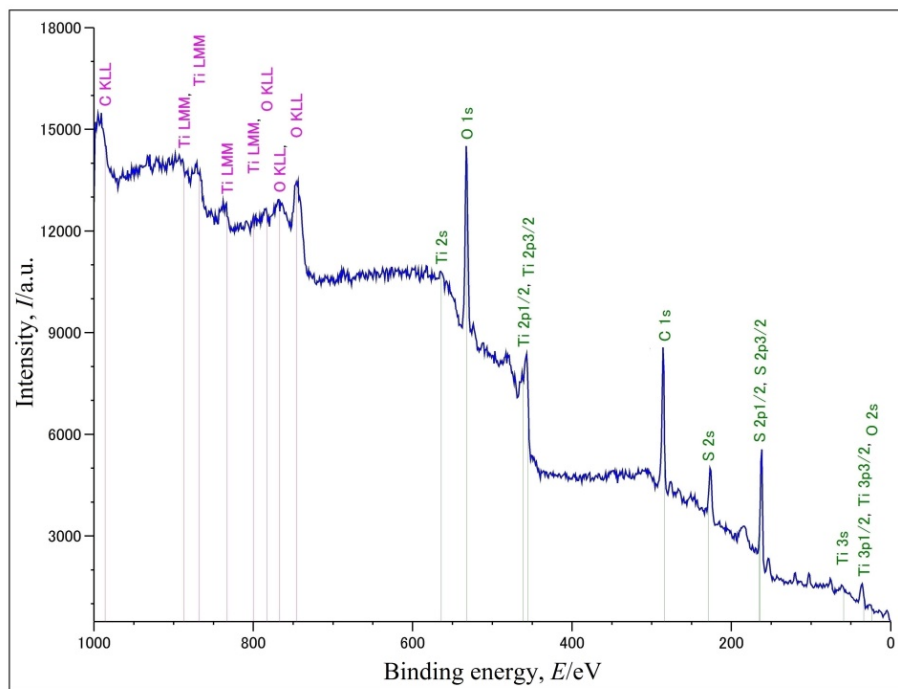
weight gain measurements and XRD analysis showed the feasibility of this approach that the nitrated ilmenite is converted to titanium sulfide which is an alternative material for TiO_2 in OS process.

C. Mechanism of Titanium Sulfide Formation using CS_2 Gas

Yuan *et al.*^[28] showed that CS_2 is a powerful sulfurizing agent and they utilized it for the preparation of rare earth sulfides from the commercial rare earth oxide powders in the temperature range of 1073 - 1523 K (800 °C - 1250 °C).^[28] The reaction rate of the studied gas-solid system has been affected by gas flow rate and particle sizes of the starting materials. Present results showed that the sulfurization of TiN powder was remarkably dependent on the operating temperature and time. This could be either due to the decomposition of CS_2 gas or the reaction mechanism, and the kinetics of the process was examined. The CS_2 gas can shorten the sulfurization time compared with H_2S gas; the sulfurization of oxygen-containing rare earth compounds by H_2S gas needed about 604.8 ks at 1348 K (1075 °C).^[29]

From our XRD results, the sulfurization of TiN and $\text{TiO}_{0.02}\text{C}_{0.13}\text{N}_{0.85}$ using CS_2 gas occurred very rapidly at 1473 K (1200 °C) for 3.6 ks, and a single phase of $\text{Ti}_{2.45}\text{S}_4$ was formed. In the temperature range used in present approach, CS_2 gas is decomposed to carbon and gaseous sulfur, S_2 (g) as shown in Eqs. [2] and [3]. This is proved by the existence of black carbon deposits and yellow sulfur crystals which were observed in the reaction tube. In the formation of $\text{Ti}_{2.45}\text{S}_4$ / $\text{Ti}_{2+x}\text{S}_4$, the positive charge of Ti^{3+} must be balanced with the negative charge of S^{2-} . Thus, the N^{3-} ions in TiN are favorably replaced by S^{2-} ions to form Ti_2S_3 phase at 1473 K (1200 °C). However, there existed a small deviation from the stoichiometric composition of Ti_2S_3 because of the presence of small amounts of oxygen and carbon in the product. X-ray photoelectron spectroscopy (XPS) analysis was also employed to study the presence of oxygen and carbon in the titanium sulfide sample prepared from pure TiN which has low free carbon compared to the products synthesized from TiC and/or $\text{TiO}_x\text{C}_y\text{N}_z$. Wide energy spectra taken by XPS on titanium sulfide product showed the expected existence of Ti, S, O and C, as shown in Figure 11. The binding energy of the adventitious C1s at 284.8 eV was assigned to C-C and C=C hydrocarbon bonds

