Crack Propagation Behavior of CVD Si_3N_4 -TiN Composite Examined by High-Resolution Electron Microscopy

Byong-Taek Lee*, Shinsuke Hayashi**, Toshio Hirai*
and Kenji Hiraga*

*Institute for Materials Research, Tohoku University, Katahira, Aoba-ku, Sendai 980, Japan

**Toyota Technological Institute, 2-12-1, Hisakata, Tenpaku-ku, Nagoya 468, Japan

Crack propagation behavior of a chemical vapor deposited (CVD) Si_3N_4 -TiN composite was investigated by micro-indentation fracture (MIF) and high-resolution electron microscopy (HREM) techniques. TiN fibers are homogeneously dispersed in large Si_3N_4 grains (about 8 μm in diameter), leading to an intragranular nano-composite structure, and their interfaces were directly bonded without any other phases. The main fracture mode is a mixed type of intergranular and transgranular fracture. Nanometer-sized TiN dispersed in the matrix grains interacts with cracks, generating crack bridging and microcracking which toughens the composite.

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I. Introduction

Si_3N_4 ceramics have been already employed as engine components and tool materials. But, according to speed developments of industry, there is need of improved materials which can be employed at more severe conditions and for a wide range of industrial applications. Consequently, for the improvement of mechanical properties of ceramics, the developments of various types of composite processing have been considered⁽¹⁾⁻⁽⁴⁾. There have been some studies on the synthesis of Si_3N_4 and its composite by chemical vapor deposition (CVD) method which makes it possible to produce a high purity and dense material without sintering additives. Studies on preparation, density, hardness, and other structural features of the CVD Si_3N_4 , have been reported by Niihara and Hirai⁽⁵⁾⁻⁽⁷⁾. It was indicated that properties of the CVD Si_3N_4 strongly depend on the experimental conditions such as gas flow rate and nature of gases used, chamber pressure, and deposition temperature. On the other hand, Hirai and Hayashi⁽¹⁾⁽⁸⁾ succeeded in preparing plates of Si_3N_4 containing titanium nitrides by CVD using a gaseous mixture of SiC_{14} - TiC_{14} - NH_3 - H_2 . The first atomic-scale images of the CVD Si_3N_4 -TiN composites⁽⁹⁾⁽¹⁰⁾ showed that fibrous TiN were dispersed in the Si_3N_4 matrix. Also crystallographic relationships between β - Si_3N_4 and TiN were discussed from the HREM images as well as structure of internal defects, such as, domain boundaries, planar faults and dislocations.

Recently, fracture and related toughening mechanisms of structural ceramic composites⁽¹¹⁾ were clearly examined by observing micro-indentation cracks and HREM images. Such a technique is very powerful, because one can clearly observe the fracture behavior both in the crack wake and tip zone from micro to atomic level.

The primary purpose of the present work is to investigate the microstructure of the Si_3N_4 -TiN composite prepared by CVD method, paying attention to the distribution of TiN fibers, crystal structures of Si_3N_4 grains and Si_3N_4 /TiN interfaces by HREM. Then, the crack propagation behavior of this composite is discussed by observing the indentation cracks.

II. Experimental Procedures

The Si_3N_4 -TiN composite was fabricated by CVD method. The deposits were prepared by adding TiCl_4 vapor into a SiCl_4 - NH_3 - H_2 system. The substrate was a graphite plate which was heated by electric current for the vapor deposition. Further details of the fabrication conditions of this composite were described in previous papers⁽¹⁾⁽⁵⁾⁽⁸⁾.

TEM samples were prepared from thin slices, which were mechanically polished to a thickness of about 150 μm and punched out 3 mm in diameter by an ultrasonic cutter. After polishing to a mirror plane, indents were made with a load of 0.49 N for 15 s by a Vickers indenter (Akashi MVK-VL). The back side of the indented plane was polished further up to about 30 μm in thickness by a dimple grinder and finally milled with Ar ions at an accelerating voltage of 3 kV with a glancing angle of 25 degrees. Coating by evaporated carbon was performed to prevent charge-up effects during TEM observations. TEM and HREM observations were performed with a 400 kV electron microscope (JEM-4000EX) with a resolution of 0.17 nm. Scanning electron microscope (SEM) and optical microscope were used for looking at the microstructures and fracture morphology over a wider scale. The SEM equipment was a JSM-5300 type microscope (JEOL). Fracture surfaces were observed after gold-coating of appropriate thickness.

III. Results and Discussion

1. Microstructure of Si_3N_4 -TiN composite

Figure 1 is a TEM image of the Si_3N_4 -TiN composite, which was taken with the incident beam parallel to the growth direction of the composite. Although TiN fibers are not clearly seen in this low magnification image, most of the Si_3N_4 grains show fine contrasts due to the existence of the TiN fibers. Si_3N_4 grains have a random

Fig. 1 TEM image of the CVD Si_3N_4 -TiN composite. Arrowheads indicate grain boundary.

