Microstructure and mechanical properties of TiN dispersed Si₃N₄ ceramics via in-situ nitridation of coarse metallic Ti

1. Introduction

Silicon nitride ceramics (Si₃N₄) has high strength, high toughness, low density, excellent high temperature strength, low dielectric constant and is the most important material for structural materials. In order to expand the range of further utilization of silicon nitride material, improvement of fracture toughness value lower than general metal material which is one of factors of lowering reliability is required. Si₃N₄/metal composites consisted of metal dispersions having excellent elasticity and Si₃N₄ matrix have been developed for improving the brittleness of ceramics. Among various metals, Titanium (Ti) is lightweight and has a relatively high melting point, and is used as a base for heat resistant alloys, shape memory alloys and so on.

By using these two kinds of materials, Si₃N₄ and Ti in combination, it might be used as structural material that is lightweight and excellent in high resistance and oxidation resistance. In fact, as the combination of Si₃N₄ and Ti metal, an active metal joining method using a Ti-added brazing filler was reported [1]. However, there was a problem to generate stress concentration at the joint interface and resultant residual stress that degraded bonding two phases.

A functionally-graded material (FGM), in which composition of two phases was gradually changed, was developed as a new method to improve mechanical reliability and to maintain their properties possessed by both materials. This has been studied as a way to further development of heterogeneous composite materials as well as solving the problem of stress concentration and residual stress at the joint interface of dissimilar materials. For example, Shinohara et al [2] developed a coating having thermal stress relaxation function by gradually-changed composition of partially-stabilized zirconia (PSZ) ceramic and NiCrAlY alloy to suppress thermal barrier coating degradation due to thermal stress at the interface between super alloy and ceramic thermal barrier coating under high temperature. In addition, Tsuda et al [3] fabricated a functionally graded material in which a graded layer of Ti-based ceramics was formed on the surface of a cemented carbid and introduced a gradient of thermal expansion coefficient into the material. As a result, they reported improvement of abrasion resistance and defect resistance as a cutting tool material.

However, when considering the combination of Ti with Si₃N₄, Ti easily reacts with Si₃N₄ and/or N₂ gas atmosphere during sintering to transform into titanium nitride (TiN),
so that partial Si$_3$N$_4$/TiN composite material is formed [4]. Studies on Si$_3$N$_4$/TiN composites have been reported so far, but most of them are focusing on improving electrical conductivity for addition of electrical discharge machinability to Si$_3$N$_4$. Ahmadet et al [5] fabricated the sintered composites by spark plasma sintering (SPS) of raw powder mixtures of Si$_3$N$_4$, sintering aid (oxides) and Ti powder, and analyzed the crystallography and conductivity. As a result, they obtained Si$_3$N$_4$ composite with sufficiently high conductivity that applicable to the electrical discharge machining. Huang et al [6] also produced a hot press sintered Si$_3$N$_4$/TiN composites using the in-situ nitridation reaction of Ti added to the raw powders, and reported the enhancement of bending strength of monolithic Si$_3$N$_4$ (around 400 MPa) to around 600 MP by the addition of 10 wt% Ti. Lian et al [7] reported a hot press sintering of Si$_3$N$_4$ and TiO$_2$ nanopowder mixtures in a nitrogen atmosphere. As a result, Si$_3$N$_4$/TiN nanocomposites with improved bending strength (1154 MPa) and fracture toughness and high electrical conductivity were achieved. Further, Tatami et al [8] reported the improvement of abrasion resistance for Si$_3$N$_4$/TiN nanocomposite fabricated from Si$_3$N$_4$, sintering aids and TiO$_2$ mixtures.

On the other hand, since Ti has high reactivity with Si and N during sintering, Si$_3$N$_4$/Ti composite or FGM system might contain some weak interfacial reaction phase such as TiN and/ or TiN-based compounds, which often hide fundamental Ti properties. In fact, not only materials physical properties but also consideration from the thermodynamic viewpoint concerning the reaction between Si$_3$N$_4$, Ti, TiN and TiO$_2$ have been discussed in these previous studies.