341 and used to calibrate XPS to minimize charging artifacts on the sample. Figure 12 also shows the high-
 342 resolution XPS spectrums fitting for carbon (C 1s), oxygen (O 1s), sulfur (S 2p_{3/2}), titanium (Ti
 343 2p_{3/2}) and nitrogen (N 1s). The carbon was found to be present mostly as free carbon (285.50 eV) and
 344 chemically absorbed CS₂ gas (287.00 eV) shown in Figure 12(a) on the surface of the powders and not in
 345 the structure of the synthesized product. However, oxygen could be present as non-stoichiometric TiO₂
 346 species (530.7 eV), TiO_{0.3}S_{1.5} (162.88 eV) and/or Ti₂O₃ (462.01 eV) as shown in Figures 12 (b)-(d).
 347 TiS₂ and Ti₂S₃ were the most dominant phases that could be observed in the surface analysis by XPS.
 348 The Ti 2p_{3/2} peaks located at 459.08 and 455.94 eV can be easily indexed to the binding energy of Ti₂S₃
 349 and TiS₂ phases, respectively. The peak at 161.67 eV is attributed to S 2p_{3/2} indicating the TiS₂ in the
 350 product based on the NIST XPS data.^[30] However, no significant peak for nitrogen was observed which
 351 indicates successful sulfurization of pure TiN in 3.6 ks at 1473 K (1200 °C), as presented in Figure 12(e).
 352



353
 354 Fig. 11 — Survey spectrum from titanium sulfide sample prepared from TiN showing various titanium, sulfur, oxygen peaks
 355 and a carbon peak.

