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Fabrication and mechanical properties of porous TiB_2 ceramic

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Abstract Porous material of TiB_2 with improved mechanical properties was fabricated by vacuum and pressureless sintering. The microstructure of the porous ceramic was characterized by the enhanced neck growth between the initially touching particles. This neck growth was ascribed to the selective heating of TiB_2 particles with different dimension. The porous structure prepared by the high-temperature sintering exhibited higher bending strength and fracture toughness in the present experiment. The improved mechanical properties of the sintered composites were attributable to the enhanced neck growth by surface diffusion.

Introduction

Porous materials are of significant interest due to their wide applications in filters, catalysis, separation, as well as lightweight structural components and thermal structural materials [1]. To satisfy different requirements for porous materials. Some new processing techniques were developed recently such as pulse electric current sintering, freeze-dry processing, and hydroxide decomposition methods [2–4].

The mechanical properties of porous ceramics are determined by their structure parameters, such as porosity, pore size and pore structure. Additionally, the microstructure of the solid phase related to neck growth and solid phase continuity strongly affects the mechanical properties [5, 6]. Several important issues [7, 8] regarding the neck growth between touching particles by surface diffusion and volume diffusion can significantly increase the mechanical properties with minimal increase in density. The microstructure in porous ceramics can be controlled not only by adjusting the particle size and shape of the initial powders, but also by the sintering process [9].

To date, porous ceramic, such as Al_2O_3, SiC, ZrO_2 and hydroxyapatite with porous structures, have been successfully fabricated [10–13]. Unfortunately, reports on the processing and mechanical properties of boride are very limited. Here, we report a beneficial use of the selective technical phenomenon to fabricate the porous TiB_2 with enhanced neck growth particles, which leads to improved mechanical properties.

Experimental procedure

The main experimental material is TiB_2 powder (mean particle size of 2 μm; Northwest Institute for Non-Ferrous Metal Research, Xi'an, China) and the chemical composition of TiB_2 is shown in Table 1.

In order to reduce the agglomerated TiB_2 powder to single particles, TiB_2 starting powder was milled by the wet-milling method for 4 h in a plastic bottle with agate balls and acetone as media. The resultant slurry was dried in vacuum evaporator. The dried powder was screened through 80-mesh screen. After that, the powder was

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Table 1 Chemical composition of TiB_2 starting powder material

Experimental material	Content of boride	Main impurity
TiB_2	>97.5%	O(0.92%), N(0.07%),Mg(0.09%)

pre-pressed in the cylindrical type mold with the L/D ratio of 1:2 and 30 mm diameter under a uniaxial pressure of 20 MPa. Then they were compacted by a cold isostatic press (CIP) machine at room temperature. The CIP pressures were 10 and 50 MPa and they were maintained for 200 s. The specimens were sintered for1 h at temperature range from 1800 to 2000 °C.

The sintering was performed in a vacuum chamber. The microstructure of porous material was studied by scanning electron microscopy (SEM). Flexural strengths were measured with three-point bending tests (sample size = $3 \times 4 \times 36$ mm^3 and span = 20 mm) at a crosshead speed of 0.5 mm/min. Fracture toughness was evaluated using single-edge notched bend (SENB) beams ($2 \times 4 \times 22$ mm^3, notch depth and radius of 2 and 0.2 mm, respectively) with a span of 16 mm and a crosshead speed of 0.05 mm/min. The density was measured by Archimedes' water-immersion method. Three samples were measured for each data point in present experiment.

Results and discussion

Microstructure characteristics

The green-compact billets were sintered in a furnace, in a vacuum atmosphere, at a heating rate of 10 °C/min. All specimens were held at the sintering temperature for 30 min and then cooled to room temperature at the same rate of 10 °C/min. Different sintering temperatures in a range of 1800–2000 °C were used in present experiment to produce specimens of different porosities. The pressures of 10 and 50 MPa formed compacts with relative densities of 32% and 58% (determined by the measurements of external geometry), respectively, referred to as T32 and T58 hereafter.