As pointed out here, Si$_3$N$_4$/TiN composite is expected to be utilized as a high strength material. For the development of these advanced composites consisted of Si$_3$N$_4$ ceramic and Ti metal, it is necessary to know the reaction behavior of Ti metal in silicon nitride in detail. The knowledge concerning the behavior of morphological change of TiN particles transformed from Ti in the sintered body produced by in-situ reaction of Ti with Si$_3$N$_4$ and N$_2$ gas, and the effect of the dispersed particles on the physical properties of the TiN composite can be expected to contribute to microstructures and physical properties control of Si$_3$N$_4$/TiN composite materials.

In this study, the effect of the morphology and transformation behavior of Ti particles to TiN grains in the hot press sintered body by changing the heating rate for the Si$_3$N$_4$ and Ti powder mixtures, which aimed to vary the total heating time during the sintering. Coarse Ti powder was used in this research to clarify the reaction behaviors and also to increase fracture toughness. The effect of these processing parameters on the phase and microstructure development, physical and mechanical properties of the sintered body was investigated and discussed.

2. Experimental procedure

2.1 Powder preparation and sintering

As a base composition of monolithic Si$_3$N$_4$ ceramic sample, α-Si$_3$N$_4$ powder (SN-E10, Ube Ind., Tokyo, Japan) was mixed with 2 wt% Al$_2$O$_3$ powder (AKP-30, Sumitomo Chem. Co. Ltd., Tokyo, Japan) and 5 wt% Y$_2$O$_3$ powder (Ishizu Co., Osaka, Japan) as sintering additives. As a composite sample, 10 wt% of Ti powder (TS-450, Toho Titanium Co. Ltd., Kanagawa, Japan) having a particle size of 45 μm or less was added to the monolithic composition. Each powders were placed in a resin bottle together with Si$_3$N$_4$ balls having diameter of 3 mm and ethanol as a mixing solution, and mixed by a wet ball mill for 24 h. The obtained slurry was dried using a vacuum evaporator. Then, the dried powder was aggregated by dry ball mill. After that, the mixed powders were passed through a sieve using a 500 μm sieve.

Then, 20 g of each raw powder mixture was put into graphite die with (44 mm of diameter) and hot press sintered at 1650°C for 0.5 h under 30 MPa of uniaxial pressure in N$_2$ gas atmosphere. The heating rate were changed in these experiments at 25, 30 and 40 °C-min$^{-1}$. The sintered samples were cut by diamond disc, grinded by #100 diamond grinding stone and polished by 9 to 0.5 μm of diamond slurry to obtain mirror surface. Hereafter, materials ID is denoted as SN_xx or SNTi_xx, where the SN and SNTi corresponds to the monolithic and 10wt% Ti added Si$_3$N$_4$ samples, and xx corresponds to the heating rate, 20, 30 and 40 °C-min$^{-1}$, respectively.

2.2 Material evaluations

The crystallographic phase of raw powders and sintered bodies were determined by X-ray diffraction method (XRD, D8 Advance, Bruker AXS GmbH, Karlsruhe, Germany). The β-type Si$_3$N$_4$ phase ratio (here as β) in the samples was calculated from XRD peak intensity of each phases of α-Si$_3$N$_4$ (ICDD PDF 010716479) and β-Si$_3$N$_4$ (ICDD PDF 000331160) using equation 1, where the α and β are the intensity (i.e. α + β = 1.0), α$_{(101)}$ and β$_{(101)}$ are the intensity of each peaks of the α- and β-Si$_3$N$_4$, respectively.

\[
\frac{\beta}{\alpha + \beta} = \frac{\beta_{(101)} + \beta_{(210)}}{\alpha_{(210)} + \alpha_{(201)} + \beta_{(101)} + \beta_{(210)}}
\]  

The density of samples were measured by Archimedes’ method using samples immersed in toluene for 24 h. The microstructure were observed by using ultra high-resolution field emission scanning electron microscope (FE-SEM, SU-9000, Hitachi High-Technologies Co., Tokyo, Japan), and elemental analysis were carried out by energy dispersive X-ray spectrometer (EDX, X–Max100TLE, HORIBA Ltd., Kyoto, Japan) coupled in FE-SEM.