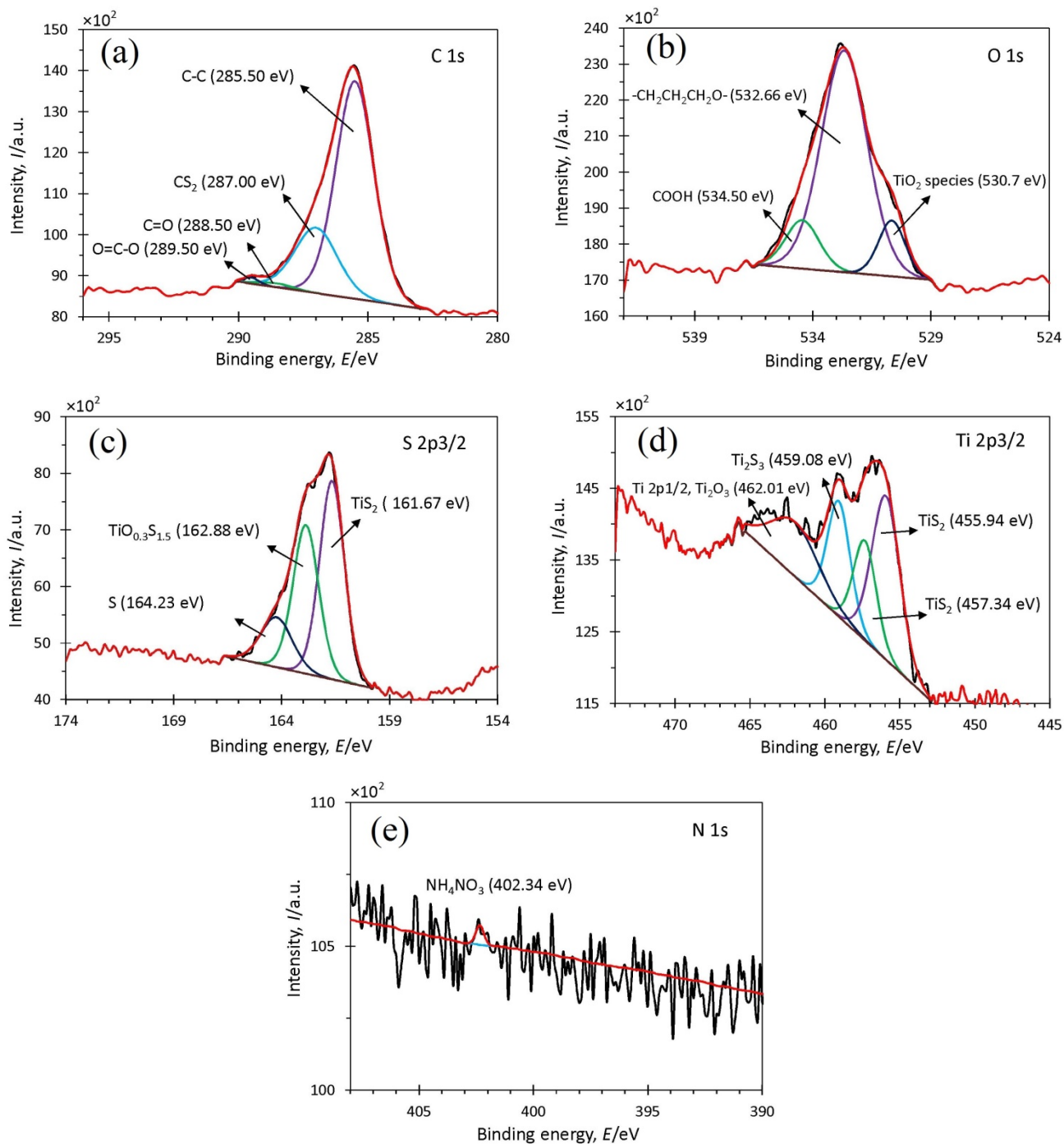
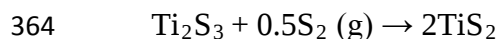
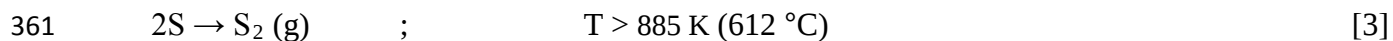
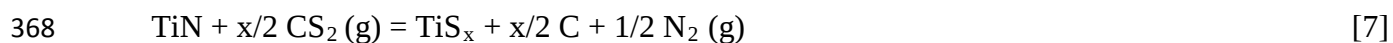


Fig. 12 — High-resolution XPS spectra for (a) C 1s, (b) O 1s, (c) S 2p_{3/2}, (d) Ti 2p_{3/2} and (e) N 1s.

To simplify the reaction mechanism in the formation of single phase of $\text{Ti}_2\text{S}_3/\text{Ti}_{2+x}\text{S}_4$ crystals from TiN and/or $\text{TiO}_{0.02}\text{C}_{0.13}\text{N}_{0.85}$, the key reactions of titanium sulfide formation can be described in the following sequence.



366 Apart from the formation of yellow sulfur crystals such as S_8 , the carbon deposited as the black carbon
367 and condensed in the reaction tube. The overall reaction for TiN may be also explained as:



369 where x is the molar ratio of S to Ti in the product.

370 *D. Microstructural Characterizations and Analyses of Products*

371 Detailed microstructural investigations using SEM and EDX analysis were conducted on starting
372 materials and the sulfurized samples. From the XRD results, it has been found that titanium sulfide was
373 formed from either TiN, TiC or TiO powders after sulfurization at 1473 K (1200 $^\circ\text{C}$). Figure 13 indicates
374 the SEM images of TiN, TiC and TiO powders before ((a), (b), (c)) and after ((d), (e), (f)) the
375 sulfurization process by CS_2 gas. As is seen in Figure 13(d)(e) and (f), well-crystallized hexagonal
376 shaped plates of titanium sulfide were formed in all the cases. The color and morphological changes were
377 significant enough to distinguish the products obtained from the starting powders. The EDX chemical
378 analysis from regions 1 to 5 in Figures 13(d) – (f) are summarized in Table I.

