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Toughening mechanism of alumina-matrix ceramic composites with the addition of AlTiC master alloys and ZrO_2

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Abstract

Titanium carbide and aluminium are introduced in alumina matrix in the form of AlTiC, which is a kind of master alloy. Alumina-matrix ceramic composites are prepared by using transient liquid phase and hot-press sintering. Significant improvements in mechanical properties have been attained due to the good toughening effect of AlTiC master alloys and ZrO_2. The microstructures and toughening mechanisms of the fabricated alumina-matrix ceramic materials are analysed using a scanning electron microscope, a transmission electron microscopy and an electron probe microanalysis, respectively. Results show that the microstructures of ‘‘intracrystalline shape’’ and ‘‘intercrystalline shape’’ are formed and ‘‘sublattice’’ exists in the composites, which may extend crack path and restrain intracrystalline failure, thus improving the fracture toughness of the composites.

Keywords: D. ZrO_2; Alumina; Al–Ti–C master alloys; Transient liquid phase

1. Introduction

Alumina-matrix ceramic materials are one of the most widely used materials in the world due to their high hardness, good chemical inertness and excellent wear resistance with which metal cannot compare. Alumina is cheaper and more resourceful than other typical ceramic materials such as SiC, Si_3N_4 and ZrO_2. However, the brittleness of alumina-matrix ceramic material restrains its further application.

With the development of toughening methods such as transformation toughing [1], whisker reinforcements [2], grain bridging [3] and so on, the bending strength and fracture toughness of alumina-matrix ceramic materials are improved significantly. However, there are still many defects in the whole fabrication process of alumina-matrix ceramic products. For example, the bridging of metal particles is adverse to the chemical inertness of alumina-matrix ceramic materials, whiskers cannot be dispersed evenly in the ceramic matrix materials [2], and the effect of transformation toughing decreases as the temperature increases [4]. In addition, these methods cost much and decrease the hardness of alumina-matrix ceramics. With the emergence of new materials, the toughening additives capable of improving the performance of alumina-matrix ceramic materials is diversified [5–11]. Research on TiC/Al_2O_3 has been carried out for many years, but it is still difficult to evenly disperse TiC into alumina-matrix ceramic materials [5]. The purpose of this work is to disperse TiC into alumina-matrix ceramic materials in the form of AlTiC master alloys, and then a small amount of ZrO_2 is simultaneously introduced in alumina-matrix ceramic materials to improve their hardness and fracture toughness. The microstructures and toughening mechanisms of the fabricated alumina-matrix ceramic materials are analysed and discussed.

2. Experimental procedure

Commercial α-Al_2O_3 powder of high purity ($\geq$99%) and small grain size (0.5–3 μm) was used as the starting material. Al–Ti–C and ZrO_2, supplied by the Department of Materials Science and Engineering, Shandong University, were used as

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Table 1
Compositions and mechanical properties of the samples

Specimens	Compositions (vol.%)	Hv (GPa)	σ_f (MPa)	K_{IC} (MPa m$^{1/2}$)
A	100%Al_2O_3	17.8 ± 1.5	130.0 ± 20	3.13 ± 0.8
AT	90%Al_2O_3 + 10%Al–Ti–C	20.0 ± 1.3	302.0 ± 12	3.90 ± 0.5
ATZ	85%Al_2O_3 + 5%ZrO_2 + 10%Al–Ti–C	23.5 ± 1.5	344.6 ± 17	5.30 ± 0.3

additives. The alloy used in the present study has the composition Al–5Ti–0.25C. The grain sizes of ZrO_2 are in the range from 300 to 500 nm. The compositions of the alumina-matrix ceramics and their mechanical properties are shown in Table 1. The time of milling for composites was 80 h. The specimens were heated up to 1450 °C (30 °C min^{-1}) under a pressure of 28 MPa for an hour by hot-pressing in a graphite die under nitrogen atmosphere.

