FULL PAPER

Simultaneous synthesis of TiN–Si₃N₄ composite powders from TiSi₂ in NH₃ atmosphere

Hanan ALHUSSAIN¹,⁴, Takuto MISE², Kohei KOBAYASHI² and Hajime KIYONO³,†

¹Division of Regional Environment Systems, Graduate School of Science and Engineering, Shibaura Institute of Technology, Koto-ku, Tokyo, 135–8548, Japan
²Division of Applied Chemistry, Graduate School of Science and Engineering, Shibaura Institute of Technology, Koto-ku, Tokyo, 135–8548, Japan
³Department of Applied Chemistry, College of Engineering, Shibaura Institute of Technology, Koto-ku, Tokyo, 135–8548, Japan
⁴Department of Chemistry, Imam Mohammad Ibn Saud Islamic University (IMSIU), PO Box 90950, Riyadh 11623, Saudi Arabia

The NH₃ nitriding process of TiSi₂ micrometer-sized powders were investigated in this paper. TiSi₂ powders were heat-treated under NH₃ flow in a temperature range of 1,100 to 1,300 °C. The composition and morphology of the resulting composites were characterized by X-ray powder diffraction, scanning electron microscopy with energy-dispersive X-ray spectroscopy, and transmission electron microscopy. Under NH₃ flow, TiSi₂ grains were first transformed into TiN and Si. Subsequently, Si was transformed into Si₃N₄ and SiO₂ fibers. From this process, mixed materials comprising TiN particles with Si₃N₄ fibers were obtained.

Key-words : Nitridation, Titanium silicide, Titanium nitride, Silicon nitride, Ammonia

1. Introduction

Silicon nitride (Si₃N₄) is an important high-temperature structural material due to its superior hardness, toughness, thermal shock resistance, corrosion resistance, and oxidation resistance.¹,²,³,⁵–⁷ These factors, coupled with its high creep resistance¹,²,⁷ and resistance to attack by a wide range of molten metals, make this material attractive for application to thermocouple sheaths and for components handling molten aluminum.⁸ However, the high hardness and fracture toughness of Si₃N₄ also lead to difficulties in machining.² Titanium nitride (TiN) has been extensively studied as an additive to Si₃N₄ because of its outstanding properties, such as its hardness, electrical conductivity, chemical durability, and high melting temperature. The combination of TiN and Si₃N₄ yielded improved electrical and mechanical properties, including wear resistance, fracture toughness, and flexural strength,²,³,⁵,⁶,⁹,¹⁰ providing a broad scope for the use of TiN–Si₃N₄ composites.²,³,⁹,¹¹,¹²

The preparation of particulate composites using conventional processing techniques frequently causes agglomerates. In the form of an initial fracture, these may eventually become structural defects. The production of composites via simultaneous synthesis methods can reduce the number of process steps and result in composites that are more homogeneous.

Intermetallic compounds (metal-metalloid) serve as candidates that can be used as starting materials in simultaneously mixed powders. The unique features of titanium silicide (TiSi₂) potentially render it a suitable material for simultaneously synthesizing TiN–Si₃N₄ mixed powders.

Manukyan et al.¹⁰ have illustrated the combustion synthesis of a composite using titanium silicides (Ti₅Si₃, TiSi and TiSi₂) as the initial raw materials for the preparation of hot-pressed samples under low (up to 5 MPa) nitrogen pressure. Moreover, Mailé et al. reported the influence of temperature, grain size, and holding time on the nitriding rate of TiSi₂ powder and identified chemical mechanisms at temperatures between 1,000 and 1,200 °C for durations up to 50 h using a direct nitriding process under nitrogen gas flow.¹³,¹⁴ They did not, however, investigate the optimum conditions for achieving the highest percentage of reaction ratio without additives (a ratio of 48.8 % was achieved). The researchers also reported nitridation enhancement by the addition of nickel⁵ for which they achieved a 96.3 % reaction ratio. However, the resulting samples included a Ni₃Ti₂Si₇ impurity.