379 Based on quantitative EDX analyses of the samples, regions 1, 2, and 3 are clearly identified as
380 titanium sulfide crystals. This means that the resulting products from the sulfurization of TiC and TiO
381 contained some parts of unsulfurized/undesired impurities. For instance, Point 4 in Figure 13(e) and
382 Point 5 in Figure 13(f) were analyzed in the samples prepared from TiC and TiO powders; respectively,
383 and determined as undesired particles. The formation of nano-sized carbon fibers, as showed with an

384 arrow 4 in Figure 13(e), could be either originated from the decomposition of CS₂ gas or residual carbon
385 from TiC. The sample prepared from TiC powder contained relatively higher contents of carbon (9.3
386 wt.%), compared with the samples synthesized from TiO and TiN. As a consequence, the SEM images
387 demonstrated that the morphology of the titanium sulfide particles formed from TiO, TiC and TiN was
388 entirely similar, although some impurities such as carbon fibers were observed in the sample synthesized
389 from TiC powder. Furthermore, the transformation of TiN to the single phase of Ti_{2.45}S₄ has been proved
390 with the morphological investigations. The presence of N in the EDX analysis of the TiN sulfurized
391 sample could be indicating there is a TiN which has not reacted. Thus, the N content of the TiN
392 sulfurized sample at 1473 K (1200 °C) for 3.6 ks was measured by LECO analysis and it was about
393 0.06wt% which could be lowered more by increasing the sulfurization time. The hexagonal-like particles
394 of titanium sulfides produced from TiN in 3.6 ks are fairly homogeneous compared to the crystals
395 synthesized from TiC and TiO. The formation of hexagonal plates of sulfides from TiC and TiO powders
396 needs longer reaction times of 7.2 ks and 10.8 ks compared to TiN powder that allow the particles to
397 grow further.