The sintered specimens were machined with a grinding machine. Standard test pieces (3 mm × 4 mm × 36 mm) were obtained through rough grinding, finish grinding with diamond wheels, and polishing. Three-point-bending mode was used to measure the bending strength with a span of 20 mm and at a crosshead speed of 0.5 mm/min. The bending strength was calculated by the following formula [12]

$$\sigma_f = \frac{3PL}{2bh^2} \quad (1)$$

where σ_f is bending strength (MPa) and P is load (N) under which the samples break, b and h are width and height (mm), respectively, and L is span (mm).

Vickers hardness was measured on polished surface with a load of 9.8N for 5 s with a micro-hardness tester (MH-6). Fracture toughness measurement was performed using indentation method with a hardness tester (Hv-120), and results were obtained by the following formula [13]

$$K_{IC} = 0.203a^{1/2}\left(\frac{c}{a}\right)^{-3/2} 1.8544\frac{P}{(2a)^2} \quad (2)$$

where K_{IC} is fracture toughness (MPa m$^{1/2}$) and P is load (N) under which the indentations come into being, $2a$ and $2c$ are length of indentation diagonal and the whole length of crack route (mm), respectively.

The micrograph of indentation cracks on polished surface of pure alumina, generated under a load of 10 kg and with a holding time of 15 s, is shown in Fig. 1 (enlarged by 400 times), and that of ATZ specimen, generated under a load of 20 kg and with a holding time of 15 s, is shown in Fig. 2 (enlarged by 400 times).

Microstructural observations of the composites were done by using a Scanning Electron Microscope (HITACHI S-570), a Transmission Electron Microscope (Philips Tecnai 20U-TWIN) and an Electron Probe Microanalyzer (JCXA-733), respectively.

3. Results and discussion

3.1. Mechanical properties of the composites

The mechanical properties of the samples are shown in Table 1. As we can see from the table, the hardness, bending strength and fracture toughness of the composites are better than that of pure alumina. They are 20.0 GPa, 302.0 MPa and 3.90 MPa m$^{1/2}$, respectively, for AT specimen, and 23.5 GPa, 344.6 MPa and 5.30 MPa m$^{1/2}$, respectively, for ATZ specimen. The mechanical properties of the composites are improved by virtue of the introduction of AlTiC master alloys and ZrO_2. For one reason, the sintering temperature of the composites was 1450 °C, which was higher than the melting point of Al. Al may, therefore, have melted and produced a liquid phase, which

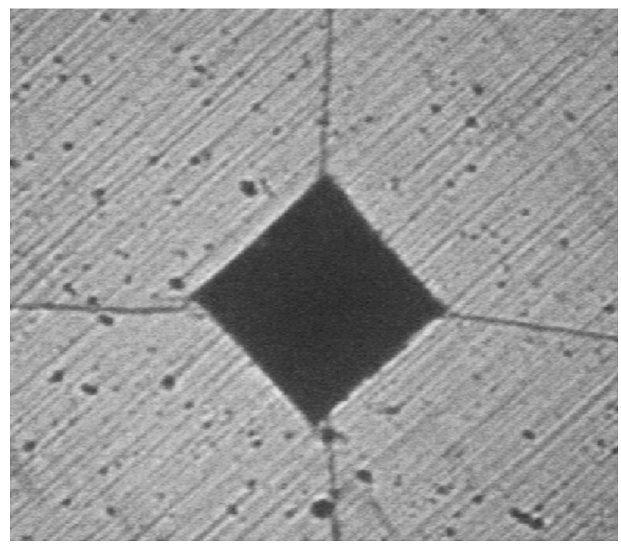

Fig. 1. Micrograph of indentation cracks of pure alumina (10 kg, 15 s, 400 times).