The Vickers hardness (Hv) was measured using a Vickers Hardness Tester (FV-310e, Future-tech Corp., Tokyo, Japan) on the polished surface with an indentation load of 98 N and holding time of 15 s. Further, the fracture toughness ($K_{IC}$) were evaluated by the indentation fracture (IF) method [9] using the Eq. (2) with the same condition as that of Hv measurement.

\[
K_{IC} = 0.203 \left( \frac{c}{a} \right)^{\frac{3}{2}} a^{\frac{1}{2}} H_v
\]

where, $c$ and $a$ are the length of median crack and half of diagonal of indentation.

The Young’s modulus ($E$) were determined by the ultrasonic pulse echo method using a digital storage oscilloscope (DSOX3052T, Keysight, Tokyo, Japan) and an ultrasonic
The Young's modulus value was calculated by Eq. (3) [10].

\[ E = \frac{V_L^2 \rho}{V_S^2 - V_L^2} \tag{3} \]

where, \( \rho \) is bulk density of sample, and \( V_L \) and \( V_S \) are sound velocity of measured longitudinal and transverse waves.

3. Results

3.1 Phase development and sinterability

Under the present experimental condition, well-sintered samples were obtained by hot press sintering at 1650°C for 0.5 h at a heating rate from 25 to 40 ºC·min\(^{-1}\) in a N\(_2\) gas flow. On the other hand, sufficiently densified sintered bodies were not obtained when the hot press was carried out under an Ar or vacuum conditions. Therefore, the samples sintered under the N\(_2\) atmosphere have been further investigated hereafter.

Fig. 1 shows the XRD patterns of sintered bodies and raw powders. In a raw mixed powder, \( \alpha \)-type of Si\(_3\)N\(_4\) (ICDD PDF: 010716479) was only identified with sintering additives and metallic \( \alpha \)-type of Ti (ICDD PDF: 010773482). On the other hand, the both \( \alpha \)- and \( \beta \)-type of Si\(_3\)N\(_4\) (ICDD PDF: 000331160) peaks were identified from the whole samples after sintering. In addition, TiN (ICDD PDF: 030650565) was identified from the composite samples (SNTi) instead of metallic Ti. It is generally known for the silicon nitride ceramic that the \( \alpha \)-Si\(_3\)N\(_4\) of raw powder transformed to \( \beta \)-Si\(_3\)N\(_4\) during singeing by following dissolution and re-precipitation mechanism [11]. In the case of Ti added sintered body, the \( \alpha \)-Ti peak was disappeared and nitrided metal phase as TiN appeared under the whole sintering, i.e. under the heating rate condition. Also, the titanium silicide phase that was often reported [5] was not identified in the present investigation.

As mentioned above, in this study, an \( \alpha / \beta \) mixed phase was obtained by the hot press sintering. Therefore, the \( \beta \)-ratio, which is the fraction of \( \beta \)-phase in the sintered Si\(_3\)N\(_4\), was calculated from the XRD results using the Eq. (1). And the relationships between the \( \beta \)-ration and the heating rate of sintering was shown in Fig. 2 together with that between the relative density and the heating rate. In the case of monolithic Si\(_3\)N\(_4\), the \( \beta \)-ratio was 30-50% depend on the heating rate while the density was 3.236, 3.230 and 3.201 g·cm\(^{-3}\) at a heating rate of 25, 30 and 40 ºC·min\(^{-1}\), respectively. On the other hand, the \( \beta \)-ratio for the Ti-added samples was around 26 to 38 %, which values were slightly lower than that of monolithic Si\(_3\)N\(_4\).