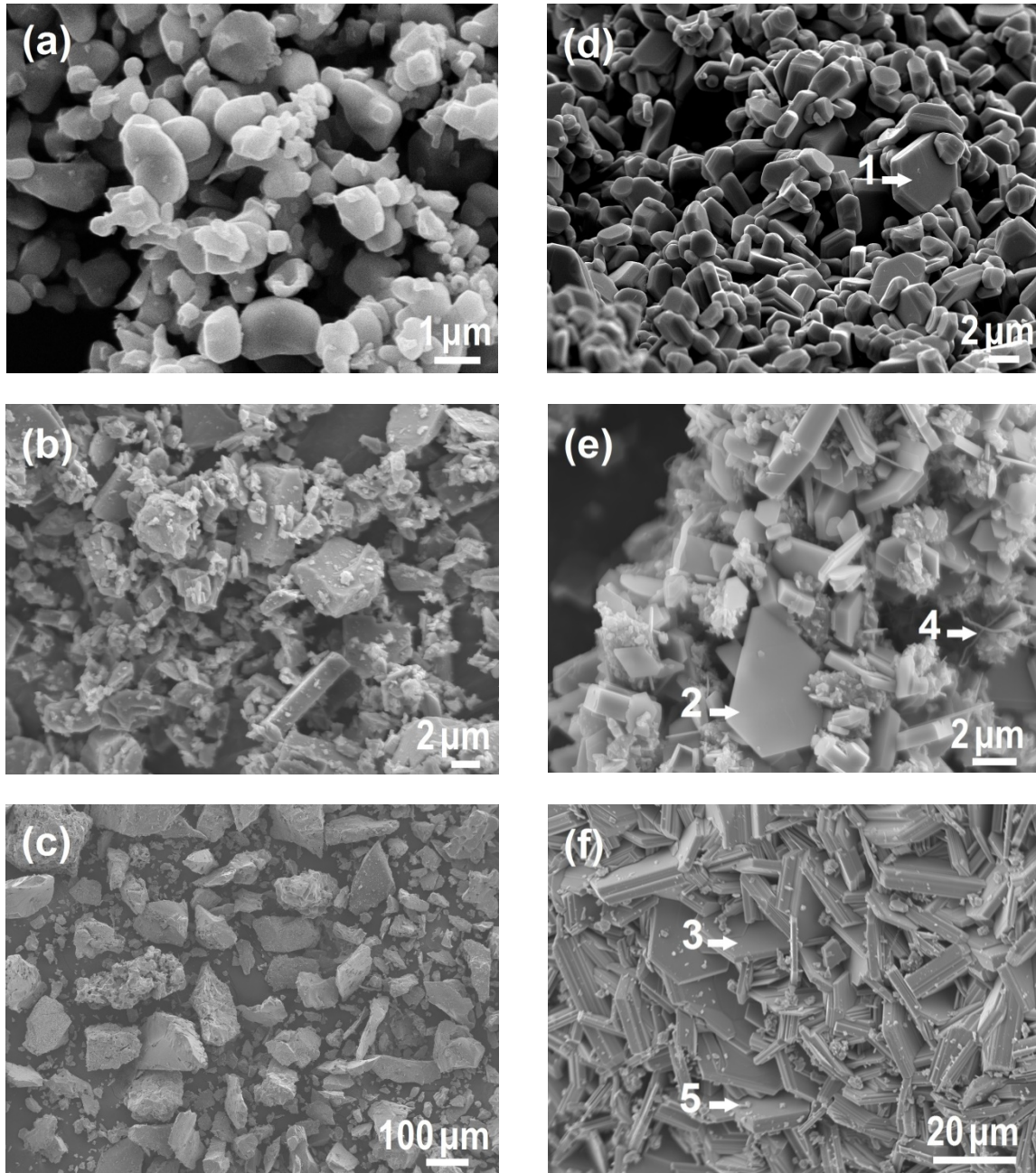
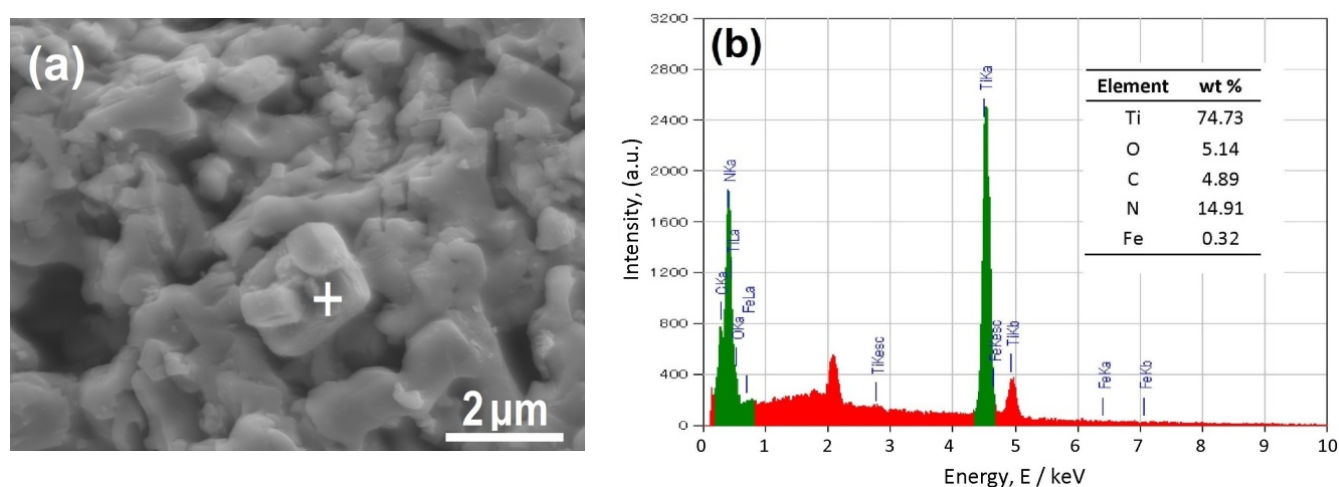


Fig. 13 — SEM morphology of as-received powders before the sulfurization (a) TiN, (b) TiC and (c) TiO powders and after the sulfurization process at 1473 K (1200 °C) for (d) 3.6 ks from TiN, (e) 7.2 ks from TiC, and (f) 10.8 ks from TiO.

