Agglomerates of faceted single crystal grains of titanium nitride (TiN) with a size of 1–100 μm were synthesized by heating TiO₂, FeTiO₃, or TiO and Na in a boron nitride (BN) crucible at 1000–1100 °C under an argon atmosphere. Water soluble sodium borates were also produced as a melt phase during the heating. The yield of TiN prepared from TiO₂ at 1100 °C was 77%. Wavelength-dispersive X-ray analysis of the TiN single crystal grains revealed that the composition was almost stoichiometric, and the oxygen content was less than 1.2 at %. The TiN formation could be regarded as a sort of metathesis reaction, in which the oxygen of TiO₂ and the nitrogen of BN were exchanged.

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Key-words : Titanium nitride, Single crystals, Low-temperature synthesis, Solid nitrogen source

1. Introduction

Titanium nitride (TiN) has a high melting point (2950 °C), high hardness, excellent chemical and thermal stability, and high electrical and thermal conductivities. Owing to these attractive properties, it has been widely used in the industry as a material for producing cermet,¹ and electrodes and diffusion barrier layers for electronic devices.⁴,⁵ TiN is generally synthesized by direct nitridation of Ti in nitrogen gas (N₂) above 1200 °C⁶ and also by carbothermal reduction nitridation, wherein a mixture of TiO₂ and carbon are heated at 1200–1400 °C in N₂.⁷ TiN obtained by these methods is usually a powder with a particle size of 1–40 μm.⁸ Fine TiN powder (40–170 nm) was synthesized at relatively lower temperatures (700–1100 °C) from a vapor phase reaction of TiCl₄ with a mixture of ammonia and hydrogen.⁹ The same reaction carried out at 1600–2200 °C yielded single crystals of TiN with a maximum size of 2 × 2 × 2 mm.¹⁰ Synthesis of TiN powder with solid nitrogen sources has also been reported.¹¹-¹⁵ Fine TiN powders with a particle size of 10–40 nm, were prepared at 500–650 °C by Huang et al. using NaNH₂ and TiO₂ [11], and by Ma et al. using NH₄Cl, TiO₂, and Mg.¹² Polycrystalline complexes and powder mixtures of TiN and TiB₂ were produced from a mixture of boron nitride (BN) and Ti powders by combustion synthesis,¹³ high energy ball milling,¹⁴ and hot pressing (1800 °C, 30 MPa).¹⁵ In the present study, TiN was prepared by heating TiO₂, FeTiO₃ or TiO and Na in a BN crucible which was used both as a solid nitrogen source as well as a container. The crystalline phases and morphologies of the obtained samples were investigated, and the mechanism of TiN formation has been discussed.

2. Experimental procedures

Powders of TiO₂ (purity 99.99%, Rare Metallic Co., Ltd.), FeTiO₃ (purity 99.9%, Kojundo Chemical Laboratory Co., Ltd.), and TiO (purity 99.5%, Junsei Chemical Co., Ltd.), and a BN crucible (outer diameter 8.5 mm, inner diameter 6.5 mm, depth 18 mm, purity 99.5%, Showa Denko Co., Ltd.), and Na chunk (purity 99.95%, Nippon Soda Co., Ltd.) were used as starting materials. For each sample, approximately 0.5 mmol of an oxide source powder was weighed in air and put into the BN crucible. Then, five times the molar amount of Ti in the oxide source, Na was weighed in an argon filled glove box (O₂ and H₂O ≤ 1 ppm) and put into the BN crucible. The crucible was sealed in a stainless-steel container (SUS316, outer diameter 12.7 mm, inner diameter 10.5 mm, height 90 mm), heated to 900–1100 °C in an electric furnace for 4 h, and the temperature was held for 10 h. The furnace was then cooled to room temperature by shutting off the power to the furnace heater. The crucible was taken out from the container in the glove box and placed in another container and heated in vacuum at 300 °C for 12 h in order to remove excess Na from the sample by evaporation. The
sample was then washed with distilled water or with dilute hydrochloric acid (ca. 2 mol/L) and water. The washed sample was dried at about 80 °C in air.