In the present study, we aim to achieve a high reaction ratio in using TiSi₂ to synthesize TiN–Si₃N₄ mixed powders under ammonia (NH₃) gas flow while allowing for lower temperature and shorter time without the use of a catalyst. NH₃ gas has two kinetic merits as a nitriding...
2. Experiment

A high-purity micrometer-sized TiSi₂ powder (C-54 stable phase; 99.9% purity; 150μm diameter; Kojundo Chemical Laboratory Co.) was used in this study. Approximately 30 mg of starting material was used in each experiment. A horizontal tube furnace with an inner diameter of 30 mm was employed with a heating rate of 5 °C/min under the flow of NH₃ gas (50 ml/min; 99.999% purity). For the reaction of the samples with NH₃, two boats of different sizes were positioned, as shown in Fig. 1. During the experiment, we found that better results were obtained when the sample was placed facing the source of the ammonia gas. Hence, this position was adopted. Sample numbers, heating temperatures, holding time, and crystalline phases were observed in the resulting samples via X-ray diffraction (XRD; see Table 1). The crystalline phases of the samples were identified using XRD (Rigaku RINT, TTR-200). The morphologies and compositions of the samples were characterized via scanning electron microscopy with electron dispersive spectroscopic analysis unit (SEM-EDS; JEOL JSM-7400F) and transmission electron microscopy (TEM; JEOL JEM-2010FX).

3. Results

Based on the isothermal Ti–Si–N ternary phase diagram at 1,100 °C and the prediction of the phase formation reported in, partial nitridation of TiSi₂ was proceeded by Eq. (1) and complete nitridation by Eq. (2).

\[
\begin{align*}
2\text{TiSi}_2 + 2\text{NH}_3 (g) & \rightarrow 2\text{TiN} + 4\text{Si} + 3\text{H}_2 (g) & (1) \\
6\text{TiSi}_2 + 22\text{NH}_3 (g) & \rightarrow 6\text{TiN} + 4\text{Si}_3\text{N}_4 + 33\text{H}_2 (g) & (2)
\end{align*}
\]

The theoretical weight gains from Eqs. (1) and (2) were 13.4 and 49.2%, respectively. Figure 2 shows the XRD patterns of the starting material and heat-treated samples at various temperatures for 1 h in an NH₃ atmosphere. For clarification, all XRD patterns obtained from the entire sample without the removal of white material on the surface will be mentioned in context. At 1,100 °C [Fig. 2(b)], small peaks corresponding to TiN and Si were observed in addition to the peaks for the starting material and the

| No. | Temp. (°C) | Holding time (h) | Weight gain (%) | Phase detection from XRD analysis |
|-----|------------|------------------|-----------------|-----------------------------------|
|     |            |                  | [Theoretical (49.2%)] | TiSi₂ TiN Si₃N₄ Si                  |
| 1   | 1100       | 1                | 0.5             | + + + +                              |
| 2   | 1200       | 1                | 20.3            | + + + +                              |
| 3   | 1300       | 0                | 17.4            | − − + +                              |
| 4   | 1300       | 1                | 42.6            | − + + +                              |
| 5   | 1300       | 4                | 49.3            | − + + +                              |
| 6   | 1300       | 10               | 50.9            | − + + +                              |
| 7   | 1350       | 1                | 37.4            | − + + +                              |

Table 1. Weight gain, phase composition, and coding of resulting nitridation samples

Fig. 1. Schematic of the sample position in the furnace.

Fig. 2. XRD patterns of (a) the starting material and samples after heat-treatment under NH₃ flow at (b) 1,100 °C, (c) 1,200 °C, (d) 1,300 °C, and (e) 1,350 °C for 1 h.
weight gain after the heating reached approximately 1%. The formation of TiN and Si suggested that partial nitridation [Eq. (1)] occurred under these conditions. At 1,200 °C [Fig. 2(c)], the peaks of TiN and Si were significantly increased, and small peaks of TiSi2 remained. At 1,300 °C [Fig. 2(d)], peaks for α- and β-Si3N4 were observed in addition to the TiN and Si peaks. When the temperature was increased up to 1,350 °C [Fig. 2(e)], the observed crystalline phases were TiN and α- and β-Si3N4. The disappearance of Si peaks and the appearance of Si3N4 peaks suggested complete nitridation had been achieved at 1,300 °C and above. Accordingly, we decided to conduct the nitridation process at 1,300 °C.