The XRD patterns showed that $\text{Ti}_{2.45}\text{S}_4$ / $\text{Ti}_{2+x}\text{S}_4$ was the crystalline phase formed from the sulfurization of TiN and $\text{TiO}_{0.02}\text{C}_{0.13}\text{N}_{0.85}$ powders at 1473 K (1200 °C) for 3.6 ks. The microstructure of the oxycarbonitride before and after the sulfurization was meticulously analyzed to provide accurate and reliable point analysis via EDX method. The SEM morphology and its corresponding EDX point analysis of the iron-free oxycarbonitride synthesized from ilmenite are shown in Figure 14. The titanium

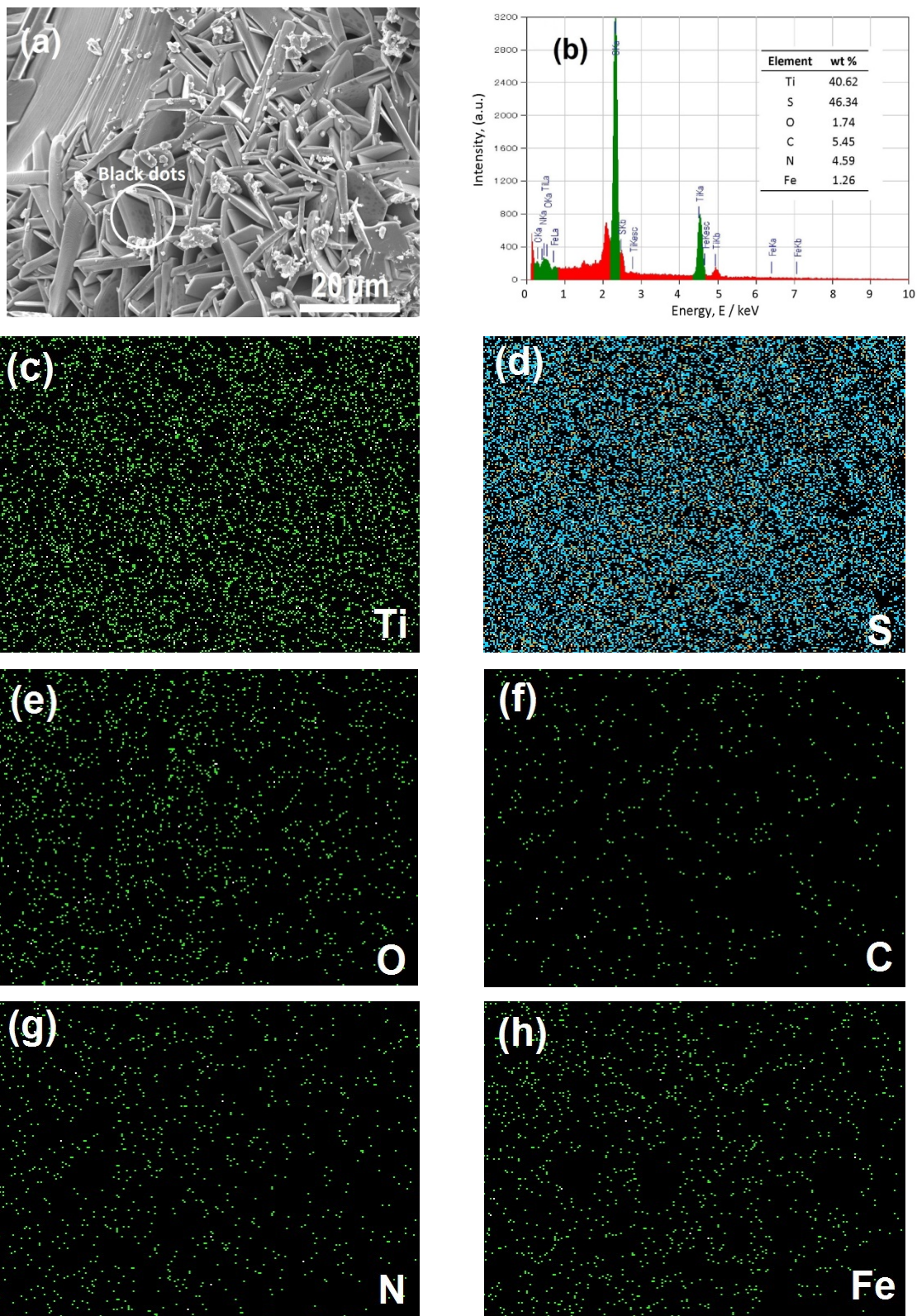
405 oxycarbonitride crystals are observed in cubic shapes with porous microstructures (Figure 14(a)), and the
 406 EDX analysis provided in Figure 14(b) showing that Fe content is very low (0.32 wt.%) in the
 407 synthesized cubic oxycarbonitride powder by CTRN process. With regard to the latter Figure, low iron
 408 contamination of the sample prepared from ilmenite is a strong evidence for the viable iron removal by
 409 the CTRN followed by aeration leaching. Details of the CTRN and iron removal process by using NH_4Cl
 410 solution are described elsewhere.^[20,21,31]



