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Mechanical properties and microstructure of TiB_2 ceramic influenced by ZrB_2 additive①

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[Abstract] Since some transition metal diborides have the same crystal structure with TiB_2, which can react with TiB_2 to form solid solution by adequate technique. With ZrB_2 used as additive, the TiB_2-ZrB_2 solid solution was prepared by hot pressing. The effects of additive content on mechanical properties of composite were investigated. The microstructure analyzing were employed by EPMA, SEM and TEM. It is shown that TiB_2 can partly form solid solution with ZrB_2 and redound to gain uniform grains, which results in the increase of mechanical properties.

[Key words] solid solution; TiB_2- ZrB_2; mechanical properties; microstructure
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1 INTRODUCTION

Possessing of special physical and chemical properties, titanium diboride ceramics are a sort of important engineering materials. Based on its extremely high melting temperature and chemical stabilization, good wear resistance, high hardness and elastic modulus, TiB_2 is prospectively used as cutting tools, light-weighted armors, grinding materials, additive for hard alloys and highly wear resistant and temperature resistant components, etc.[1]. Differed from most of other structural ceramics, TiB_2 is a good electric conductor, which makes it as a good candidate for corrosion resistant electrodes and evaporation boats for liquid metals. Titanium diboride ceramics can also be machined by electrical discharge machining method. However, the high melting temperature and low mass transport of TiB_2 are the main obstacles for the consolidation of polycrystalline bulk material[2, 3]. In order to gain full dense pure TiB_2 sample, high sintering temperature(above 2 000 ℃) and pressure-assistant sintering techniques(such as hot pressing and hot isostatic pressing) are required. Due to the high sintering temperature for densification, an undesirable grain growth also takes place according to *c* axis direction in the sintering process of TiB_2 single phase ceramic, which sharply degrades the mechanical properties[4, 5].

For improving the sintering performance of TiB_2, some transition metals that have good wetting capability with TiB_2, such as Fe, Co and Ni, were used to reduce the sintering temperature and gain dense materials. It is obvious that metallic binder can decrease sintering temperature but lower the hardness of composites[6, 7]. Otherwise, some ceramics (such as SiC[8], Si_3N_4[9], TiC[10], B_4C[11], Al_2O_3[12] and ZrO_2[13, 14], etc.) used as secondary phases were studied to improve the mechanical properties of composites. It is shown that although the mechanical properties of composites can be effectively enhanced, some unique properties of TiB_2, like high electric conductivity, are lost due to big adding content.

The solid solution modified technology is a kind of methods that improves the properties of ceramics by replacing some ions of matrix with dopant. At present, this technology has succeeded in many structural and functional ceramics[15]. In transition-metal diboride compounds, the ZrB_2 and TiB_2 have the same crystalline structure and close crystalline parameters. Thus, they may form solid solution with each other in some extent by suitable method. In this paper, ZrB_2 is selected as doping additive to form solid solution with TiB_2 matrix by solid reaction and the TiB_2-ZrB_2 composites are finally consolidated by hot pressing. The microstructure analyzing are carried out by EPMA, SEM and TEM. Then, the influence of adding content on the mechanical properties and microstructures of composites are investigated.

2 EXPERIMENTAL

TiB_2 powders were prepared by SHS (self-propagating high-temperature synthesis) method[16]. In order to gain the uniform particle size, the TiB_2 powders were milled in WC-Co container for 4 h with WC-Co balls. ZrB_2 were synthesized by self-propagating thermal explosion method at 1 473 K, using pure zirconium and amorphous boron powders. The as-synthesized products were milled in agate mortar and then sifted by 180 mesh sieve. According to mole

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fraction, the TiB_2 and ZrB_2 were mixed to composites powder with certain ratio. The mixtures were agitated by ball milling in alcohol for 24 h in a polyethylene container with agate balls. The mass ratio of ball to mixture was kept in 1∶1. After dried and sifted, the mixtures were packed into 20 mm × 30 mm graphite dies and compacted by hot pressing. Hot pressing sintering was conducted in argon atmosphere, with hot pressing temperature of 2 073 K, applied pressure of 30 MPa and sintering time of 60 min.