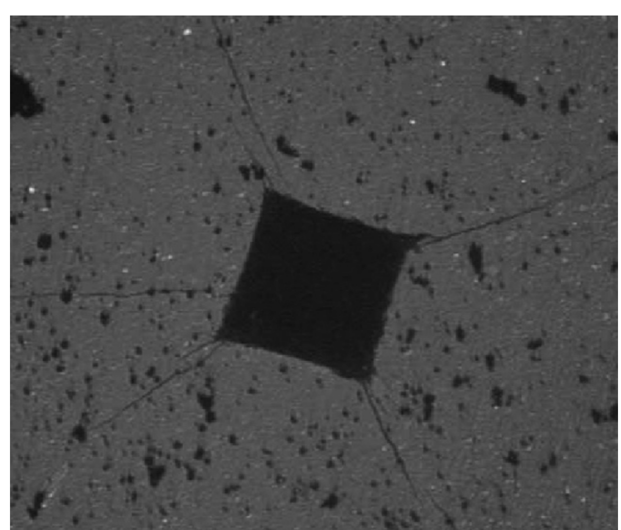

Fig. 2. Micrograph of indentation cracks of ATZ specimen (20 kg, 15 s, 400 times).

promoted the densification rate of the composites. An increased densification rate contributes to the improvement of mechanical properties of the composites. For another, AlTiC master alloys may react with alumina, and thus interfacial reactions take place on the boundaries of the composites, which may strengthen the grain boundaries.

3.2. Scanning electron microscopy (SEM) of the composites

SEM micrograph of the fracture surfaces of pure alumina is shown in Fig. 3, those of AT and ATZ specimen are shown in Fig. 4 and Fig. 5, respectively. The fracture mode of pure alumina is mainly intergranular failure, and the mean grains size is about 15 μm. The introduction of AlTiC master alloys and ZrO_2 makes the microstructures of the composites finer and more homogeneous. This is because AlTiC master alloys prevent the grains of alumina-matrix ceramics from abnormal growing when infiltrating into alumina [11]. The fracture surfaces of AT and ATZ specimen are irregular, and the fracture mode turns to the combination of transgranular failure and intergranular failure as AlTiC master alloys and ZrO_2 are introduced in alumina, as is shown in Figs. 4 and 5. The bondings of grains become stronger when the fracture mode turns to the combination of transgranular failure and intergranular failure, which may bring on the improvement in bending strength and fracture toughness.

3.3. Transmission electron microscopy (TEM) of the composites

The microstructures of the composites are observed by using a high resolution transmission electron microscope (Philips Tecnai 20U-TWIN). Particulates with different shapes are found in ATZ specimen. Figs. 6 and 7 show the microstructures characterized as ‘‘Feather-shape’’ and ‘‘Cluster round’’, respectively. ‘‘Crystal shape of inside grain’’ is shown in Fig. 8. The microstructure of ‘‘Feather-shape’’ is well arranged, and the profile is clear and like a twin crystal. The mechanism of microstructure formation is still unclear and it needs further research.

It can be clearly seen from Fig. 7 that many small grains surround a big one, which is mostly alumina. The small grains

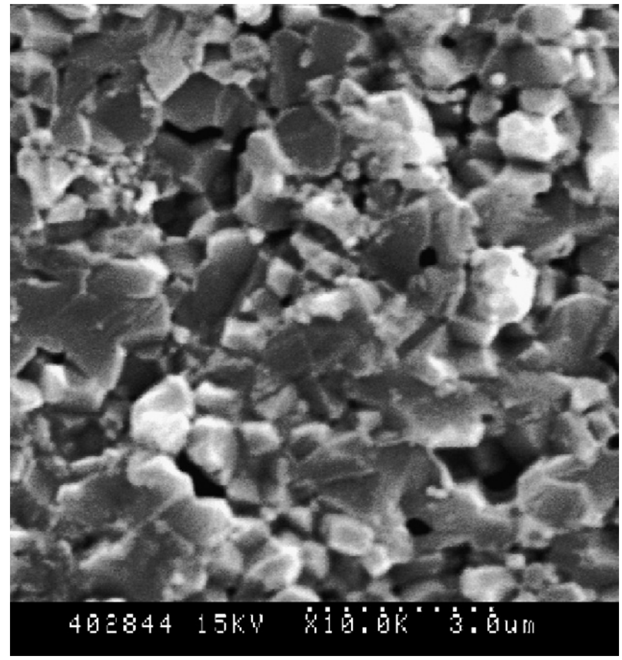

Fig. 4. SEM micrographs of the fracture surfaces of AT specimen.