411 Fig. 14 — SEM micrograph and EDX analysis of the iron-free oxycarbonitride synthesized from ilmenite by CTRN process at
 412 1523 K (1250 °C) under an $\text{H}_2\text{-N}_2$ atmosphere: (a) SEM image and (b) EDX spectrum of marked point.

413 Figure 15 shows the SEM micrograph and the corresponding EDX maps of the titanium sulfide
 414 prepared from the sample shown in Figure 14. Hexagonal layered structure of titanium sulfide was
 415 observed as a result of the reactions that took place in a CS_2 gas atmosphere at 1473 K (1200 °C) for 3.6
 416 ks. The EDX maps (Figures 15(c) to (h)) proved the existence of titanium sulfide crystals judged from
 417 the enriched levels of Ti and S elements in the product. The EDX spectra given in Figure 15(b) showed
 418 that surface S:Ti molar ratio was ~ 1.70 , which is close to the expected $\text{Ti}_{2.45}\text{S}_4$ phase. However, oxygen,
 419 nitrogen and particularly carbon contents (Figure 15(b)) were slightly high, whereas they were very low
 420 for the sample prepared in a similar way from pure TiN. An explanation for this observation was the
 421 presence of TiC in solid solution with TiO and TiN phases. The surface of titanium sulfide crystals was

422 covered with numerous small black particles (circulated in Figure 15(a)) that could be impurities such as
423 carbon. It was reported that presence of TiC in oxycarbonitride positively affected the chlorination
424 process in the production of TiCl_4 .^[21] For the future study of industrial application, nevertheless, low-
425 carbon oxycarbonitride powder was required for the production of commercial grade titanium metal by OS
426 process.^[7]



427 Fig. 15 — SEM micrograph and EDX maps of the titanium sulfide sample prepared from iron-free oxycarbonitride using CS_2
 428 sulfurization at 1473 K (1200 °C) for 3.6 ks: (a) SEM micrograph, (b) EDX spectra of (a), (c)-(h) EDX maps.

429 It is well known that the presence of carbon (≥ 0.1 wt.%) as an impurity gives adverse effect on the
430 quality of the metallic titanium and makes it brittle due to the formation of carbide in the structure of
431 titanium and its alloys.^[32,33] In XRD profiles, no significant peaks related to TiC and TiO phases were
432 identified. However, low concentrations of surface oxygen and carbon were detected in SEM/EDS
433 analyses, indicating that oxygen and particularly carbon are the main impurities in the final product. The
434 EDS surface analyses for these light elements are not suitable for precise evaluation. Thus, carbon and
435 oxygen contents of the samples sulfurized at 1473 K (1200 °C) were determined using LECO elemental
436 analyzers. Table II illustrates the oxygen and carbon contents of the samples.

