Microstructural Characterization of a Hot Pressed Si$_3$N$_4$–TiN Composite Studied by TEM

Byong-Taek Lee, Dong-Hwi Jang and Taek-Soo Kim

Chungnam Research Center for Nano Materials, School of Advanced Materials Engineering, Kongju National University, Kongju 314-701, Korea

Microstructures and material properties of TiN reinforced-Si$_3$N$_4$ composites, fabricated by hot pressing and using Si$_3$N$_4$, TiN and sponge Ti powders, were investigated. The sponge Ti powders in the Si$_3$N$_4$–TiN-sponge-Ti compacts are fully nitrided into TiN without residual Ti phase, but some residual pores remain. The Si$_3$N$_4$ grain boundaries, Si$_3$N$_4$/TiN interfaces and triple regions are covered with an amorphous phase. However, some reaction compounds estimated to be Si$_3$W$_8$Ti$_2$ phase are observed around fine TiN particles. The values of electrical resistivity, fracture strength and fracture toughness of the composite are 1.2 x 10$^{-2}$ Ω•cm, 362 MPa and 5.3 MPam$^{1/2}$, respectively. The main reason for the relatively low mechanical properties is the existence of microcracks at the interface of Si$_3$N$_4$/large TiN grains, as well as the microstructure of fine, rod-like Si$_3$N$_4$ grains.

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1. Introduction

To widely use sintered Si$_3$N$_4$ as an industrial material, low cost of production and good mechanical properties are required. Recently, TiN ceramics have received much attention because it affords the possibility for the improving fracture toughness, as well as electric discharge machining (EDM), due to its good electrical conductivity and high value of hardness. This approach is an attractive alternative to the high cost, of diamond machining, as it shows the way to make Si$_3$N$_4$ ceramics at low cost by an EDM process similar to that of common metallic machining. Furthermore, TiN particles dispersed in a Si$_3$N$_4$ matrix body can lead to the remarkable microcracking phenomenon at the crack process zone, which is due to the difference in lattice parameters and thermal expansion coefficient between Si$_3$N$_4$ and TiN grains. A Si$_3$N$_4$–17 mass% TiN composite was synthesized in situ by gas pressure sintering (GPS) at 2000°C for 3.5 hours, using Si and sponge Ti powders. The fracture toughness was high, having a value of 10 MPam$^{1/2}$ due to the microcracking, crack deflection and crack bridging mechanisms.

In some published papers, Si$_3$N$_4$ and TiN raw powders were used to synthesize the electroconductive Si$_3$N$_4$–TiN composites by hot pressing, S. Boskovic et al. reported that an electroconductive Si$_3$N$_4$–TiN composite fabricated by liquid-phase sintering, in which the electrical resistivity decreased drastically with increasing TiN content. In our previous work, the GPSed Si$_3$N$_4$–TiN composites have been successfully synthesized from Si and TiN powders, with the composites having sufficient electrical conductivity. However, the mechanical properties of the composites decreased with increasing TiN contents, caused by the existence of many pores and fine, rod-like Si$_3$N$_4$ grains. Thus, in this work, we used sponge Ti and fine TiN powders to fabricate hybrid TiN particles in a Si$_3$N$_4$ matrix. Up till now, although there have been many reports on the Si$_3$N$_4$–TiN systems, no detailed microstructural characterization appears to have been carried out. Therefore, the focus of this work is on the relationship between microstructure and mechanical properties of a Si$_3$N$_4$–46 mass% TiN composite.

2. Experimental Procedures

For the synthesis of an electroconductive Si$_3$N$_4$–TiN composite, fine Si$_3$N$_4$, sponge type Ti and TiN (30 mass%) powders were used, together with 6 mass% Y$_2$O$_3$ and 2 mass% Al$_2$O$_3$ powders as the sintering additives. They were mixed in ethanol using a ball mill and Si$_3$N$_4$ balls as milling media. The mixtures were dried on a hot plate while stirring. The powder mixtures were densified at 1850°C for 2 hours under 150 MPa pressure in the N$_2$ gas atmosphere by hot-pressing. The distribution of TiN particles and crystal phases were identified by back-scattered SEM and XRD techniques, respectively. Using TEM (JEOL-2010), the detailed internal microstructures such as grain boundaries and interfacial structures of the composites were examined. The Vickers hardness was measured by indenting with a load of 500 g, while the bending strength was measured by 3-point bending method of specimens measuring 3 x 4 x 30 mm$^3$. For the measurement of electrical resistivity of the composites, gold-palladium paste was coated on the specimen which was measured at room temperature using a Napsen RT8A8 instrument with a 4-point probe. The fracture toughness ($K_{IC}$) was calculated by the indentation method using a load of 20 kg. The propagated crack and fracture surface made by Vickers indentation and 3-point bending test, respectively, were observed by SEM.