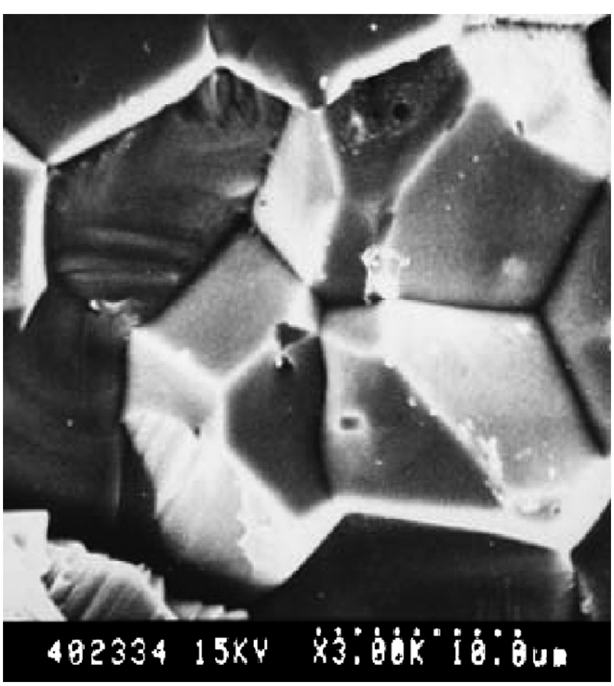

Fig. 3. SEM micrographs of the fracture surfaces of pure alumina.

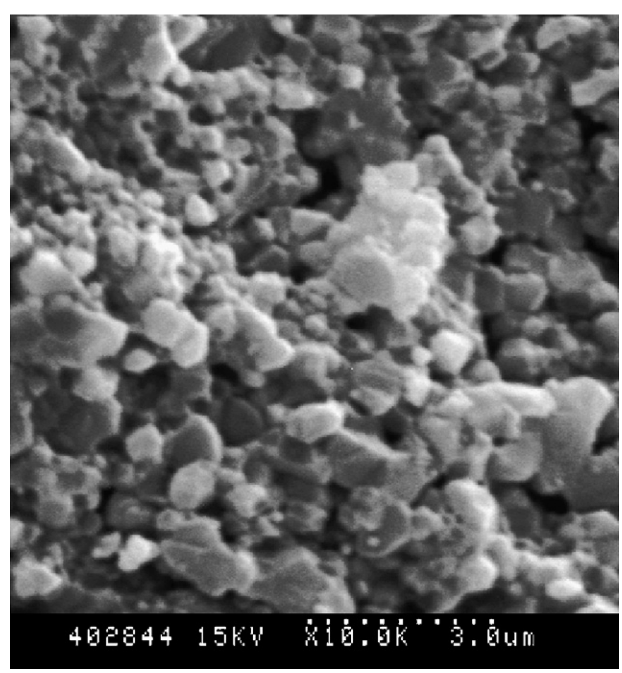

Fig. 5. SEM micrographs of the fracture surfaces of ATZ specimen.

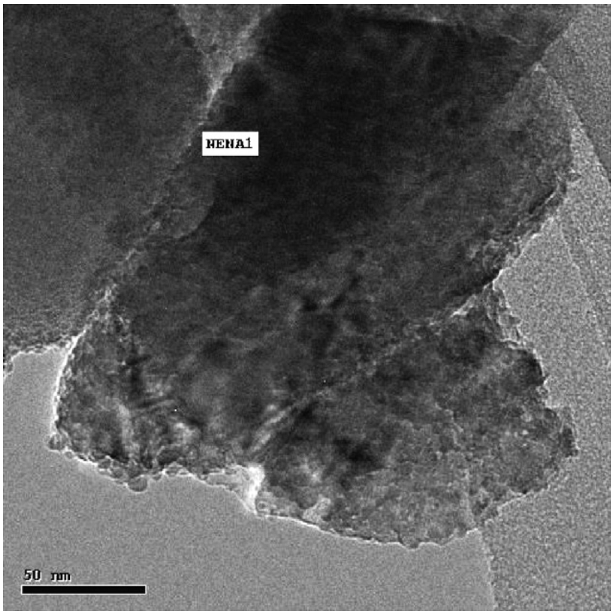

Fig. 6. ‘‘Feather-shape’’ microstructure of ATZ specimen.