The as-sintered specimens were cut and polished into 4 mm × 3 mm × 30 mm and 5.0 mm × 2.5 mm × 30.0 mm for mechanical properties test. The bending strength of specimen was determined by three-point bending method with load rate of 0.05 mm/min. Five samples were tested in each group of specimens to gain the average value. The fracture toughness was tested by the single-edge notched beam (SENB) method. The proportion of sample size was: $c/w = 0.4 \sim 0.6$, $w/s = 0.25$, $B \approx 0.5\ w$, where c is the depth of notch, s is span, B and w is the width and thickness of sample. The hardness (HRA) was measured by indentation technique with applied load 588 N. The densities of samples were determined by Archimedes method. The microstructure characterization of specimens were carried out by scanning electron microscopy (JEOL SX-40), transmission electron microscopy (Philips TEM/STEM) and electron probe micro-analyzer (Philips, JCXA-733).

3 RESULTS AND DISCUSSION

3.1 Sintering performance and mechanical properties

The relative density and hardness (HRA) of as-sintered specimens are shown in Fig. 1. Fig. 2 shows the bending strength and the fracture toughness of specimens. It can be known that the addition of ZrB_2 can improve the relative density in contrast with additive-free specimen. The curve of relative density appears maximum value at 8% ZrB_2. The HRA of composites have the same trend with relative density. The hardness of TiB_2-8% ZrB_2 is 94.75 HRA. In addition, the macro hardness is closely related not only to material nature but also to the density of specimen. It is beneficial to improving the hardness by decreasing the porosity of composites. Compared with the specimen without additives, the bending strength, ranging from 300 MPa to 450 MPa, declines along with the increase of additive content. But the fracture toughness increases significantly with the content of ZrB_2. The fracture toughness of TiB_2-8% ZrB_2 (mole fraction) reaches 7.63 $MPa \cdot m^{1/2}$.

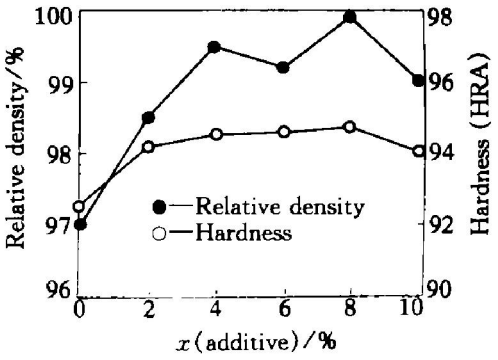

Fig. 1 Relative density and hardness vs additive contents

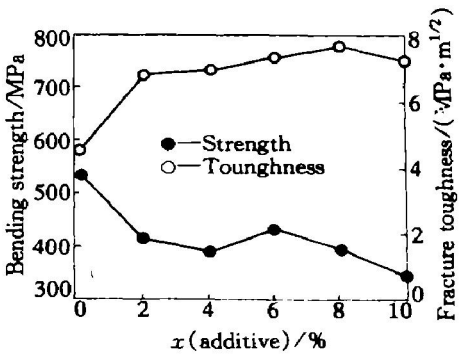

Fig. 2 Bending strength and fracture toughness of TiB_2 ceramic containing different additive contents

3.2 Electron probe micro-analysis

The EPMA results of TiB_2-8% ZrB_2 (mole fraction) are shown in Fig. 3. As shown in Fig. 3(a), some Ti-rich region and Zr-rich region are existed in the specimen. It can be easily convinced that ZrB_2 is partly solved in the matrix of TiB_2. Fig. 3(b) is the line distribution of elements. It indicates that it has a gradient distribution of Zr along the wedge to the center of TiB_2 grain. This phenomenon implies that the solution of element Zr in TiB_2 grain is formed by mutual diffusion of ZrB_2 and TiB_2, which results in the formation of Ti-rich region and Zr-rich region at the two sides of interface.

3.3 Microstructures

The SEM images of pure TiB_2 and TiB_2-8% ZrB_2 (mole fraction) specimens, which were prepared by hot pressing at 2 073 K and 30 MPa for 60 min, are shown in Fig. 4. It is found that with the average grain size larger than 20 μm, the grains in pure TiB_2 remarkably grow. In the TiB_2-8% ZrB_2 (mole fraction) sample, the grains are small and uniform with the average grain size smaller than 5 μm. This phenomenon indicates that ZrB_2, as an additive, can effectively inhibit the growth of TiB_2 grains during hot pressing.