Figure 1 shows the microstructures of porous TiB_2 specimens sintered from different compacts at a temperature of 1850 °C. Because of the low sintering temperature, the original morphology of TiB_2 grains produced by the compaction can be clearly seen. A number of voids and small flaws existed in the specimen, due to a loose connection between the TiB_2 grains. However, these voids and small flaws were reduced greatly with the increasing temperature, indicating a better connection between the TiB_2 grains. The weak interface strength in porous TiB_2 ceramic sintered from T32 compacts originated from TiB_2 grains and their poor connections (Fig. 1a). Because of the progress of densification and grain growth, highly packed regions densified faster than the less-dense regions, as shown in Fig. 2a and b, where the ceramic grains clearly have grown in neck area but the connections between the particles are still the porous structures.

TiB_2 grains and their connections affect the microstructure uniformity of sintered porous TiB_2 ceramics, especially for the specimens with low porosity, as shown in Fig. 1. The loose connections between the TiB_2 grains in T32 compact led to a nonuniform microstructure, and a number of small flaws existed in the sintered porous body (arrows in Fig. 1a). However, the microstructure of the specimen sintered from T58 compact is more uniform relative to that from T32 compact.

Since TiB_2 belongs to the covalently bonded solids, the intrinsic diffusivity is very low and, therefore, the Peierl's stress is high for the movement of dislocation. According to the literature [14, 15], the dominant sintering mechanism for TiB_2 is surface diffusion and subsidiary volume diffusion at such an experimental sintering condition. The surface diffusion does not result in shrinkage but in the formation of solid bonds between adjacent particles. With the temperature increases, the enhanced surface diffusion was enhanced and bridges between particles were well developed (arrows in Fig. 2b), suggesting the diffusion is sufficient and effective at elevated temperature. The temperature at 2000 °C, however, promoted neck formation between particles by diffusion, giving rise to the microstructure.

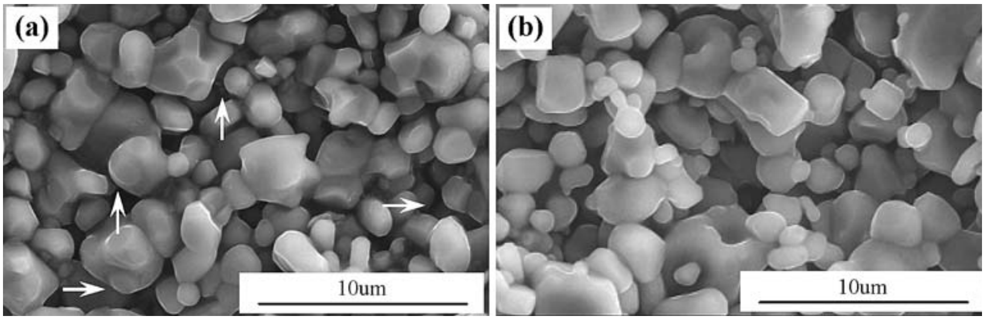

Fig. 1 SEM micrographs of initial TiB_2 specimens from (**a**) T32 compact (porosity 32.5%) and (**b**) T58 compact (porosity 28.4%) at 1850 °C/1 h

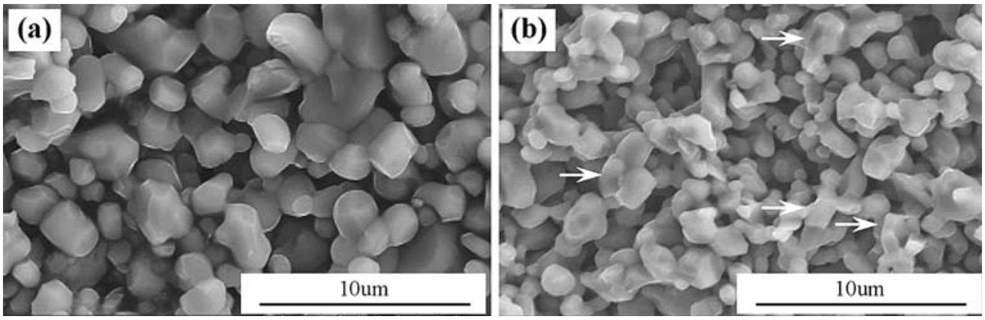

Fig. 2 SEM micrographs of TiB_2 specimens sintered from (**a**) T32 compact (porosity 30.2%) at 1900 °C/1h and (**b**) T58 compact (porosity 15.8%) at 2000 °/1 h