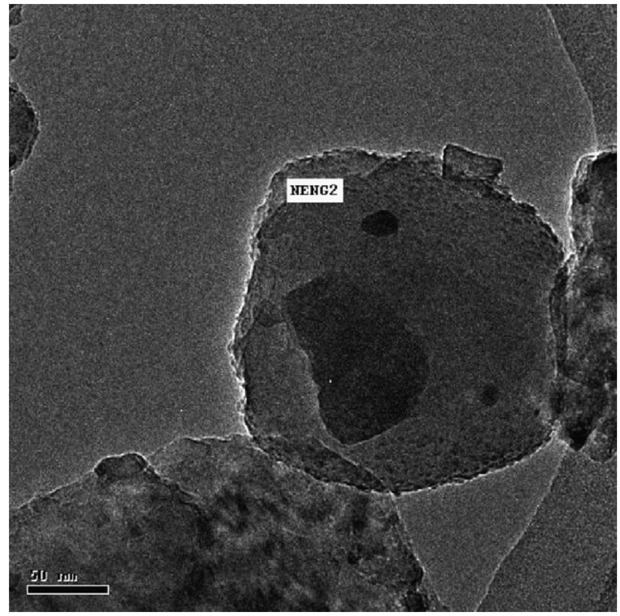

Fig. 8. ‘‘Crystal shape of inside grain’’ microstructure of ATZ specimen.

are additives as confirmed though an analysis of their spectra. This ‘‘surrounding’’ of alumina matrix by the additives prevents alumina from growing. The results indicate that when 10 vol.% AlTiC is added to alumina-matrix ceramics as seed crystals, the AlTiC master alloys prevent alumina grain growth and the fracture mode of composites changes from intracrystalline failure to promiscuous mode, which consists of intracrystalline failure and intercrystalline failure.

It has been reported that Al–Ti–C master alloys are composed of Al and TiC phases and the following reaction will tack place when AlTiC master alloys and ZrO_2 are introduced in alumina matrix [11]

$$2Al + N_2 \rightarrow 2AlN \quad (3)$$

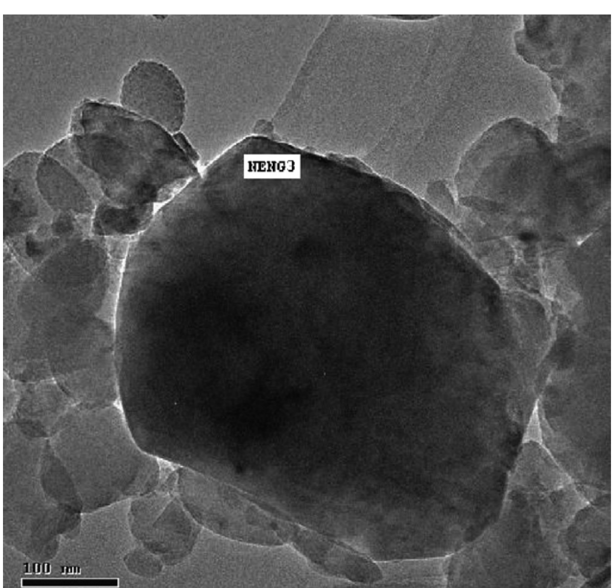

Fig. 7. ‘‘Cluster round’’ microstructure of ATZ specimen.

where Al is from AlTiC master alloys and N_2 is the protection atmosphere. Based on thermodynamics analysis of the reactive equation, the following ranking can be expressed:

$$\Delta G_T^{\circ} = -2.536 \times 10^5\ \mathrm{J} < 0 \quad (4)$$

where ΔG_T° is the Gibbs free energy of reaction (3). The existence of AlN contributes to refinement of the new fabricated composites and thus results in strengthening of the grain boundaries.

