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ARTICLE

Toughening Effect of ZrB_2 in Al_2O_3-ZrB_2 Nanocomposite Ceramics

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Abstract: The Al_2O_3-ZrB_2 nanocomposite ceramics were prepared and the mechanical properties of the process parameters' effect were studied. The results show that for various applied sintering temperatures of Al_2O_3 ceramics, a maximum Vickers hardness of 18 970 MPa and high reliability are attained at 1500 ℃ and at atmosphere sintering. The fracture toughness is (5.2±0.3) MPa $m^{1/2}$. In addition, the sample is not well densified at the sintering temperature. Scanning electron microscopy (SEM) shows that fine ZrB_2 particles disperse and are pinned at grain boundaries to inhibit grain boundary movement effectively. While larger ZrB_2 particles distribute between $A1_2O_3$ particles uniformly and occupy Al_2O_3 particles growing space to hinder the matrix grains, which greatly promote the densification of the ceramic and improve the microstructure. 20% ZrB_2/Al_2O_3 composite ceramics exhibit a relative density above 98% at (450 ℃, Vickers hardness of 18 070 MPa, and fracture toughness of (6.7±0.2) MPa $m^{1/2}$ Fracture morphology indicates that trans-granular fracture occurs in the nanocomposite ceramic with high toughness.

Key words: atmospheric sintering; nano alumina ceramic; nanocomposite ceramics; toughening

As we all know, Al_2O_3 ceramic is a representative of the advanced ceramics industry, which has a series of advantages such as high melting point, high hardness, corrosion resistance, heat resistance and good electrical insulation properties, so it can be used in demanding conditions. Furthermore, Al_2O_3 ceramic has become one of the important and widely used base materials in the science and technology field because of its mature production technology, production volume and low price.[1-2] Al_2O_3 ceramic is usually applied to the structure parts to withstand mechanical stress, tool material, wear parts, bio-ceramics field, aerospace, energy, aerospace, chemical, electronics, and so on. The research of Al_2O_3 ceramic is of great importance for science and technology workers, and it has become an extremely rapid development field in the last 20 years. [3,4] In these 20 years, the research of ZrO_2 particle toughening Al_2O_3 ceramic materials is more and more, and some of the research have been applied to the practice. But in these studies, zirconia is usually used to toughen alumina, and certain powder is required: either both nano powder[2,3,5], or nano ZrO_2 powder and micron Al_2O_3 powder with formation of "intragranular" structure after sintering[3,6]. However, the reports of ZrB_2 toughened alumina ceramic are few, especially the study of less-micron ZrB_2 toughened nano-alumina.

The present paper employs atmospheric sintering, high purity nano Al_2O_3 powder and micron ZrB_2 powder to produce Al_2O_3 ceramic and ZrB_2/Al_2O_3 composite ceramics and study the microstructure and mechanical properties.

1 Experiment

A kind of high purity nano-Al_2O_3 (Shanghai, purity of 99.99%) and micron ZrB_2 (Lanzhou University and Technology, purity of 98%) containing a small amount of ZrO_2, as shown in Fig.1 were selected as starting materials and their properties are listed in Table 1.

There is a clear difference before and after treatment of Al_2O_3 powder. Firstly, we pre-processed a large amount of Al_2O_3

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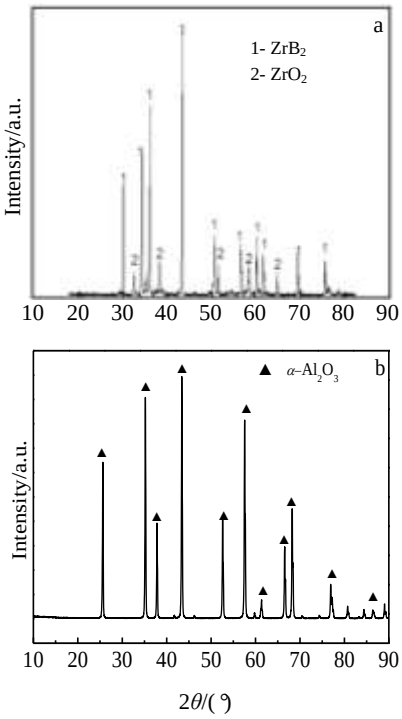