In contrast, the density values (3.321, 3.281 and 3.331 g·cm\(^{-3}\) at 25, 30 and 40 ºC·min\(^{-1}\), respectively) was slightly higher than the monolithic samples. In spite of the complex reaction of Ti phases among the sintered bodies, the theoretical density of Ti added sample was calculated by assuming 12.6 wt% of TiN dispersion in Si\(_3\)N\(_4\) ceramic, which value was calculated by the nitridation of 10 wt% of Ti into TiN, resulted in the value of 3.362 g·cm\(^{-3}\) as the theoretical density of the samples. The relative densities were then obtained and reached to 95 TD% or more under all the sintering conditions (Fig. 2.b), indicating that a sufficiently densified sample was obtained. In the case of monolithic Si\(_3\)N\(_4\), the relative density tended to decrease with increase in heating rate as shown in Fig. 2.b, however, both \( \beta \)-ratio and relative density of Ti dispersed sample showed lower values for the sample obtained from 30 ºC·min\(^{-1}\).

![Fig. 1](image1.jpg)

**Fig. 1** XRD patterns of sintered bodies and raw powders for (a) monolithic (SN) and (b) Ti-added Si\(_3\)N\(_4\) (SNTi) ceramics

1. ábra Szinterelt és nyers porok röntgendiffraktogramjai (a) monolitikus (SN) és (b) Ti adalékolt Si\(_3\)N\(_4\) (SNTi) kerámiák

![Fig. 2](image2.jpg)

**Fig. 2** Effects of heating rate on (a) \( \beta \)-ratio and (b) relative density for sintered samples

2. ábra Felülfutó sebesség hatása (a) a \( \beta \)-arányra és (b) a reális sűrűségre a szinterelt mintákban
3.2 Microstructure

Fig. 3 shows a SEM image of Ti particle in the raw mixture powder. The average diameter of Ti particles in the raw mixture powder were 5.83 µm which was smaller than the raw Ti particles (<45 µm) by ball milling. It was also observed that raw Si₃N₄ and additives powders, which primary size was much smaller than that of Ti, were adhered around large Ti particle.

Fig. 4 shows the optical image on the polished surface of the sintered body. The surface of monolithic Si₃N₄ was smooth, and a few pores were observed (Fig. 4a). On the other hand, large particles of several tens of micrometers were found to disperse in the matrix of the Ti-added composite sample (Fig. 4b). The color of these large particles were gold, which was the typical color of the TiN compound, and is consisted with the result of XRD analysis.

To evaluate structures of dispersed phase in more detail, SEM observation and EDS analysis for the formed TiN particles were carried out, and the results are shown in Fig. 5. The Ti particle used as raw powder had a dense structure, however, porous structure and inner grain boundaries were observed in Ti-derived particles. Ti and N was detected from the corresponding Ti-derived particles by EDS. Nitrogen was found also in the center of the particle, indicating that N penetrated to the central part of Ti particles. From the matrix region, Si, Al and Y as well as N derived from Si₃N₄ and additives were detected. Based on the above results as well as the XRD (Fig. 1), it was clear that the metal Ti particles used as a raw material was nitrided during sintering to form TiN, thus obtained material by this sintering method was Si₃N₄/TiN composite.

Fig. 6 shows the relationships between heating rate and equivalent diameter of dispersed TiN particle in the sintered bodies, where the diameter was calculated by the image analysis method from obtained SEM images. The diameter value of the dispersed phase was 12.29, 10.25 and 9.98 µm at the heating rate of 25, 30 and 40 ºC∙min⁻¹, respectively, and tended to decrease as the heating rate increased. The diameter of the dispersed particle was approximately two times larger than that of used Ti raw powder, which was 5.8 µm, showing the particle size increase was governed after the hot press sintering.
4. Discussion

Generally, sintered Si$_3$N$_4$ is well known to be formed by a dissolution of a phase in liquid phase by sintering additives and followed re-precipitation and growth as to be β phase grains [11]. In the present study, the mixed phase of α- and β-Si$_3$N$_4$ was observed a mentioned before (Fig. 1). In this study, we selected a sintering condition with a relatively higher heating rate (> 25 ºC·min$^{-1}$), lower sintering temperature (1650°C) and shorter holding time (~ 0.5 h) compared to the commonly used condition of Si$_3$N$_4$ sintering, above 1800°C [11]. For this reason, unlike the commonly obtained sintered body with single β-phase, the present samples contained the both β- and α-phases. Nevertheless, sintered samples were fairly densified, more than 95% of relative density (see Fig. 2). This phenomenon was often reported for the Si$_3$N$_4$ sintered by pulse electric current sintering (PECS, also described as SPS) which enables rapid and short-time sintering [5, 12].