In general, an aggregate of fine-grained crystals increases in average grain size when heated at elevated temperature. As the average grain size increases, it is

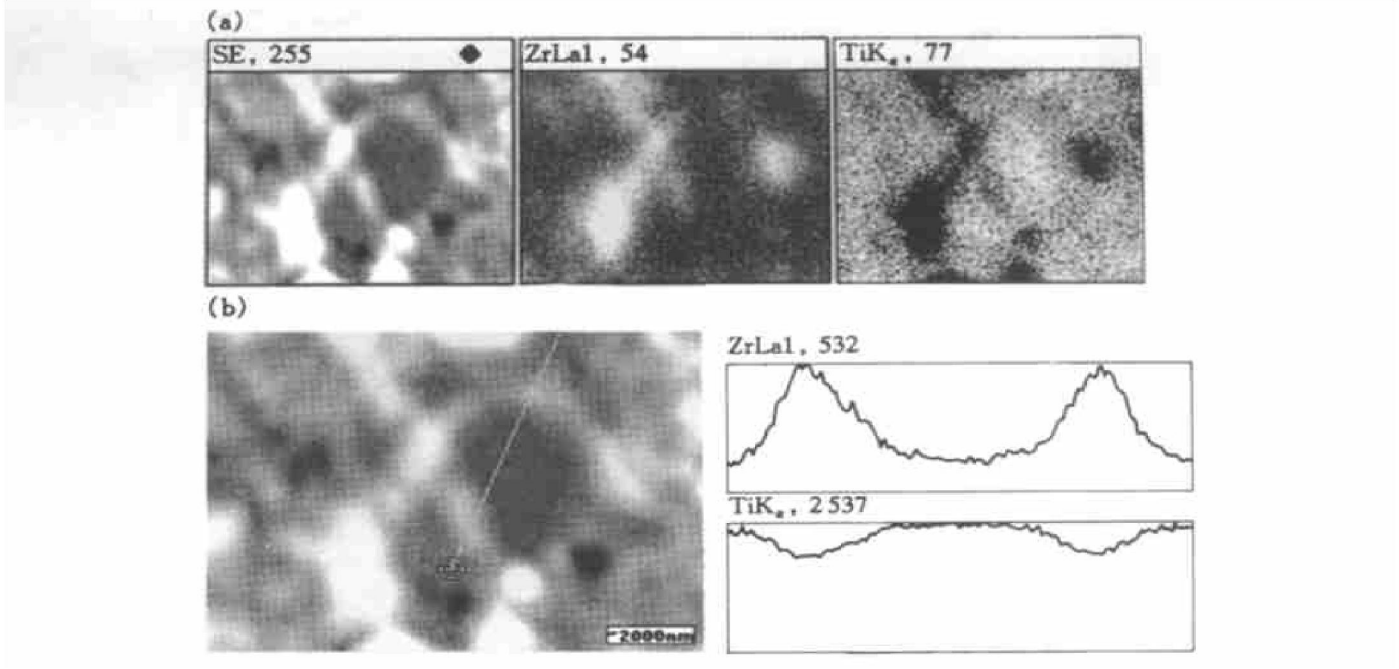

Fig. 3 Results of EPMA analysis for TiB_2-8% ZrB_2(mole fraction)
(a) —SE image and element surface distribution; (b) —Line analysis for TiB_2 grain wrapped by solid solution

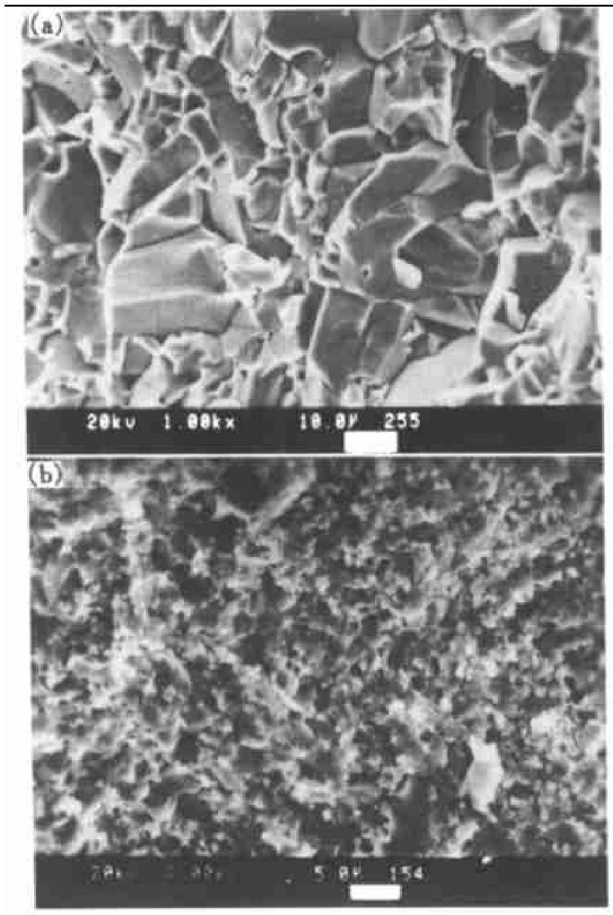

Fig. 4 SEM images of pure TiB_2 and TiB_2-8% ZrB_2(mole fraction) hot pressed at 2 073 K, 30 MPa for 60 min
(a) —Pure TiB_2(× 1000); (b) —TiB_2-8% ZrB_2