3. Experimental Results

Figure 1 shows SEM images of raw Ti (a) and TiN starting powders (b) for this present work, as well as back-scattered SEM image of the hot-pressed Si$_3$N$_4$–TiN composite (c). The Ti powders of 50 μm in average size, are divided into two types, i.e., a fine, porous-type (marked with an arrow), and a coarse, round-type (marked with arrowheads). Raw TiN powders with irregular shapes are fine, and less than
In average size. In the Si$_3$N$_4$–46 mass%TiN composite, the Si$_3$N$_4$ matrix was observed to have a gray color, and the TiN particles are seen to be distributed homogeneously, having dark-gray contrast, although their original color was gold. TiN particles in the composite are classified into large or fine TiN particles. The large TiN particles were nitrided from Ti powders during hot pressing, whereas the fine TiN particles started from the raw TiN particles. Despite the short time of hot-pressing, the sponge Ti powders were fully nitrided into TiN, so that no residual Ti phase was observed in the composite. Some residual pores are observed in the large TiN particles (as indicated with arrowheads). An important observation is that some Si$_3$N$_4$ phase penetrated into large TiN particles (as indicated with arrows), which may have originated from sponge Ti powders during ball milling.

Figure 2 shows a XRD profile of the Si$_3$N$_4$–46 mass%TiN composite. Although α-Si$_3$N$_4$ powders were used as a raw powder, no α-Si$_3$N$_4$ peaks were detected due to the phase transformation during hot pressing. The peaks of TiN particles, having a typical NaCl structure, were detected without residual Ti and their reaction compounds.

Table 1 summarizes the material properties of the Si$_3$N$_4$–46 mass%TiN composite. Although the hardness values are high e.g., 1665 Hv, the values of relative density, fracture strength and fracture toughness are comparatively low being 98.6%, 362 MPa and 5.3 MPa m$^{1/2}$, respectively. In particular, the reason for the low mechanical properties is mainly caused by the low relative density of the composite. However, the electrical resistivity is a sufficiently low value, being $1.2 \times 10^{-2}$ $\Omega$cm for the EDM processing, since the TiN particles, as an electrical conductor, are homogeneously dispersed in Si$_3$N$_4$ matrix as showed in Fig. 1(c).

Figure 3(a) is a TEM micrograph of the Si$_3$N$_4$–46 mass%TiN composite. Most of the Si$_3$N$_4$ grains with a gray color are seen to have various shapes i.e., hexagonal, elongated hexagonal and rod-like shapes, caused by the crystallographic random orientation.$^{12}$ TiN particles on the other hand are seen to have dark contrast and rounded shapes in the composite.$^{10}$ However, the average diameter of Si$_3$N$_4$ grains is less than about 2 $\mu$m. This is a finer size than that of

<table>
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<tr>
<th>Relative density (%)</th>
<th>Fracture strength (MPa)</th>
<th>Fracture toughness (MPa m$^{1/2}$)</th>
<th>Electrical resistivity ($\Omega$cm)</th>
</tr>
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<tr>
<td>98.6</td>
<td>362</td>
<td>5.3</td>
<td>$1.2 \times 10^{-2}$</td>
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Fig. 1  SEM micrographs of sponge Ti (a) and TiN (b) powders, and back-scattered SEM micrograph of the hot pressed Si$_3$N$_4$–46 mass%TiN composite.

Fig. 2  XRD patterns of the hot pressed Si$_3$N$_4$–46 mass%TiN composite, using Cu Kα radiation.
cracks are observed at the interfaces between Si$_3$N$_4$ and fine TiN particles. As shown in the diffraction pattern insert that was taken from the dark circle in Fig. 4(a), the diffuse ring pattern is observed in all of the triple regions caused by the existence of amorphous phase that was constructed with Y–Si–Al–O components (Fig. 4(c)). Figure 4(b) is an enlarged image of the local region as marked with a dark circle Fig. 3(a) which was observed at near the fine TiN particles of the composites. From the EDS analysis (Fig. 4(d)) and selected area electron diffraction pattern taken from the region marked ‘P’ in Fig. 4(b), the region with dark contrast is thought to be a Si$_{10}$Ti$_3$W$_2$ reaction compound, in which the W component may be an impurity in the raw TiN powders. However, at the interface near the Si$_{10}$Ti$_3$W$_2$ reaction compounds, no large cracks are observed.

Figure 5 presents HRTEM micrographs of a Si$_3$N$_4$–46 mass%TiN composite (a) and a Si$_3$N$_4$/TiN interface (b) adjoining fine TiN particles. Thin amorphous layers of about 1–2 nm in thickness are observed at the grain boundary and interface, but the amorphous regions become thicker near the triple regions. Furthermore, there are no special crystallographic orientations at the junction regions, since they exist with random orientations in the sintered body.