Fig.1 XRD patterns of Al_2O_3 (a) and ZrB_2 (b)

particles to make them get together (Fig.2a), but they dispersed after ethanol treatment, which reduced the force between the particles, so the aggregates were dispersed (Fig.2b). The grain size of Al_2O_3 is about 100 nm. Fig.2c is a scanning electron micrograph of the ZrB_2 powder. The individual particles are relatively large (10 μm), average particle size of most of other particles is about 0.3 μm and they uniformly dispersed in the conductive adhesive.

The high-purity nano-Al_2O_3 powder (99.99% purity) and micron ZrB_2 powder, according to the ratio shown in Table 2 were loaded into a four steel mill pot. After stirring with a spoon, corundum balls (according ball and raw material ratio is 2:1) were used to mill for 8 h on QM-2SP20-CL planetary ball mill (Nanjing University Instrument, Nanjing, China). After milling, artificial granulation was conducted. Then we let the powder through 60 mesh sieve and dried it in a thermostatic oven for 2 h and loaded a die a steel mold for dry pressing at 450 MPa with Guo-long four-column universal hydraulic machine of Nantong China. After forming, the sample was a cylinder with size Φ25 mm×7 mm (named as green). Then we put the green into the TC-17X sintering furnace whose heating source was composed of 24 $MoSi_2$ rods (bar) atmospheric sintering at 1500 ℃ or 1450 ℃, heating rate is 15 ℃ /min. The sintering system is shown in Fig.3.

The sintered ceramic material samples were ground and polished with sandpaper 600, 800, 1000, 1200, 1500 and 2000 mesh. Vickers hardness was measured with MVC-1000JMT1 micro Vickers hardness tester with load of 200 gf, holding time of 15 s, equipped with 400 optical microscope. The phase composition of the sintered composite materials or the raw materials was analyzed by X-ray diffraction (XRD) (D8ADVANCE X-ray diffraction, Rigaku Company). Material microstructure morphology, polished surface and fracture morphology of the sample were detected by JSM-6700F field emission scanning electron microscope (FESEM, JEOL Company, Japan).

2 Results and Discussion

2.1 Sintering system

Fig.4 and Fig.5 shows the Vickers hardness and relative density of materials at different temperatures, respectively. At 1500 ℃, the Al_2O_3 ceramic's Vickers hardness is 18 970 MPa, and it almost remains the value. But, the ZrB_2-Al_2O_3 ceramic's Vickers hardness is 18 070 MPa, which is lower than Al_2O_3 ceramic's, and also almost remains the level. At 1400 ℃, the relative density of both ceramics is more than 99%. Therefore, the two samples, sample A of pure Al_2O_3 sintered at 1500 ℃, and sample B of ZrB_2 (20wt%) + Al_2O_3 (80 wt%) sintered at 1450 ℃, were selected to determine the properties of toughened.

2.2 Phase composition and microstructure of Al_2O_3 ceramics

SEM image of the sample A is shown in Fig.6a. We can see obviously that its quality is not very good, mainly because the sintering temperature is not enough to completely form porcelain, and the grain size is 200~300 nm. When the purity of Al_2O_3 increases, and the sintering temperature increases too, grains grow rapidly. It can be seen from the fracture surface topography in Fig.6b that the fracture mode is obvious intergranular fracture.

2.3 Phase composition and microstructure of ZrB_2-Al_2O_3 composites

Since the sintering quality of sample A is not very good, we adjusted the sintering temperature and added the second phase of ZrB_2 particles to obtain good microstructural and mechanical properties. ZrB_2 particle dispersion can toughen the material. From the XRD patterns (Fig.7) of sample B shows that the phase transformation toughening phenomenon

Table 1 Starting materials properties

Starting materials	Density/g·cm^{-3}	Thermal expansion coefficient/×10^{-6} K^{-1}	Poisson's ratio	Modulus of elasticity/GPa	Grain size	Purity/%
Al_2O_3	3.98	8.4	0.26	400	<200 nm	99.99
ZrB_2	6.085	5.9	0.2422	387	0.1~10 μm	99