Fig. 2 TEM images showing the distributions of the TiN fibers in the Si_3N_4 matrix. The incident beam is parallel to [001] (a), and tilted with a large angle from the [001] direction (b).

orientation and irregular shape with an averaged diameter of about $8\text{ }\mu\text{m}$ which is markedly larger than that of Si_3N_4 composites sintered by conventional techniques.

Figure 2(a) and (b) are TEM images showing the distribution of TiN fibers in the Si_3N_4 matrix. Figure 2(a) was taken with the [001] incident electron beam. As can be seen in this image, the TiN fibers indicated by arrowheads have an ellipsoidal section with a major diameter of about 15 nm and are homogeneously dispersed in the Si_3N_4 matrix. On the other hand, Fig. 2(b) is an image taken with the incident beam tilted at a large angle from the [001] direction. From this image, we can see that these TiN have fiber-like shapes and that they lie along the [001] direction of the Si_3N_4 matrix.

In the present HREM observations, it is also confirmed that the Si_3N_4 grains have both α - and β -type structures. Generally, crystal structure of CVD Si_3N_4 closely depends on the deposition temperature, that is, the structure of Si_3N_4 deposited at low temperatures was amorphous, while that deposited at high temperatures was crystalline of α or β type. Hiraga *et al.*⁽⁹⁾, observing images of CVD α - and β - Si_3N_4 on the atomic scale discussed their atomic structures in comparison with multislice calculations as functions of the crystal thickness and the objective lens defocus.

The interface structure between TiN and Si_3N_4 in the composites was also investigated since it plays a main role on the mechanical properties. Figure 3 is a HREM image taken with the incident beam parallel to the [001] direction, showing a cross section of a TiN fiber embedded in a β - Si_3N_4 grain. From this image, we can directly determine the crystallographic orientation relations between the Si_3N_4 matrix and TiN fiber. It is clear, as also indicated in a previous report⁽¹⁰⁾, the fiber axis of the TiN crystallites is always $\langle 110 \rangle$, being parallel to the [001] direction of Si_3N_4 , and the orientation relation in the observed plane of Fig. 3 is given as $[1\bar{1}0]_{\text{TiN}} // [001]_{\text{Si}_3\text{N}_4}$ and $[110]_{\text{TiN}} // [100]_{\text{Si}_3\text{N}_4}$.

2. Fracture behavior of Si_3N_4 -TiN composite

In order to characterize the fracture mode and to identify the main toughening mechanisms, SEM observations of the fracture surface, and TEM observations of the indentation crack profile were carried out. Figure 4 is a SEM image showing the typical fracture morphology after bending test. In Fig. 4(a), it is noticed that this CVD sample has a columnar structure with a thickness of about $100\text{ }\mu\text{m}$. Figure 4(b) is an enlarged image of the square region in Fig. 4(a). From this images, one can clearly see both intergranular and transgranular fractures, which can be seen as a sharp columnar grain (marked with an arrowhead) and tearing (marked with a white arrow) on the fracture surface, respectively. Further details of the fracture mode were provided by observing indentation paths.

Figure 5 shows an optical micrograph showing cracks formed around a Vickers indentation, with 9.8 N load. The average hardness value was 1550. In this case, cracks

Fig. 3 HREM image taken with the $[001]_{\text{Si}_3\text{N}_4}$ incidence, showing the cross section of a TiN fiber embedded in $\beta\text{-Si}_3\text{N}_4$.

Fig. 4 (a) SEM image showing the fracture morphology after bending test at room temperature. (b) magnified image of the square region in (a).

Fig. 5 Optical micrograph of the sample indented at room temperature using a load of 9.8 N for 30 s.

are generated at various places and microcracks (indicated with arrowhead) are noticed. This feature is different from those of the other ceramics, in which cracks start from four corners of the diamond indentation. In this case, main cracks propagate with various directions, and some microcracks were born around the indentation. Although a quantitative estimation of the fracture toughness of this composite was difficult since the crack propagation direction was not straight, it can be thought that this composite has a comparatively high fracture toughness from the ratio of the crack length to the indentation diagonal length.

Figure 6(a) is a TEM image showing two cracks (indicated with A and B) around an indentation. It is clearly

Fig. 6 (a) TEM image showing crack propagation at room temperature. (b) Enlarged micrograph of the crack A in Fig. 6(a).

seen that the main paths propagate intergranularly with frequent deflections as indicated with large arrows. Especially, in the crack B, it is observed that the cracks are branched in the wake zone. And the phenomenon of microcracking occurs both near the indentation and at the crack tip, as indicated with small arrows. The microcracks are better seen in the enlarged image of the crack A in Fig. 6(b). In this image, strong strain contrasts are also noticed around the indentation.