4.1 Effect of Ti addition to Si$_3$N$_4$ on physical properties

Fig. 7 shows the relationship between the heating rate and the Young’s modulus. In the Si$_3$N$_4$ monolith, the Young’s modulus tended to decrease slightly with increase in heating rate. On the other hand, Young’s modulus of Ti-added samples slightly increased with the heating rate. The theoretical Young’s modulus of the Si$_3$N$_4$ composite containing 12.6 wt% of TiN (by considering complete transformation of Ti to TiN as mentioned before) was estimated by the Hill’s equation [13], and the value was calculated to be 325 GPa. However, the observed Young’s modulus of the present samples was lower than the calculated value, which was around 270 GPa (30 ºC·min$^{-1}$) to 305 GPa (40 ºC·min$^{-1}$).

As found by the SEM investigation, the present composites contained aggregated but porous polycrystalline TiN regions (see Fig. 5) which dispersed in dense Si$_3$N$_4$ matrix. It imply us that the porosity of the TiN particles might affect on the decrease in density of the sintered samples, and then resultantly on the decreased Young’s modulus. Thus, at first, the density of TiN particle ($d_{\text{TiN}}$) dispersed in sintering body was calculated from the relationship between density and mass concentration by the Eq. (4).

$$d_{\text{TiN}} = \frac{W_{\text{TiN}}d_c d_m}{(1-W_{\text{TiN}})(d_m-d_c)+W_{\text{TiN}}d_m}$$

Where $d_m$ and $d_c$ is the measured density of monolithic Si$_3$N$_4$ and TiN dispersed Si$_3$N$_4$ composite, respectively, and $W_{\text{TiN}}$ is the mass concentration of TiN in the sintered body (12.6 wt%). Further, the porosity in the TiN particle region ($P_{\text{TiN}}$) was taken into account and was calculated from the relationship between the density and the porosity by Eq. (5),

$$P_{\text{TiN}} = 1 - \frac{d_{\text{TiN}}}{d_{\text{TiN}}^{\text{th,TiN}}}$$

where, $d_{\text{TiN}}^{\text{th,TiN}}$ is the theoretical density of TiN (5.45 g·cm$^{-3}$).

Then, the Young’s modulus of porous TiN grain ($E$) was calculated using the Eq. (6) [14] representing the porosity dependency of the elastic modulus of the porous body.

$$E = E_0 (1 - P_{\text{TiN}})$$

Where $E_0$ is the Young’s modulus of fully-densified TiN (390 GPa). Table 1 shows the calculated porosities of the TiN particle and Young’s modulus. The porosity of TiN particle was estimated to 13, 32 and 24% at 25, 30 and 40 ºC·min$^{-1}$, respectively. These values seems to be reasonable by considering porous morphology of TiN grains observed by SEM image in Fig. 5. On the other hand, the Young’s modulus of the porous TiN particles was estimated to be about 294, 265 and 339 GPa at 25, 30 and 40 ºC·min$^{-1}$, respectively. High porosity and low Young’s modulus were observed for the sample sintered at 30 ºC·min$^{-1}$, which was due to the low density for the sample.

### Table 1

<table>
<thead>
<tr>
<th>Heating rate / ºC·min$^{-1}$</th>
<th>$P_{\text{TiN}}$ / %</th>
<th>$E$ / GPa</th>
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<tr>
<td>25</td>
<td>24</td>
<td>294</td>
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<tr>
<td>30</td>
<td>32</td>
<td>265</td>
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<tr>
<td>40</td>
<td>13</td>
<td>339</td>
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</table>

4.2 Effects of large and porous TiN grain on the mechanical properties

Fig. 8.a shows the relationship between heating rate and the Vickers hardness. The hardness of the Si$_3$N$_4$ monolithic
was about 18 GPa, and the effect of the heating rate was not confirmed. The hardness of TiN dispersed samples was around 15 GPa, which was slightly lower than Si₃N₄ monolith. However, as discussed above, the Hv of composites was reasonable by considering the fact that large but porous TiN particles were dispersed in.