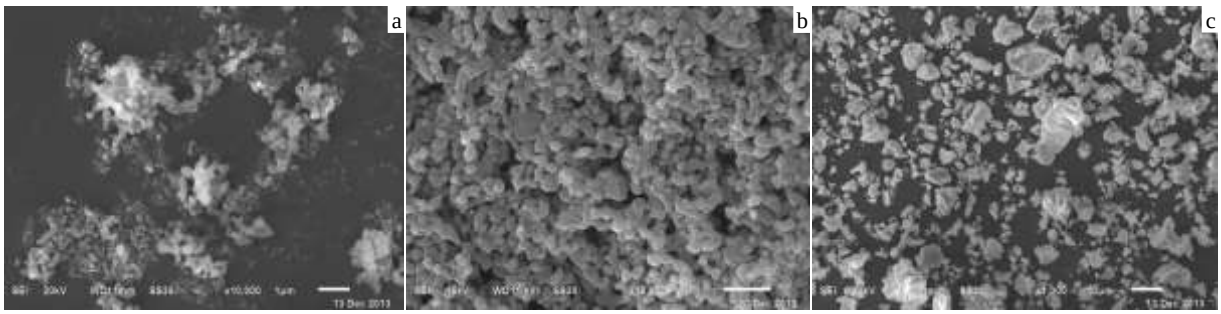

Fig.2 Starting materials' SEM images: (a) α-Al_2O_3 before treating, (b) α-Al_2O_3 after treating and (c) ZrB_2

Table 2 Experimental ratio and sintering parameters

Samples	Composition, φ/%		Sintering parameters		
	Al_2O_3	ZrB_2	Sintering temperature/ ℃	Molding pressure/MPa	Insulation time/h
A	100	0	1500	450	8
B	80	20	1450	450	8

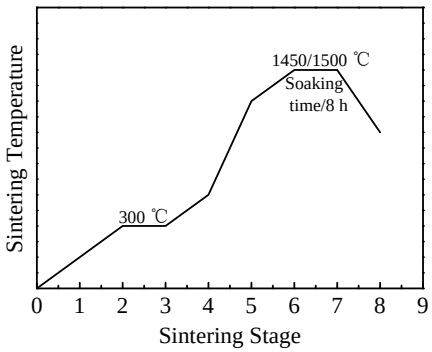

Fig.3 Curve of atmospheric sintering system

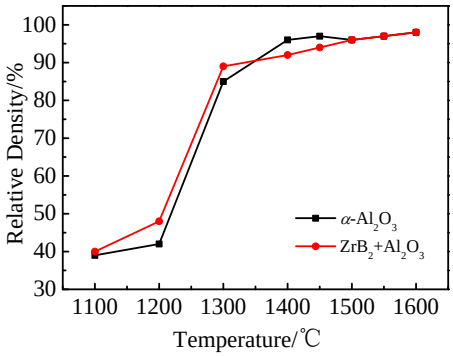

Fig.5 Relative density of materials at different sintering temperatures

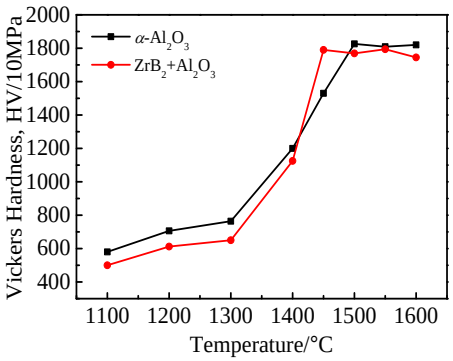

Fig.4 Vickers hardness of materials at different sintering temperatures

does not exist. The main reason of particles toughening is second phase particles of high elastic modulus added in the ceramic matrix. The thermal expansion coefficient and elastic modulus of the second phase and the matrix are mismatched, so when the fracture stress increases, the part of the fracture energy is absorbed. The absorbed fracture energy has the dual effect of strengthening and toughening.