Figure 7 is a HREM image, showing the crack propagation near the indentation, together with an electron diffraction pattern. One can clearly see the main crack propagating into a Si_3N_4 grain and several microcracks, as indicated with small arrows. Strain contrast due to the plastic deformation was observed around the indentation even at room temperature. Figure 8(a) and (b) are enlarged images of the square regions marked with A and B in Fig. 7, respectively. In Fig. 8(a), one can clearly see some edge dislocations, by viewing along arrows, together with the strain contrast on the background. This type of dislocations were not observed in this sample before indentation, therefore they may be considered due to the indentation process. On the other hand, in Fig. 8(b) showing a portion of crack tip zone, it can be seen that microcracks propagate along random directions rather than along definite planes in Si_3N_4 . By viewing along white arrows, a few edge dislocations are seen at the terminal sites of the microcracks (marked with dark circles). They are caused by displacements of a half of lattice distance, as indicated with lines. The contrast difference between the regions marked with "S" and "T" results from a slight change in the crystallographic directions, induced by the crack propagation. Figure 9 is a TEM image showing crack propagation near the indentation in a Si_3N_4 grain which was taken with the incident beam tilted at a large angle from the [001] direction of the Si_3N_4 grain. Similarly to Fig. 2(b), TiN fibers were homogeneously dispersed in Si_3N_4 matrix, and cracks pro-

Fig. 7 TEM image showing cracks near the indentation site.

pagated transgranularly from the indentation site (marked with I). Although cracks are not clear because of the large tilt on the edge of the cracks, their existence was confirmed by electron beam tilting. Also, in this case, microcracking were observed along various direction around the indentation site as indicated with arrows. Particularly, the crack 'A' is divided into two cracks, interacting with the TiN fibers.

Fig. 8 (a) Enlarged micrograph of the square region A in Fig. 7. Arrows indicate edge type dislocations. (b) Enlarged micrograph of the square region B in Fig. 7. White arrows indicate edge dislocations.

Fig. 9 TEM image showing crack propagation near the indentation site.

Some important informations were obtained from observations of the crack tip. Figure 10 is a TEM image showing a crack-tip zone, taken with the electron beam along the [001] direction of Si_3N_4 . In this image, TiN fibers dispersed in the Si_3N_4 matrix were clearly observed (indicated with arrowheads) and the crack propagated around the TiN fibers. This feature corresponds to the crack bridging model proposed by Bannister⁽¹¹⁾.

Fig. 10 TEM image around a crack-tip zone, showing crack bridging by TiN fibers. Arrowheads indicate the TiN fibers.

Fig. 11 TEM image of the wake- and tip-zone of the crack, showing microcracking and crack bridging by TiN fibers.

Figure 11 also shows a TEM image of crack tip and crack wake zones, taken with the same beam incident direction of that of Fig. 10. From this image, one can clearly see microcracking and crack bridging phenomena both in the wake and at the tip zone of the crack interacting with the dispersed TiN fibers.

As deduced from Figs. 9, 10 and 11, it can be considered that in the interaction between cracks and TiN fibers, the difference in thermal expansion coefficients and lattice mismatch between the Si₃N₄ matrix and the TiN fibers play a fundamental role in fracture. It is expected that this composite has excellent high temperature properties because of the homogeneous dispersion of the TiN fibers in the Si₃N₄ matrix and their direct bond at the Si₃N₄/TiN interfaces without any impurity. However, the sizes of Si₃N₄ grains in this composite (Fig. 1) were quite large compared with that of Si₃N₄ fabricated by conventional sintering processes. Thus, one target for further improvement of the mechanical properties in this composite system can be pointed out in the control of its matrix grain size.

IV. Conclusion

Microstructure and fracture behavior of a CVD Si₃N₄-TiN composite were characterized as follows.

- (1) Si₃N₄ grains have a columnar structure parallel to their growth direction, with a grain size of about 8 μ m.
- (2) TiN fibers are homogeneously distributed in the Si₃N₄ matrix and their axes are nearly parallel to the [001]

direction of Si₃N₄. Most of their cross sections have an ellipsoid shape of about 15 nm in diameter.

(3) Most of the Si₃N₄ grains have the β -typed hexagonal structure, but also the α -typed trigonal structure was observed. The TiN fibers have a NaCl-type structure.

(4) Grain boundaries and interfaces show a direct bond without any impurity phase.

(5) The main fracture mode is a mixed type of intergranular and transgranular fracture.

(6) Toughening mechanisms are possibly crack bridging by the dispersed TiN fibers and microcracking.

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