Fig. 8.b shows the relationship between heating rate and fracture toughness measured by the indentation fracture method. The fracture toughness of the monolithic Si₃N₄ showed a tendency to slightly decrease with increase in heating rate. On the other hand, the TiN dispersed samples showed an opposite tendency, and the value increased to 5.8 MPa∙m¹/² at 40 °C·min⁻¹ which was higher than the toughness value of the monolithic Si₃N₄ sintered at the same condition.

To discuss the mechanical properties of the present Si₃N₄/ TiN composites from viewpoint of the crystalline phase of Si₃N₄ matrix, i.e. the effect of α/β phase, the relationships between these mechanical properties and β-ratio of Si₃N₄ matrix were shown in Figure 9. It is reported that the α-Si₃N₄ single crystal has 1.3 times higher hardness value than that of β-Si₃N₄ [15]. It is thus easily predicted that hardness declined as the β-ratio increases. In fact, Kawaoka et al [12] reported that the hardness and the Young’s modulus decreased while the fracture toughness increased when the β-ratio increased for the spark plasma sintered Si₃N₄.

In the present study, however, the hardness of both monolithic and TiN dispersed Si₃N₄ did not depend strongly on the β-ratio (Fig. 9.a) although the value was higher for the monolithic Si₃N₄, which was, as discussed above, due to the dispersion of porous TiN phase. The reason of this behavior is regarded as the trade-off relation between the decreased hardness due to the density degradation and the increase in hardness due the increased α-Si₃N₄ ratio in the samples.

It is well-known that fracture toughness of sintered Si₃N₄ generally increases with grain growth of β-Si₃N₄ particles, especially formation of elongated large β-grains, resulting in high fracture toughness for high β conversion ratio [12]. In the present case, the toughness value seemed to be higher for the higher β-ratio. However, the correlation between the β-ratio and the fracture toughness was not distinct (Fig. 9.b).

For the TiN dispersed samples, it was considered that the fracture toughness value seemed to be affected more by the characteristics of the dispersed TiN; Sample SNTi_40 (40 °C·min⁻¹) showed the highest toughness and the lowest porosity in dispersed TiN (P_{TiN} = 13%, see Table 1), while the SNTi_30 (30 °C·min⁻¹) containing porous TiN (P_{TiN} = 32%) exhibited the lowest toughness among the composites. These fact imply us that the microstructural characteristic of dispersed TiN grains, i.e. porous structure, is more dominantly affect on the fracture toughness than the β-ratio of matrix.

4.3 Microstructural characteristics of dispersed TiN particles

Although the Ti particle of the raw powder was large (Fig. 3), Ti-derived grains in the sintered body were polycrystalline but porous structure as explained before (Fig. 4.c). Thus it is said that the present Si₃N₄ based composite has a unique structure, where porous TiN grains were dispersed in Si₃N₄ matrix. The reason why such a complicated structure is formed will be discussed below. It should be considered that the Ti particles expanded during the reaction (transformation) to TiN. The mass increase rate when Ti (molecular weight: 47.96 g·mol⁻¹
density: 4.51 g·cm⁻³) transforms to TiN (weight: 61.96 g·mol⁻¹, density: 5.45 g·cm⁻³) is 1.29, while the volume increase rate is calculated to be 1.068, which corresponds to only 2.2 % (1.022 times) increase in equivalent particles diameter. However, in this study, average grain size of dispersed TiN in the sintered Si₃N₄ (SNTi_25; 25 °C·min⁻¹) was 2.1 times larger than that of used raw Ti particles (see Fig. 6). Therefore, it is not able to explain the reason of larger TiN by the chemical reaction (nitridation of Ti), and it is considered to be a minor role.