Mechanical properties and mechanisms

Table 2 shows the variation of relative density of porous TiB_2 ceramic before and after sintering in different sintering conditions, which shows that the density increases with the rise of sintering temperature. Figure 3 shows the dependence of relative density on sintering temperature of TiB_2 porous network. Because of the lower density of T32 green compacts, the T32 billets required a higher temperature to reach the same density as that of the T58 billets.

Figures 4 and 5 show the dependence of bending strength and fracture toughness on the relative density of porous TiB_2 ceramic sintered from the compacts prepared by different pressures. In general, the mechanical properties of porous TiB_2 followed the expected trend; that is, fracture strength and toughness increased with increasing relative density. However, bending strength and fracture toughness of porous TiB_2 sintered from T58 compact were higher those from the T32 compact. The difference in strength and toughness between the specimens sintered from two different compacts was small when the relative density of porous TiB_2 was $<60\%$, but this difference became more apparent as the relative density greater higher than 70%. This indicated that high compaction pressures improve the mechanical properties of porous TiB_2 ceramics.

As shown in Fig. 4, the strength of T32 and T58 samples having 20% porosity retain high strength of 200 and 180 MPa, respectively. The high strength must be related to the growth of the interparticle contacts (neck growth) by surface diffusion. At the initial stage of densification, the surface diffusion is small and the difference in boundary defects for different compacts is small; the resultant interface bonding and mechanical properties of porous TiB_2 display limited differences between the two compacts. As densification progresses, the sintering shrinkage increases and the difference in boundary defects and the resultant interface bonding increases.

Table 2 Variation of relative density before and after sintering at different temperature

Sample	Sintering conditions	Compacted relative density, (TD%)	Sintered relative density, (TD%)
T32	1800 °C, 1 h	32.4	72.5 (3 samples)
T32	1900 °C, 1 h	32.5	75.6 (3 samples)
T58	1950 °C, 1 h	58.6	82.4 (3 samples)
T58	2000 °C, 1 h	58.8	86.8 (3 samples)

Generally, high mechanical strength is desirable simultaneously with high porosity for almost all applications of porous ceramics. The relationship between strength and porosity have been investigated by many researchers, and a number of models have been proposed to explain the strength-porosity behaviors. Based on the assumption that the fracture strength of porous ceramics is determined by the minimum solid area, one of the simplest expressions was given by Rice as follows:

$$\sigma = \sigma_0 \exp(-bP) \tag{1}$$

where σ is the strength of a nonporous structure, σ the strength of the porous structure at a porosity P. This expression indicates that strength will increase with decreasing of porosity, this agrees with our results.

Fracture toughness is a property that materials resist to the propagating of cracks. For a porous ceramic material, when a crack meets an open pore in a porous ceramic

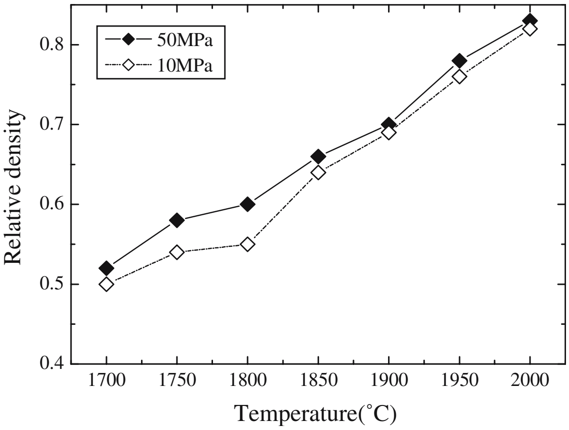

Fig. 3 Dependence of relative density on sintering temperature of TiB_2 porous network