The crystalline phases in the sample were identified by powder X-ray diffraction (XRD) in air or under Ar atmosphere using a diffractometer (Bruker Japan Co., Ltd., D2 PHASER, Cu Kα). The lattice constants and weight fraction of the phases were refined by Rietveld analysis of the powder XRD patterns using the TOPAS software package (Bruker AXS Inc.). The diffraction angle was corrected using Si powder (SRM640c, NIST) as an internal standard. The single crystals contained in the samples were measured with a single-crystal X-ray diffractometer (Bruker AXS Inc., D8 QUEST, Mo Kα). The morphologies of the products were observed with an optical microscope and a scanning electron microscope (SEM, Keyence Corporation, VE-8800). The chemical compositions of the samples were measured by wavelength dispersive X-ray (WDX) analysis using an electron probe micro analyzer (EPMA, JEOL Ltd., JXA-8200).

3. Results and discussion

**Figure 1** shows the powder XRD patterns of the samples prepared by heating TiO2 and Na in a BN crucible at 900, 1000, and 1100 °C for 10 h, followed by removal of Na by evaporation. In the samples prepared at 1000 and 1100 °C, TiN was formed as the main phase, and TiB2 and Na3BO3 were present as secondary phases. A diffraction peak observed at 31.6° in both XRD patterns was not identified. The XRD pattern of the sample prepared at 900 °C matched well with that of NaTiO2 except for the unidentified diffraction peak at 31.6°.

Other than TiO2 which has a O:Ti molar ratio of 2:1, FeTiO3 and TiO having O:Ti molar ratios of 3:1 and 1:1, respectively, were also used as Ti sources. The powder XRD patterns of the samples prepared at 1100 °C after removal of Na are shown in **Fig. 2**. The sample prepared from FeTiO3 consisted of TiN, Fe, and Na3BO3, but no TiB2. TiN, TiB2, TiO, Na4TiO3, Na2TiO3, and NaB2O5 were found to be present in the sample made from TiO, and the amount of TiB2 was greater than that in the sample prepared from TiO2 [Fig. 1(a)].

**Figure 3** shows the powder XRD patterns of the samples prepared by heating oxide Ti sources and Na in the BN crucible at 1100 °C followed by removal of Na and by washing with distilled water or a hydrochloric acid solution and water. The water-washed sample prepared from TiO2 was composed of TiN and a small amount of TiB2. The Na3BO3 and the unidentified phase were removed by the washing. The molar ratio of TiN to TiB2 was evaluated to be 9.1:0.9 by Rietveld analysis of the XRD pattern. From the TiN/TiB2 ratio and the mass of the obtained...
product, the yield of TiN was calculated to be 77% against the Ti content of the starting TiO2 powder.

The water-washed sample prepared from FeTiO3 consisted of TiN and Fe. After washing with a dilute HCl solution, only TiN remained while the Fe was dissolved and removed. The yield of TiN was calculated to be 62%.

The water-washed sample from TiO contained TiN as the main phase and TiB2, TiO, and an unidentified phase as minor phases. The lattice constants of TiN prepared from TiO2, FeTiO3, and TiO were 4.2432(1), 4.2423(1), and 0.9(5) at %, respectively. Although all these single crystals were prepared from the oxides, their compositions were stoichiometrically closer to that of TiN, and their oxygen content was low.