Magnified SEM and elemental mapping images of inside of TiN grains in the sintered body for SNTi_25 (heating rate of 25 °C·min⁻¹) and SNTi_30 (30 °C·min⁻¹) are shown in Figs. 10.a and 10.b, respectively. It was clearly seen that the Ti-derived grain was polycrystalline structure with grain boundaries. In addition, some finer particulates which size is around 1 µm or less can be seen within the grains (see arrows in SEM images of Fig. 10). From element mapping results, Ti and N was uniformly detected from the whole area except pores, grainboundary and finer particles mentioned above, which results well agree to the fact previously discussed that the Ti was converted to the TiN during sintering. On the other hand, Si was found in the finer particles inside of the TiN and at some part of grain boundaries of TiN. Oxygen was also detected from not all but some region of Si detected (particulates and grainboundary). In addition, Al was often detected from the grain boundary phase together with Si and O (see Figs. 10.a and 10.b). These results implied that the particulates inside of TiN was SiO₂ and Si, which might be formed or precipitated by the complicated reaction during sintering. At the grainboundary of formed TiN, SiO₂ or Al-Si-O compound were also precipitated during the reaction.

From these facts, it was considered that Si, Al, Y and O elements in Si₃N₄ and additives (Al₂O₃ and Y₂O₃) might diffused into the Ti particles during the nitridation reaction or into the formed TiN phase at the late stage of sintering. In the TiN regions, some oxides consisted of SiO₂ or Al-Si-O were found as mentioned above. These silica-based oxides were known to have lower melting temperature and to form glassy phase, and thus liquid phase of these oxides might exist during sintering that promoted reaction of TiN with Al and/or O and formation of Al-Si-O phases at the boundaries among TiN regions. Based on these results, the formation of coarse and porous TiN grains within Si₃N₄ matrix as well as enlargements of TiN grain size.

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**Fig. 10** Magnified SEM image of the center of TiN grain and corresponding elemental mapping images of Ti, Si, N, O, Al and Y for the samples (a) SNTi_25 and (b) SNTi_30.
more than primary Ti particles might be considered due to the combination of several factors as described follows.

Reaction and followed solid solution formation of constituent elements, especially Si-O and/or Si-Al-O based compounds near the Ti particles, should be taken place at first. In fact, grain boundary phases containing Si and O as major elements and Al, Y and Ti as minor elements. These grain boundary phases seemed to be generated form a liquid phase, and they were penetrated and precipitated into the internal grain boundary of polycrystalline TiN particles produced from Ti, thereby dividing primary Ti particles and increasing the equivalent diameter of Ti-based particles. The fine particulates within TiN, which were consisted mainly from Si-O or Si (Fig. 10), were considered to be formed by precipitation during sintering followed by the diffusion of corresponding elements in the raw materials into Ti particles.

Before or at the same time, nitridation of metallic Ti might be taken place by the direct reaction of Ti with N, atmosphere, or by the reaction with SiN₄ particles, because the reactivity of Ti with nitrogen is thermodynamically high. Reaction of nitrides with liquid phase might promote further diffusion of elements, such as Y etc. into the TiN, which could be seen in small amount but uniform distribution of Si, O and Y within the TiN particles existing as solid solution or precipitates as fine particles within TiN (see for example Si, O and Y in Fig. 10 a).

In addition, the effect of pressurization, i.e. mechanical uniaxial pressing during sintering should be considered. In this study, sintering was performed by hot press method at a high temperature of 1650°C, which corresponded to 0.99 Tm of Ti metal, extremely close to the melting point of Ti (Tm = 1668°C). At this temperature, Ti was sufficiently softened, and hence it might easily react with other components including SiN₄, nitrogen and formed oxide glassy phases.

In the case of nano-sized TiN dispersed dense SiN₄ composites, it was reported that the addition of several tens of volume percents of TiN was necessary to achieve the enhanced toughness [6, 7]. In this study however, SiN₄ composites containing porous TiN grains, in which the porosity of around 20 vol%, exhibited decreased hardness while slightly increased fracture toughness compared to the porous structure of dispersed TiN grains. However, matrix itself was mostly densified of over 95% under the present sintering conditions.

6. Acknowledgements

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Reference

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