437 As listed in Table II, the minimum content of carbon was about 0.14 wt.% in the sample prepared
438 from TiN at 1473 K (1200 °C) for 3.6 ks, whereas it became the largest (9.74 wt.%) for the sample
439 prepared from TiC powder at the same temperature for 7.2 ks. The measured C content in TiC sample
440 after the sulfurization for 7.2 ks is in good agreement with the reaction presented in Figure 1 ($\text{TiC} +$
441 $\text{S}_2(\text{g}) = \text{TiS}_2 + \text{C}$). In contrast, the sulfurized samples from TiO and TiN at 10.8 ks contained 0.195 wt.%
442 and 0.20 wt.% carbon, respectively. This indicates that the higher carbon concentration in the sample
443 prepared from TiC was probably due to the decomposition of TiC and not from CS_2 . The decomposition
444 reaction of TiC precipitates carbon as given in Figure 1. In addition, this higher carbon concentration
445 validates the existence of carbon fibers in the microstructures observed by SEM/EDX analyses for
446 samples synthesized from TiC. The residual oxygen was also observed in the samples prepared from TiN
447 and TiO powders. The oxygen contents of the samples sulfurized for 3.6, 7.2 and 10.8 ks were also
448 determined by LECO analysis and were 20.15 wt.%, 19.23 wt.% and 16.80 wt.%, respectively. The
449 presence of oxygen indicates that TiO has not been fully reacted and some unreacted TiO particles could
450 be found in the product prepared from TiO powder. The highest oxygen content in Table II was 16.8
451 wt.% for the sample sulfurized from TiO for 10.8 ks; however, it was only 1.24 wt.% and 0.25 wt.% for
452 the samples prepared from TiN for the sulfurization time of 3.6 and 10.8 ks, respectively. Thus, longer

453 sulfurization time resulted in the lower oxygen levels of the samples, although carbon content slightly
454 increased due to decomposition of CS₂.

455 The S:Ti molar ratio for the low-oxygen sample prepared from TiN at 1473 K (1200 °C) in 3.6 ks
456 was also precisely evaluated by energy-dispersive X-ray fluorescence (EDXRF) spectrometer, and the
457 molar ratio of S:Ti was obtained about 1.35 which is close to the Ti₂S₃ product. In case of the sample
458 prepared from TiO_{0.02}C_{0.13}N_{0.85} at 3.6 ks, oxygen and carbon contents were 1.8 wt.% and 1.4 wt.%,
459 respectively. The higher carbon concentration in this sample was due to TiC phase in titanium
460 oxycarbonitride sample. As mentioned earlier, the presence of a small amount of TiO in oxycarbonitride
461 sample was also practically negligible and the oxygen content of the product from TiO_{0.02}C_{0.13}N_{0.85} was
462 very low as intended and the remaining oxygen in the final product could be reduced by OS process in Ti
463 metal powder production.

464 IV. CONCLUSIONS

465 The authors proposed to produce commercial grade Ti metal powder from sulfurized iron-free titanium
466 oxycarbonitride prepared from ilmenite. The main objective of this study was to produce a single phase
467 of titanium sulfide from iron-free TiO_{0.02}C_{0.13}N_{0.85}. The formation of titanium sulfide Ti_{2+x}S₄/TiS₂ via
468 CS₂ gas sulfurization of TiO, TiC, TiN and TiO_xC_yN_z powders were investigated in the range of 1173 -
469 1523 K (900 °C - 1250 °C) for 1.8 - 10.8 ks. It was possible to completely convert pure TiN, TiC, TiO
470 and TiO_{0.02}C_{0.13}N_{0.85} to titanium sulfide at 1473 K (1200 °C). The XRD and weight gain measurements
471 showed that the extent of sulfurization increased with increasing temperature and time. In addition, the
472 microstructural assessments showed that the product prepared from TiC powder contained high
473 concentration of carbon (9.74 wt.%), whereas it was much lower for the products synthesized from either
474 TiN or TiO powders. High carbon concentration of the sample prepared from the sulfurization of TiC
475 powder might be due to the decomposition of TiC, not to CS₂ gas. The optimum conditions for the

sulfurization process were at 1473 K (1200 °C) and 3.6 ks in order to produce a single phase of $\text{Ti}_{2.45}\text{S}_4$ ($\text{Ti}_{2+x}\text{S}_4$) from TiN and $\text{TiO}_{0.02}\text{C}_{0.13}\text{N}_{0.85}$ with low impurity of oxygen (1.4 wt.%) and carbon (1.8 wt.%).

ACKNOWLEDGMENTS

The financial supports from Grant-in-Aid for Scientific Research (B) Number 17H03434, the Center for Engineering Education Development (CEED) of Hokkaido University, Japan Student Services Organization (JASSO) Scholarship and Universiti Sains Malaysia (USM) Fellowship (APEX1002/JHEA/ATSG4001) are gratefully acknowledged. Titanium oxycarbonitride synthesis was made possible by support from USM through the Research University Individual (RUI) Grant (No. 1001/PBAHAN/814273).

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