obvious that some grains must shrink and disappear. An equivalent way of looking at grain growth is the rate of disappearance of grains. The energy of the driving force of the process in the fine-grained material and the large-grain-size product resulting from the decrease in grain-boundary area and the total boundary energy is different. The immigration of grain boundary and decrease of boundary curvature lead to the growth of fine grains. Thus, the speed of grain growth can be revealed by the rate at which the boundary moves. However, there is a space-charge atmosphere of lattice defects associated with the boundary and solute segregation in actual structure of a ceramic grain boundary. The effect of these lattice defects and impurity atmosphere is to sharply reduce the moving velocity of grain boundary at low driving forces. The influence of this atmosphere becomes stronger as the grain size increases, the solute segregate concentration increases and the average boundary curvature decreases[17]. As shown in Fig. 3(b), the additive reacts with TiB_2 grains to form solid solution at the interface of two phases in ZrB_2 doped TiB_2 system. This reaction leads to the replacement of some Ti^{2+} by Zr^{2+} at interface. Since the moving velocity of grain boundary is greatly decreased by solid solving reaction, the grain growth of composites can be inhibited.

The results of TEM for TiB_2-8% ZrB_2 (mole fraction) are shown in Fig. 5. There are some big grains with irregular shape from the observation of TEM image. The energy dispersive analysis indicates that the composition of big grains contains a great deal of Zr, a little of Ti and free of Fe, Co, W. The result of selected area diffraction reveals that the big grain Zr-rich boride crystal solving with some titanium ionic. According to above measurement, it can be

considered that TiB_2-ZrB_2 ceramic is a kind of solid solution composites consisted of Ti-rich boride solving with some zirconium ionic and Zr-rich boride solving with some titanium ionic. The energy dispersive analysis at triangle grain boundary finds that its main composition is Ti, W, Fe, Co. The emergence of W, Fe, Co comes from the ball milling process for TiB_2. Since there does not produce low valence metallic boride during the solid solving between TiB_2 and ZrB_2, the low valence zirconium boride is not existed at the interface of TiB_2.