The TiN formation reactions at 1000–1100 °C could be represented with the crystalalline phases of the products in the Eqs. (1)–(3).

\[
\begin{align*}
9 \text{TiO}_2(s) + 8 \text{BN}(s) + 18 \text{Na}(g) & \rightarrow 8 \text{TiN}(s) + \text{TiB}_2(s) + 6 \text{Na}_3\text{BO}_3(l) & \text{(1)} \\
\text{FeTiO}_3(s) + \text{BN}(s) + 3 \text{Na}(g) & \rightarrow \text{TiN}(s) + \text{Fe}(s) + \text{Na}_3\text{BO}_3(l) & \text{(2)} \\
5 \text{TiO}(s) + 4 \text{BN}(s) + 4 \text{Na}(g) & \rightarrow 4 \text{TiN}(s) + \text{TiB}_2(s) + \text{Na}_4\text{B}_2\text{O}_5(l) & \text{(3)}
\end{align*}
\]

Considering that the transition temperatures of Na3BO3 (melting point: 636 °C) and Na4B2O5 (melting point: 677 °C),) and Na (melting point: 98 °C, boiling point: 883 °C),) the single crystal TiN grains with well-developed crystal facets could be formed/grown via a liquid phase of the sodium borates at the surface of the BN crucible.

The calculated Gibbs free energy change (\(\Delta G_0\)) for the Eq. (3) at 1100 °C is a negative value of \(-143 \text{kJ/mol}\), indicating that the reaction occurs spontaneously. The \(\Delta G_0\) values of the Eqs. (1) and (2) at 1100 °C could not be calculated because of a lack of the thermochemical data of Na3BO3 in a liquid state, while the \(\Delta G_0\) values at 600 °C were calculated to be \(-187\) and \(-120 \text{kJ/mol}\), respectively, using the thermochemical data of Na3BO3(s) although the reactions at 600 °C are thermodynamically favorable but kinetically unfavorable. The formation free energies of Na3BO3 (\(-1077 \text{kJ/mol}\) at 600 °C) and Na4B2O5 (\(-1641 \text{kJ/mol}\) at 1100 °C and 1914 kJ/mol at 600 °C),) are higher than those of TiN (\(-208 \text{kJ/mol}\) at 1100 °C) and TiB2 (\(-261 \text{kJ/mol}\) at 1100 °C),) the formation of the sodium borates and TiN, therefore, could be a metathesis, i.e. they are formed by an exchange of oxygen and nitrogen from the oxides and BN, respectively.

Table 1. Composition of TiN single crystals prepared by heating TiO2 and Na, FeTiO3 and Na, and TiO and Na in the BN crucible at 1100 °C for 10 h

| starting oxide | TiN single crystal | Total |
|---------------|-------------------|-------|
| TiO2          | 77(2)             | 23(1) | 0.6(3) | 100(2) wt% |
|                | 49(2)             | 49(2) | 1.2(6) | 100 at%   |
| FeTiO3        | 77(1)             | 25(2) | 0.5(2) | 103(1) wt% |
|                | 47(2)             | 52(2) | 0.9(5) | 100 at%   |
| TiO           | 78(1)             | 23(1) | 2.0(6) | 103(1) wt% |
|                | 48(2)             | 48(2) | 4(1)   | 100 at%   |

Fig. 4. OM (a) and SEM (b, c) images of the sample prepared by heating TiO2 and Na in the BN crucible at 1100 °C for 10 h.
The main driving force of the reaction is probably the large free energy of formation of the sodium borates. For the sample prepared at 1100 °C, the observed ratio of TiN to TiB₂ (9.1:0.9) and TiN yield (77%) were close to the theoretical ratio (8:1) and yield (89%) expected as per Eq. (1). The difference in the yield could be attributed to a loss of TiN fine particles during the washing process, and to the minor unidentified phase formation in the sample.

4. Conclusions

The new processing method proposed in the present study could be useful for low temperature production of faceted TiN single crystal grains which could be useful as abrasives. Agglomerates of TiN single crystal grains with a size of 1–100μm were obtained by heating TiO₂, FeTiO₃, or TiO and Na in a BN crucible at 1000–1100 °C for 10 h. The compositions of the grains were close to the stoichiometric composition of TiN. Generation of sodium borates (Na₃BO₃ and Na₄B₂O₅) which have large formation free energies is likely to be the driving force behind TiN formation.

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