**Figure 3** shows the XRD patterns of the samples following heat-treatment with various holding times at 1,300 °C in NH3 atmosphere. There was a trace of α-Si3N4 in the no-holding time sample (no. 3) in Fig. 3(a). However, in the patterns with increasing holding times shown in Figs. 3(b) and 3(c), which correspond to holding times of 1 (no. 4), and 4 (no. 5) h, respectively, the intensity of the Si peaks decreased, while the intensity of the α-Si3N4 peaks did not undergo any significant change. After a 10 h holding time [Fig. 3(d)], the decreased Si peak intensity became more noticeable.

**Figure 4** shows photographs of the starting material and samples after heat-treatment at various temperatures and holding times. When comparing the starting material image [Fig. 4(a)] with the sample at 1,100 °C for 1 h [no. 1, Fig. 4(b)], only a change in color to dark gray was observed. In the sample at 1,200 °C for 1 h [no. 2, Fig. 4(c)], the sample’s color had changed to golden brown and a fluffy white material appeared and covered the samples’ surface. As the temperature increased to 1,350 °C [Fig. 4(d)], the sample’s color returned to gray.
increasing holding time [Figs. 4(e)–4(g)] at the same temperature (1,300 °C), the white layer decreased and the color of the samples, located under the white layer, changed from gray to golden brown. The XRD pattern of this white material yielded a wide amorphous peak [Fig. 4(h)]. Usually, the color of TiN is golden brown, but previous studies have reported that its color varies not only with composition (TiNx colors vary from titanium gray to golden brown as the x value increases from 0 to 1) but also with lattice expansion and distortion.\(^{20-22}\) TiN is an interstitial compound, and in sample no. 1 [Fig. 4(b)], it was in its initial stages of formation, as can be seen from the XRD result of the sample [Fig. 2(b)]. Thus, the dark gray color was probably a result of the large amount of sub-stoichiometric TiN\(_{1-x}\), where x \(\approx\) 1. At the same time, the gray color in sample no. 7 [Fig. 4(d)] could have been caused by structural distortion. A comparison of the photographs revealed that an amorphous phase began forming at 1,200 °C and its formation was likely due to a reaction with oxygen in the atmosphere.

**Figure 5** shows SEM micrographs of the starting material [Fig. 5(a)]; samples (no. 1, 2, 4 and 7) which are shown in Figs. 4(b)–4(e) respectively. In the starting material photograph [Fig. 5(a)], the typical shape of the starting material and a particle approximately 30 μm in diameter is shown, which is smaller than the average TiSi2 particle. For the sample heated at 1,100 °C [Fig. 5(b)], the surface image of a TiSi2 particle is shown. Almost no difference existed in the microstructure between the starting sample and the sample heated at 1,100 °C. In the sample heated at 1,200 °C [Fig. 5(c)], particles with a size of approximately 1 μm and with twisted fiber were found. At 1,300 °C [Fig. 5(d)], the number of particles increased and the particles agglomerated; additionally, the twisted fibrous material increased, and several of the fibers grew in width and length. When the temperature increased to 1,350 °C [Fig. 5(e)], most of the fibers on the surface became longer, wider, and more linear than those at lower temperatures. The fluffy materials were twisted fibers, which are similar to those observed in Fig. 5(d).

**Figure 6** shows SEM micrographs of the samples heat-treated at various holding times at 1,300 °C. By comparing SEM micrographs of samples at 1,300 °C for 0 h [no. 3, Fig. 6(a)] and 1 h [no. 4, Fig. 6(b)], both samples were observed to have particles with fibrous material on their surface. The fibrous material in the sample heated at 1,300 °C for 1 h showed a significant increase. However, comparing the SEM micrographs of the sample at 1,300 °C for 1 h with those heated for 4 h [no. 5, Fig. 6(c)] and 10 h [no. 6, Fig. 6(d)], the amount of twisted fibers was observed to have decreased, whereas the wide linear fibers had increased following an extended holding time.