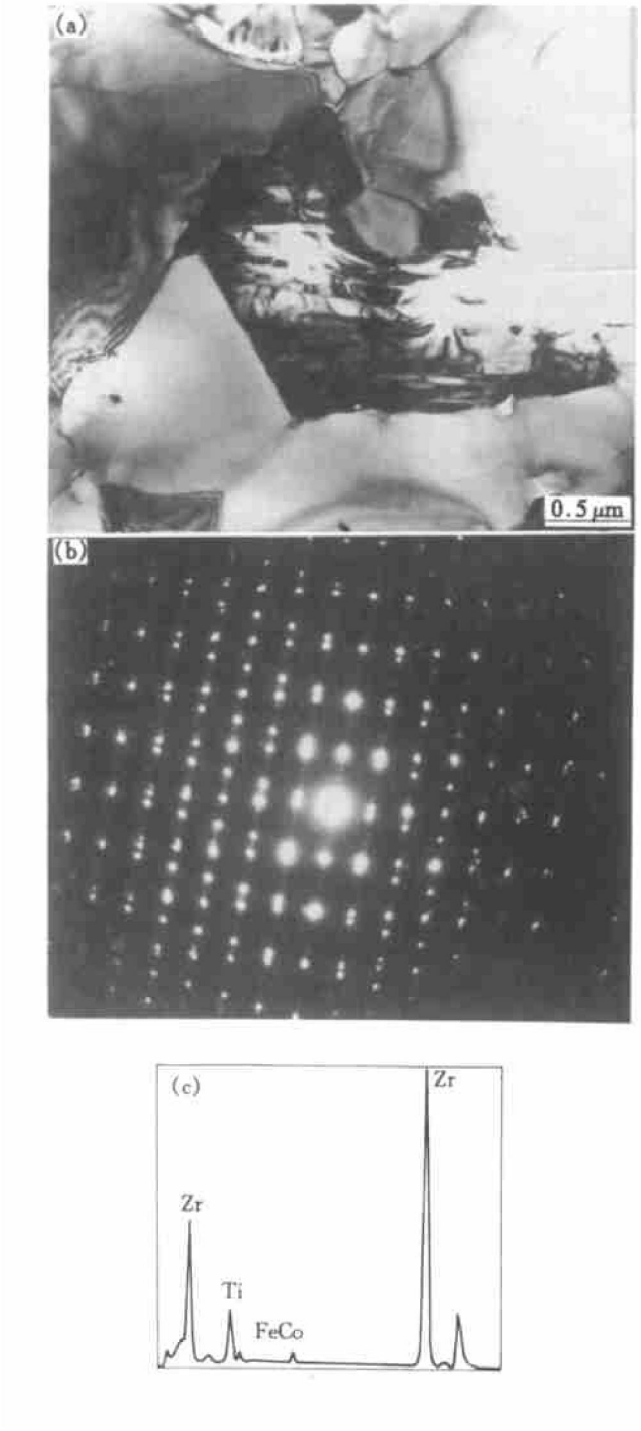

Fig. 5 Irregular grain in TiB_2-8% ZrB_2(mole fraction)
(a) —Morphology (22 000×);
(b) —SADP; (c) —EDAX

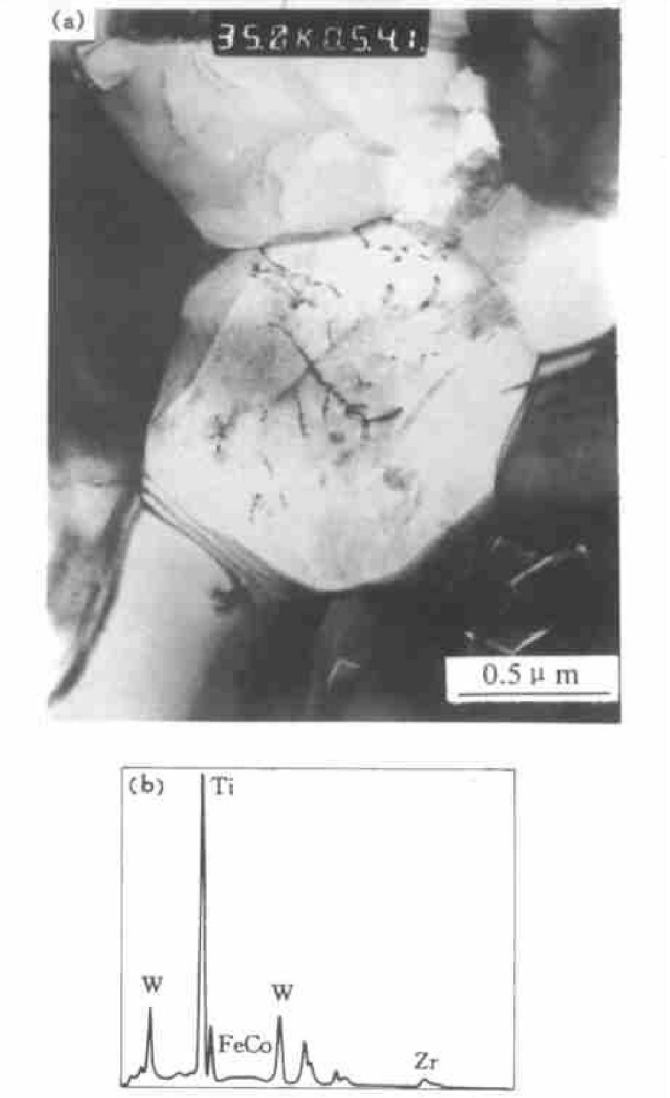

Fig. 6 Crystal morphology and grain boundary of TiB_2-8% ZrB_2(mole fraction)
(a) —Morphology; (b) —EDAX for grain boundary

4 CONCLUSIONS

1) The addition of ZrB_2 in hot pressed TiB_2 ceramics can effectively enhance their sintering performance and greatly improve the hardness and fracture toughness of the composites. The hardness and fracture toughness of TiB_2-8% ZrB_2(mole fraction) can gain 94.75 HRA and 7.63 $MPa \cdot m^{1/2}$, respectively.

2) The microstructure analysis of TiB_2-ZrB_2 composites shows that the mutual solid solving interfaces are formed by the diffusion of TiB_2 and ZrB_2. The solid reaction between TiB_2 and ZrB_2 leads to increase of some solute segregation on their interface, which is beneficial to sharp declining the moving velocity of grain boundary and forming fine-grained composites during sintering.

3) According to the measurement of phase composition and microstructure, it can be considered that TiB_2-ZrB_2 ceramic is a kind of solid solution compos-

ites consisted of Ti-rich boride solving with some zirconium ionic and Zr-rich boride solving with some titanium ionic.

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