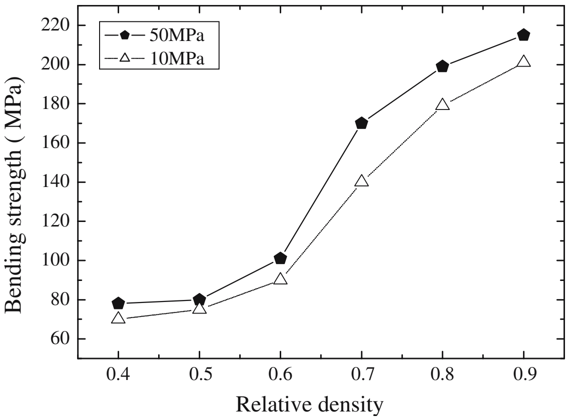

Fig. 4 Dependence of bending strength on relative density of TiB_2 porous network

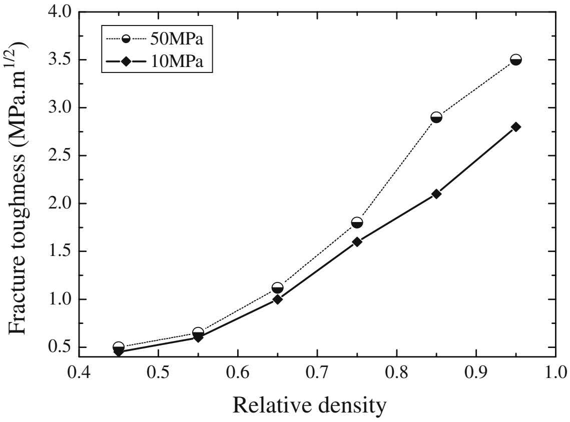

Fig. 5 Dependence of fracture toughness on relative density of TiB_2 porous network

material, the crack tip becomes blunt. This decreases the stress-concentration at the crack tip and increases the external load to propagate the crack such that the fracture toughness increases [16], which is indicated that the crack-tip blunting obviously increases the fracture toughness of porous ceramics and that the larger the pore size at the crack front, the higher the fracture toughness of porous ceramics.

The relationship between fracture toughness and relative density is shown in Fig. 5, the fracture toughness of T32 and T58 samples having 15% porosity retain high fracture toughness of 2.0 and 3.0 MPa m$^{1/2}$ approximately. As above discussed (shown in Fig. 3), the T32 billets required a higher temperature to reach the same density as that of the T58 billets, therefore higher temperature and connected particles with higher density can both enhanced the neck growth and grain-boundary strength which contributes to the increase of fracture toughness.

Mechanical properties of dense ceramics fabricated by granule powders have been investigated by several researchers [15, 17]. It was found that fracture strength and fracture toughness were different for different granules and processing conditions. Granule-related large surface defects are the controlling mechanisms for the mechanical properties of dense ceramic materials. However, the situation is different for porous materials. Recent studies [18] showed the size of artificially introduced surface defects has only a negligible influence on the strength of porous ceramics provided the defect size remains large compared with the microstructural features. In fact, the neck growth, interface bonding and connected network distribution might play a important role on mechanical properties of porous ceramics.

At the initial stage of densification, the sintering shrinkage is small and the difference in boundary defects for different compacts is small; the resultant interface bonding and mechanical properties of porous TiB_2 display limited differences between the T32 and T58 compacts (Fig. 1). As densification progresses, the sintering shrinkage increases and the difference propresses, the sintering shrinkage increases and the difference in boundary defects and the resultant interface bonding increases (Fig. 2). Therefore, mechanical property differences increase with increasing relative density.

Conclusions

Effect of compaction pressure on microstructure and mechanical properties on sintered porous TiB_2 ceramics were investigated. The microstructure of the compacts prepared at lower pressures appeared to degrade the interface bonding strength of the TiB_2 grain boundaries. The strength and toughness of porous TiB_2 sintered from the compacts prepared at 10 MPa were substantially lower than those compacted at 50 MPa. The high mechanical properties are related to the growth of the neck growth by surface diffusion in high temperature.

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