**Figure 7** shows the EDS analysis (with an accelerating voltage of 15 kV) results of the sample heat-treated at 1,300 °C for 4 h (no. 5). Figure 6(c) shows the SEM micrographs of the same sample. The sample had twisted and wide linear fibers on the surface of the globular agglomerate material. By comparing the globular agglomerate parts [arrowed areas in Figs. 7(a) and 7(b)] using Ti mapping (red parts in Fig. 7) and the corresponding SEM image, the globular agglomerate material was attributed to TiN [detected by XRD; Fig. 3(c)], as shown in Fig. 7(b). Additionally, comparing Si mapping (the yellow parts in Fig. 7) with the twisted and wide linear fibers on the surface of the globular agglomerate material in the SEM micrograph [Fig. 7(a)] indicated that these fibers could be attributed to silicon compounds [see Fig. 7(c)]. And, by comparing the EDS results of the long linear fibers in Fig. 7(d) (circled part), the fibers were observed as appearing only in the Si mapping [Figs. 7(e) and 7(f)]. Furthermore, the SEM and EDS results indicated that the fibrous material was composed of Si compounds.

TEM images of the sample heated at 1,300 °C for 4 h (no. 5) are presented in Fig. 8(a). Two types of fibers were found: twisted fibers (with atoms that displayed only a short-range order [Fig. 8(b)]) and birch trunk-shaped crystalline fibers (with atoms that displayed a linear and long-range order [Fig. 8(c)]). High-resolution TEM observation is shown in Fig. 8(d). Well-defined atomic planes showing periodic fringes without a disordered structure were clearly observed, indicating the crystalline structure of the fiber. The lattice spacing between neighboring atomic planes was approximately 0.39 nm, similar to the (110) planes spacing of α-Si\(_3\)N\(_4\) \(\{d = 0.387 \text{ nm}\}\) (ICDD 41-0360) or β-Si\(_3\)N\(_4\) \(\{d = 0.380 \text{ nm}\}\) (ICDD 33-1160) [data provided by the International Center for Diffraction Data (ICDD)], indicating that the crystalline fibers corresponded to α- or β-Si\(_3\)N\(_4\). XRD results also revealed that the sample contained α- and β-Si\(_3\)N\(_4\) [Fig. 3(c)]. In addition, since the amorphous Si is usually difficult to form, the amorphous fibers were also attributed to SiO\(_2\).

From the abovementioned analysis results, we can conclude that a mixture of TiN particles and Si\(_3\)N\(_4\) fibers were obtained by this nitridation.

### 4. Discussion

Based on our previous results and a previous study on Si\(_3\)N\(_4\) formation,\(^{23}\) the nitridation mechanisms of Ti and Si were estimated as follows, where the XRD results [Fig. 2(b)] at 1,100 °C revealed that TiN and Si phases had formed. In relatively low-temperature conditions, titanium diffused more rapidly than silicon toward the surface of the TiSi2 particles and reacted with NH\(_3\) to form TiN [Eq. (1)], which had a globular shape. The remaining silicon coagulated and formed a silicon phase, as observed by XRD. Fibrous materials are generally formed by the reaction of gas-phase chemical species. Subsequently, with the unavoidable presence of oxygen contaminating the nitriding system (e.g., as a residual gas in the tube of furnance\(^{20,24}\)), silicon reacted with O\(_2\) and formed SiO\(_2\), as shown in Eq. (3). The reaction was estimated using the Gibbs free energy (ΔG) of Eqs. (3) and (4) and calculated using HSC chemistry (v. 9),\(^{25}\) as shown in Fig. 9.

\[
\text{Si} + \text{O}_2(g) \rightarrow \text{SiO}_2(s)
\]
Another portion of the Si reacted with O\textsubscript{2} to yield SiO [Eq. (4)], which was re-oxidized into SiO\textsubscript{2} [Eq. (5)].

\begin{align*}
2\text{Si} + \text{O}_2(g) & \rightarrow 2\text{SiO}_2(g) \quad (4) \\
2\text{SiO}_2(g) + \text{O}_2(g) & \rightarrow 2\text{SiO}_2(s) \quad (5)
\end{align*}

Equations (4) and (5) explain the appearance of the white SiO\textsubscript{2} layer covering the sample surface (Fig. 4). SiO\textsubscript{2} is typically formed as an amorphous phase at temperatures lower than 1,300 °C. In this study, the amorphous SiO\textsubscript{2} was not detected by XRD. The suggestion that Si reacted with O\textsubscript{2} rather than NH\textsubscript{3} to directly form Si\textsubscript{3}N\textsubscript{4}, as in Eq. (6), is supported by the fact that the $\Delta G$ values of Eqs. (3) and (4) were more negative compared to that of Eq. (6) (see Fig. 9).
Si + 4/3NH₃(g) → 1/3Si₃N₄ + 2H₂ \hspace{1cm} (6)

As the amount of SiO₂(s) increased, Eqs. (7) and (8) became favorable, with H₂(g) forming due to NH₃ dissociation.