Fig.7a is XRD patterns of Sample B. ZrB_2 phase and α-Al_2O_3 phase can be seen in the composite materials, but the phase transformation toughening phenomenon does not occur, which is a great pity for toughening. Fig. 7b can explain the better performance of the materials when the micron ZrB_2 particles are added into the nano Al_2O_3 matrix. Micron ZrB_2 particles are not spherical, but the polygonal block. These particles uniformly distribute in the matrix. Fig.8a is the surface scanning electron micrograph of the sample B. We can see that the crystal particles are uniform and spherical. The grain size is only about 100 nm, smaller than that of the pure Al_2O_3[1,5] ceramic. Although the ZrB_2 particles are irregular in shape and size, they are still very uniformly distribute in the matrix. Fig.8b is a scanning electron micrograph of the fracture of sample B, in which the uniform grain size and dense microstructure can be seen clearly in the SEM. As a result, ZrB_2 particle size and dispersion degree, have a

significant effect on the sintering and fracture of ceramic samples: (1) the small size of the ZrB_2 pinned on the Al_2O_3 grain boundaries which inhibits the growth of the matrix grains [7-9] (Fig.8c, the arrows show the pinning phenomenon). (2) the large particle size ZrB_2 effectively suppresses matrix grain growth, and block and disperse the crack, increases the expansion path and consume more fracture energy. In Fig.8d as indicated by the arrows, the transgranular fracture occurs on the large particles. This is because the tiny ZrB_2 particles are pinned grain boundaries and make the intergranular combination very strong, forcing the crack propagation along the cleavage plane of the larger particles, and the transgranular fracture occurs. Its appearance will absorb part of the energy at break, and extremely favorable for improving the fracture toughness. The fracture mode is a mixed fracture mode with intergranular fracture as the main mode (Fig.8b).

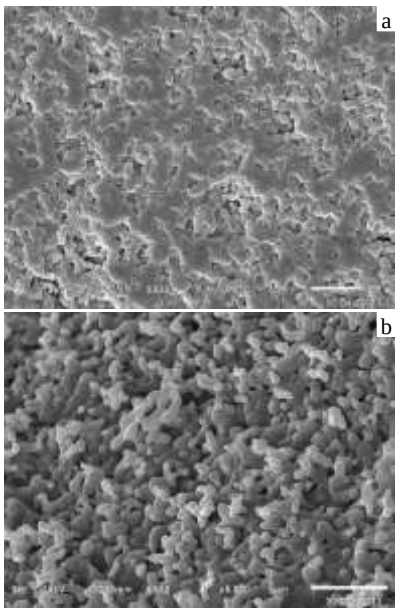

Fig.6 SEM image (a) and fracture morphology (b) of sample A (pure Al_2O_3, 1500 ℃, 8 h)