To identify the fracture characteristics of the Si$_3$N$_4$–46 mass%TiN composite, crack propagation (Fig. 6) and the fracture surface (Fig. 7), which were made respectively by micro-indentation and 3-point bend testing, are observed in the back-scattered SEM mode. In Fig. 6, the region marked ‘I’ indicates a corner of a diamond indentation site. Although the cracks propagate from the indentation corner, the remarkable micro-cracking phenomenon is observed, as well as short-range crack deflection in the crack propagation zone. On the other hand, although the fracture surface of the Si$_3$N$_4$–46 mass%TiN composite is seen to be rough and complex in shape in Fig. 7(a), the surfaces are locally divided into fine and coarse regions. From the enlarged SEM image of Figs. 7(b) and (c) that was taken from the region marked ‘P’ and ‘Q’, respectively, it is confirmed that the fine regions correspond to fracture surfaces of Si$_3$N$_4$ and fine TiN grains, whereas the coarse regions are large TiN particles. On their fracture surfaces, we did not find the remarkable pulled-out of rod-like Si$_3$N$_4$ grains which have frequently been observed in monolithic GPSed-Si$_3$N$_4$ having a bimodal microstructure.

In addition, the fracture mode of the Si$_3$N$_4$ matrix and fine TiN regions is of the mixed type, being intergranular and transgranular. The large TiN particles, which include many pores and Si$_3$N$_4$ grains, seen in Fig. 3(b) are fractured in a transgranular mode. As indicated by the arrow in Fig. 7(c), many fine, rod-type Si$_3$N$_4$ grains are observed in the large, fractured TiN particles.

4. Discussion

The electrical conductivity of Si$_3$N$_4$–TiN composites have been developed to reduce the fabrication cost by the EDM process. The sponge Ti powders used in the present work are attractive because their price is much cheaper than that of TiN powders. In general, it has been known that by increasing the TiN content, the electrical conductivity was promoted, due to the formation of TiN necks and the
Fig. 4 Enlarged TEM micrographs and EDS profiles of the Si$_3$N$_4$–46 mass%TiN composite. The EDS profiles of Figs. 4(c) and (d) were taken from the dark circle in Fig. 4(a) and the region marked 'P' in Fig. 4(b), respectively.

Fig. 5 High-resolution TEM micrographs of a Si$_3$N$_4$ grain boundary (a) and a Si$_3$N$_4$/fine TiN interface (b).
homogeneous distribution of TiN particles. As pointed out in Table 1, although the electrical resistivity of the hot pressed Si$_3$N$_4$–46 mass%TiN composite is sufficient for EDM, the mechanical properties, particularly with respect to fracture strength and fracture toughness, show poor values, due to the low relative density of the composite. Of course, the observed low relative density of this composite is mainly attributed to the existence of residual pores and the formation of interfacial cracks at, or near, the large TiN particles, as shown in Fig. 3. The formation of interfacial cracking and strong strain fields near the large TiN particles can be explained by a TEM image of the Si$_3$N$_4$/TiN interface (Fig. 8(a)) and corresponding schematic diagram (Fig. 8(b)).

During hot pressing at high temperatures, although the Si$_3$N$_4$ and TiN grains macroscopically experience a uniaxial stress field, the interface between Si$_3$N$_4$ and TiN grains experiences compressive stress, due to the difference in thermal expansion coefficients of both phases (Si$_3$N$_4$:...

![Fig. 6 Back-scattered SEM micrographs showing crack propagation in the Si$_3$N$_4$–46 mass%TiN composite.](image)

![Fig. 7 SEM fracture surfaces (a) of the Si$_3$N$_4$–46 mass%TiN composite; (b) and (c) are enlarged images of marked ‘P’ and ‘Q’ regions, respectively.](image)
3 × 10^6°C⁻¹, TiN: 9 × 10^6°C⁻¹). In this case, Si₃N₄ grains near TiN particles seemed to be deformed by compressive stresses. It is considered that the observation of a few dislocations and strain field contrast in the Si₃N₄ grains near the TiN particles is evidence for strong compressive stress field at high temperature. However, during the cooling process, many cracks spontaneously occurred at Si₃N₄/TiN interfaces, because of some tensile stress applied at the interfaces due to the volume shrinkage of large TiN particles. Thus, at interfaces near large TiN particles and in most TiN particles, many cracks and dislocations were observed in the hot-pressed Si₃N₄–46 mass%TiN composite.

In general, the average size of Si₃N₄ grains in the hot-pressed body is small compared with that of GPSed bodies. They show a tendency to become finer with increasing amounts of TiN particles, since the dispersed TiN particles restrain the growth of Si₃N₄ grains.

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