As we can see in Fig. 8, TiC with submicron dimensions, and AlN and ZrO_2 with nanometer dimension, and with minor crystal boundaries, are all surrounded by alumina grains, whose crystal boundaries are primary. The bond-strength of main crystal boundaries can be weakened by the minor crystal boundaries, producing intracrystalline failure and thus crack deflection and microcracking. As a result, the fracture toughness of the composites is improved significantly owing to the deflection of crack.

In addition, there are ‘‘sublattices’’ existing in the crystal lattice stripe-micrography of alumina grains (shown in Fig. 9). The effect of ‘‘sublattice’’ on extension of crack path is direct and distinct. When the crack extends to a ‘‘sublattice’’, which changes the direction of crystal lattice, the crack will change its direction of propagation. This extends the crack path and intracrystalline failure is restrained, and thus the fracture toughness of the composites is improved significantly.

3.4. Electron probe microanalysis (EPMA) of the composites

The distribution of TiC and ZrO_2 in Al_2O_3 matrix is difficult to observe by a scanning electron microscope (SEM) [11]. In order to analyze the uniformity of additives in the matrix material, electron probe microanalysis (JCXA-733) is used to

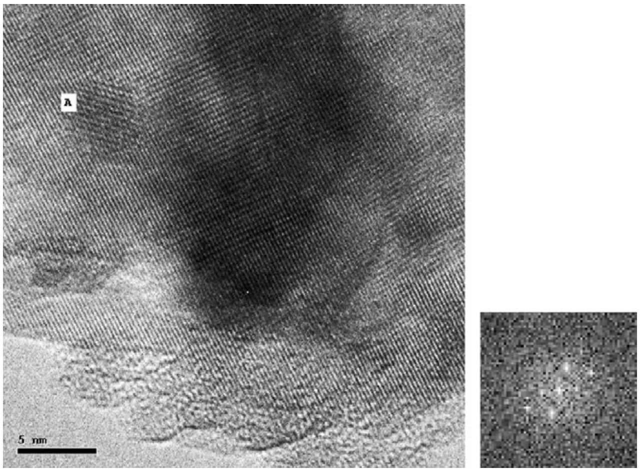

Fig. 9. ‘‘Sublattice’’ in alumina grains and its electron diffraction spot.

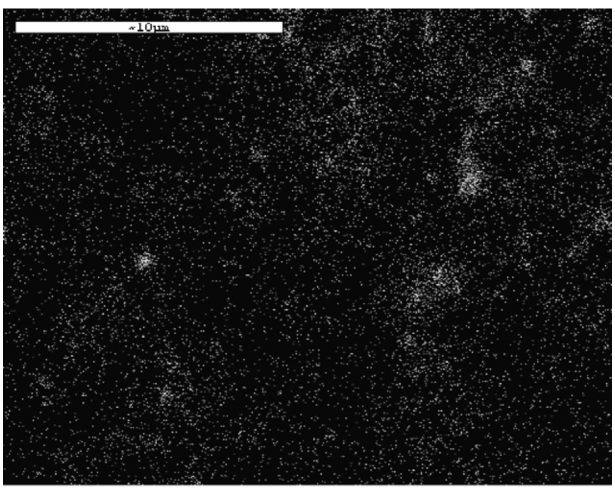

Fig. 10. EPMA photograph of Ti in ATZ specimen.

scan Ti and Zr, which exist on the surface of ATZ specimen (shown in Figs. 10 and 11). As can be seen from Figs. 10 and 11, Zr disperses evenly into the composites on the whole, but locally there exists agglomeration. The distribution of Zr is different from that of Ti. Ti disperses more evenly than Zr into alumina-matrix ceramic materials for the reason that TiC is added in alumina matrix in the form of AlTiC master alloys.