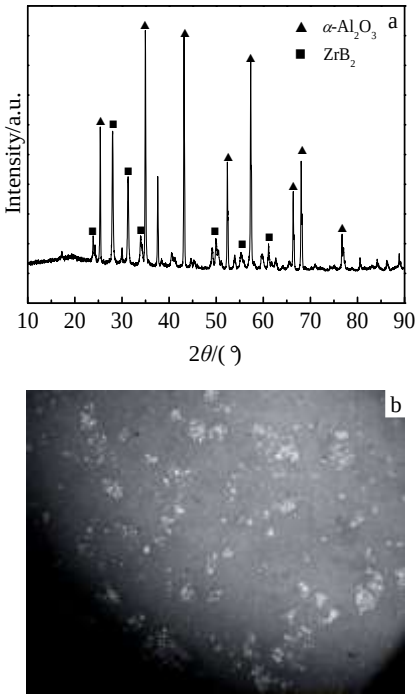

Fig.7 XRD pattern (a) and photomicrograph (b) of sample B

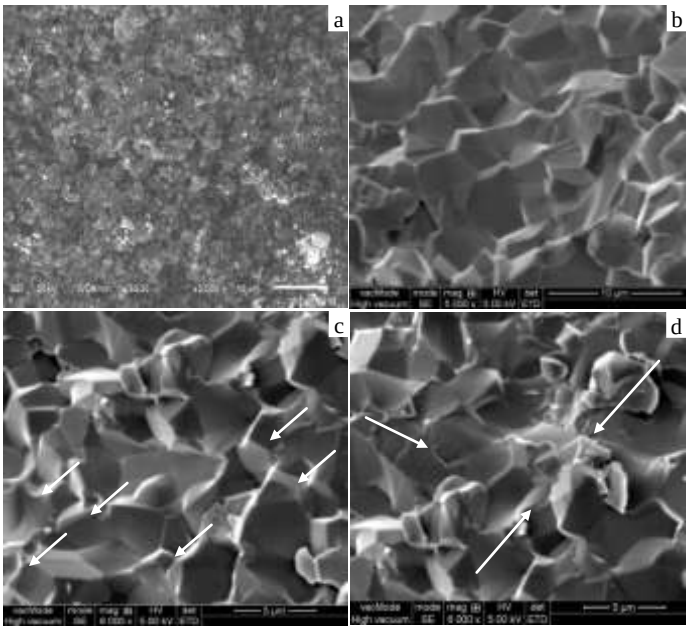

Fig.8 SEM image (a) and fracture morphologies (b, c, d) of sample B (1450 ℃, 8 h)

2.4 Ceramic toughness calculation

The toughness of the ceramics were measured and calculated by Laugier II (DCM8)[10,11] formula:

$$K_{\mathrm{Ic}} = 0.015(L/\mathrm{a})^{-\frac{1}{2}}(E/H)^{\frac{2}{3}} \quad (1)$$

$$PC^{-\frac{3}{2}}L/a < 2.5 \quad (2)$$

where, H: hardness of the materials; E: Elastic modulus of the material; P: Indentation, carry burden; L: Indentation crack length; a: Indentation radius; $C=L+a$

According to the formula, the toughness of pure alumina ceramics is (5.2±0.3) MPa·m$^{1/2}$, lower than (6.7±0.2) MPa·m$^{1/2}$ of the ZrB_2+Al_2O_3 ceramics. The results indicate that the preceding analysis of ZrB_2 nail toughening effect is correct.

3 Conclusions

1) Pure Al_2O_3 ceramic's microstructure is poor when atmospheric sintering and its fracture morphology is intergranular fracture. The Al_2O_3 ceramic has a Vickers hardness of 18 970 MPa and the fracture toughness of (5.2±0.3) MPa·m$^{1/2}$ when sintered above 1500 ℃. Correspondingly, the ZrB_2-Al_2O_3 ceramic has a Vickers hardness of 18 070 MPa and the fracture toughness of (6.7±0.2) MPa·m$^{1/2}$ when sintered above 1450 ℃.

2) The microstructure of ZrB_2+Al_2O_3 is good. ZrB_2 with small grain size is distributed in the Al_2O_3 matrix uniformly, playing the role of pinning. However, larger particles block and disperse the crack, so the fracture toughness and microstructure are improved.

3) Fracture morphology of ZrB_2+Al_2O_3 indicates that intergranular fracture is the main way of mixed fracture mode.

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ZrB_2 在 Al_2O_3-ZrB_2 复相陶瓷中的增韧性能

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摘 要：常压烧结制备了 Al_2O_3 和 20%ZrB_2/Al_2O_3(质量分数)复合陶瓷，用 XRD 和金相显微镜、SEM 分析了其相组成、微观结构、断裂形貌，并用压痕法计算了陶瓷的断裂韧性。结果表明：Al_2O_3 陶瓷自 1500 ℃开始其相对密度超过 99%，维氏硬度达到 18 970 MPa，断裂韧性为(5.2±0.3) MPa·m$^{1/2}$；20%ZrB_2/Al_2O_3 复合陶瓷在 1450 ℃时相对密度超过 98%，维氏硬度达到 18 070 MPa，断裂韧性为(6.7±0.2) MPa·m$^{1/2}$。微观形貌观察表明，ZrB_2/Al_2O_3 复合陶瓷韧性的增加是由于弥散分布的 ZrB_2 在 Al_2O_3 陶瓷基体中起到遏制裂纹扩展和钉扎双重作用的结果。

关键词：常压烧结；纳米氧化铝陶瓷；纳米复相陶瓷；增韧

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