SiO₂(s) + Si(g) → 2SiO(g) \hspace{1cm} (7)

SiO₂(s) + H₂(g) → SiO(g) + H₂O \hspace{1cm} (8)

Over time, the amount of SiO increased, and Eq. (9) occurred.

Fig. 6. SEM micrographs of samples heated at 1,300 °C for (a) 0 h (no. 3), (b) 1 h (no. 4), (c) 4 h (no. 5), and (d) 10 h (no. 6).

Fig. 7. The EDS analysis result for the sample heated at 1,300 °C for 4 h (no. 5). (a, d) SEM images of the sample; (b, e) Ti mapping; (c) Ti and Si mappings; and (f) Si mapping.
\[ \text{SiO}(g) + 4/3\text{NH}_3(g) \rightarrow 1/3\text{Si}_3\text{N}_4(s) + \text{H}_2\text{O}(g) + \text{H}_2 \quad (\Delta G_{1200 \, ^\circ\text{C}} = -3716 \, \text{kJ}) \]  

(9)

The results indicating that the amount of \( \text{Si}_3\text{N}_4 \) fiber increased over the holding time (see Fig. 6) support the occurrence of Eq. (9). Nevertheless, regarding the positive \( \Delta G \) values of Eqs. (7) and (8), the consumption of \( \text{SiO} \) via Eq. (9) was able to adequately lower \( P_{\text{SiO}} \) (\( \text{SiO} \) partial pressure), thus shifting Eqs. (7) and (8) to the right.

In previous studies using the same starting material under the flow of nitrogen gas,\(^{13,14}\) a TiN–\( \text{Si}_3\text{N}_4 \) particulate composite was obtained, and 48.8 % of the reaction ratio without additives was achieved at 1,200 °C. In this study, we obtained TiN–\( \text{Si}_3\text{N}_4 \) mixed powders with a fibrous \( \text{Si}_3\text{N}_4 \) structure under the flow of \( \text{NH}_3 \) gas. Moreover, we achieved a higher than 100 % reaction ratio owing to the presence of \( \text{SiO}_2 \). Different results occurred in the two types of atmosphere during Si nitridation. We assumed the reason for this to have been the presence of \( \text{H}_2 \) gas in the case of the \( \text{NH}_3 \) atmosphere. This conclusion was based on the following information. (1) The presence of \( \text{H}_2 \) gas during the Si nitridation process increased the nitridation rates at low temperatures and allowed for a high level of silicon-to-silicon nitride conversion within a short reaction time.\(^{26,27}\) (2) Hydrogen affected the morphology of the silicon nitride products and promoted the formation of finer, more fibrous-like microstructures compared to nitrogen alone.\(^{26,28}\) Typical electro conductive TiN–\( \text{Si}_3\text{N}_4 \) composites have a matrix phase of roughly 70–80 vol %.\(^{3}\) When the composites are fabricated, a small amount of \( \text{Si}_3\text{N}_4 \) or TiN phase should be added. Preliminary mixed powders, such as the product formed in the present study,
appear to be good raw materials for fabricating TiN–Si3N4 composites.

5. Conclusion

A simple preparation method for simultaneously synthesized TiN–Si3N4 mixed materials was obtained by the direct nitridation of TiSi2 under a NH3 gas flow (50 ml/min). Using this nitridation, we achieved a 50.9% weight gain at 1,300 °C for 10 h. The nitridation was almost completed, but other reactions, such as oxidation owing to the presence of SiO2 have occurred. The amount of SiO2 decreased alongside an increase in holding time. This high reaction ratio was presumed to have been the result of the presence of hydrogen, formed by the thermal dissociation of NH3.

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