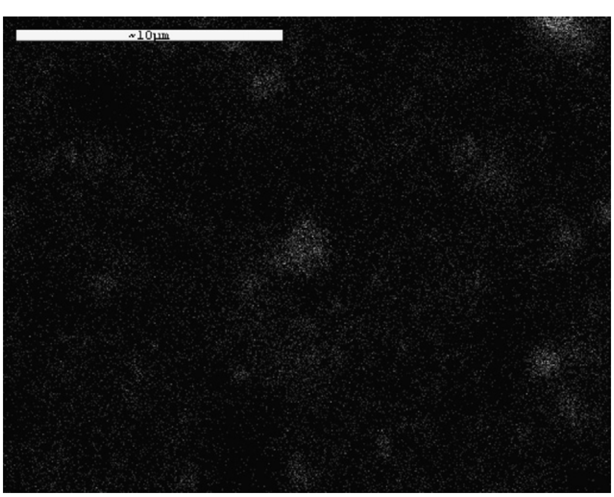

Fig. 11. EPMA photograph of Zr in ATZ specimen.

4. Conclusion

Titanium carbide is introduced in alumina-matrix ceramic materials in the form of AlTiC master alloys. Alumina-matrix ceramic materials are fabricated by hot-press sintering technology. Not only the particles of titanium carbide are dispersed evenly in alumina-matrix ceramics, but also the hardness and fracture toughness of the composites are improved. Transient liquid phase sintering is produced and the sintering temperature is decreased by the addition of AlTiC master alloys. The sizes of alumina grains are uniform and ‘‘sublattice’’ structures exist in the composites. Alumina is the main phase and smaller size of TiC, AlN and ZrO_2 disperse evenly on the boundaries of alumina grains or within the crystal grains, and thus microstructures of ‘‘intracrystalline shape’’ and ‘‘intercrystalline shape’’ are formed. The existence of a ‘‘sublattice’’ structure can restrain intracrystalline failure and improve the fracture toughness of the composites.

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References

[1] J.F. Yang, T. Ohiji, T. Sekino, et al., Phase transformation, microstructure and mechanical properties of Si_3N_4/SiC composite, J. Eur. Ceram. Soc. 21 (12) (2001) 2179–2183.
[2] K. Geng, W.J. Lu, Y.X. Qin, D. Zhang, In situ preparation of titanium matrix composites reinforced with TiB whiskers and Y_2O_3 particles, Mater. Res. Bull. 39 (6) (2004) 873–879.
[3] C.P. Ostertag, Influence of fiber and grain bridging on crack profiles in SiC fiber-reinforced alumina-matrix composites, Mater. Sci. Eng. A 260 (1–2) (1999) 124–131.
[4] D. Casellas, F.L. Cumbrera, F. Sánchez-Bajo, et al., On the transformation toughening of Y–ZrO_2 ceramics with mixed Y–TZP/PSZ microstructures, J. Eur. Ceram. Soc. 21 (6) (2001) 765–777.
[5] K. Jakus, S.V. Nair, Nucleation and growth of cracks in SiC/Al_2O_3 composites, Compos. Sci. Technol. 37 (1–3) (1990) 279–297.
[6] W. Acchar, A.E. Martinelli, C.A.A. Cairo, Reinforcing Al_2O_3 with W–Ti mixed carbide, Mater. Lett. 46 (2000) 209–211.
[7] W. Acchar, P. Greil, A.E. Martinelli, et al., Sintering behaviour of alumina-niobium carbide composites, J. Eur. Ceram. Soc. 20 (2000) 1765–1769.
[8] W. Acchar, C. Zollfrank, P. Greil, Microstructure of alumina reinforced with tungsten carbide, J. Mater. Sci. 41 (2006) 3299–3302.
[9] D.F. Lii, J.L. Huang, K.C. Twu, et al. J. Ceram. Soc. Jpn. 104 (9) (1996) 796–801.
[10] W.P. Tai, T. Watanab, J. Am. Ceram. Soc. 81 (6) (1998) 1673–1676.
[11] C.X. Liu, J.H. Zhang, X.H. Zhang, et al., Addition of Al–Ti–C master alloys and ZrO_2 to improve the performance of alumina matrix ceramic materials, Mater. Sci. Eng. A 426 (2006) 31–35.
[12] Z.H. Jin, J.Q. Gao, G.H. Qiao, Engineering Ceramics [M], Publishing House of Xian Jiao Tong University, Xian, 2000.
[13] R.F. Cook, B.R. Lawn, A modified indentation toughness technique, J. Am. Ceram. Soc. 66 (11) (1983) 200–201.