Materials Chemistry and Physics 200 (2017) 217–222

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Microstructure and mechanical properties of textured TiB_2 ceramic fabricated by combination of catalyst and hot–forging

Xin Liu [a], Jiahua Pei [a], Minjing Liu [a, *], Zhi Wang [b, **], Lixin Liu [b], Li Jing [c], Zhanjun Wu [a]

[a] School of Aeronautics and Astronautics, Faculty of Vehicle Engineering and Mechanics, State Key Laboratory of Structural Analysis for Industrial Equipment, Dalian University of Technology, Dalian, 116024, PR China

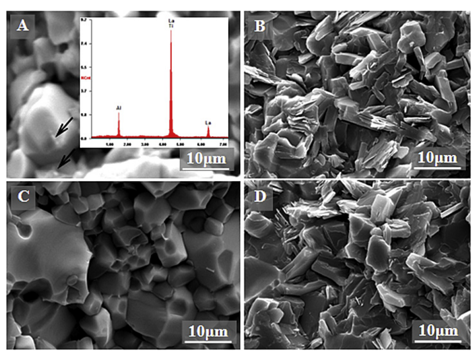
[b] Beijing Institute of Astronautical Systems Engineering, Beijing, 100076, PR China

[c] Science and Technology on Space Physics Laboratory, Beijing, 100076, PR China

HIGHLIGHTS

- It is to report textured TiB_2 ceramic fabricated using combination of catalyst and hot–forging.
- The flexural strength of the textured TiB_2 ceramic was improved obviously.
- The fracture toughness of the textured TiB_2 ceramic was improved significantly.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 6 November 2015
Received in revised form
6 July 2017
Accepted 10 July 2017
Available online 24 July 2017

Keywords:
Composite materials
Sintering
Mechanical testing

ABSTRACT

In the present work, the powder mixtures of TiB_2 containing 2.0mol.% carbon black with trace La_2O_3 and Al_2O_3 are used to fabricate textured TiB_2 ceramic using hot–pressing at 1800 °C, and then the TiB_2 ceramic is hot–forged. The results of microstructural observation indicated that the addition of the powder mixtures of Al_2O_3 and La_2O_3 was favorable to the rearrangement of the anisotropic TiB_2 grains, whereas was unfavorable to the improvement of the relative density during hot–pressing and hot–forging. The flexural strength and the fracture toughness of textured TiB_2 ceramic fabricated using the combination of oxides and hot–forging were improved significantly, whereas hardness did not show obvious change. The results here pointed to a novel method for fabricating textured TiB_2–based ceramics.

1. Introduction

Among the compounds of diborides, titanium diboride (TiB_2) has potential for a wide range of technological applications including electrodes for charge machining, cutting tools, wear–resistant parts, armor equipment and so on due to its attractive properties like high melting point, superior thermal and electrical conductivities, high elastic modulus, high hardness and good corrosion resistance [1–6]. Despite possessing useful properties, the engineering applications of monolithic TiB_2 are rather limited because of poor sinterability due

* Corresponding author.
** Corresponding author.
E-mail addresses: liumj@dlut.edu.cn (M. Liu), wangzhi1780@126.com (Z. Wang).

http://dx.doi.org/10.1016/j.matchemphys.2017.07.033

to the unavoidable presence of surface oxides, such as B_2O_3 and TiO_2 that constitutes an additional factor which hinders the densification of the TiB_2–based ceramics [1,3,7]. In particular, B_2O_3 enhances grain growth and inhibits densification by promoting coarsening at temperatures below 1800 °C [8]. At present, most research is focused on the composition design by selecting different additives to improve the sinterability. The literature [8] have confirmed that the presence of either boron carbide or carbon improved densification and reduced the temperature necessary to reach full density to 1750 °C and 1850 °C, respectively. In addition, in 1997, A. J. Gant et al. have proposed a novel method to fabricate dense ceramic matrix composites based on a supersolidus liquid phase mechanism with diffusion controlled solution reprecipitation as the predominant sintering mechanism [9–11]. Although these dense TiB_2–based ceramics have many advantages, their intrinsic characteristics such as low fracture toughness (premature failure due to brittle fracture) and low toughness–induced poor thermal shock resistance are still obstacles for their being used widely, especially for applications in severe environments [8]. For improving resistance to brittle fracture of the TiB_2–based ceramics, layered configurations have been studied as a structural option for improving the mechanical behavior and reliability of ceramics, and many of these studies draw inspiration from R. Bermejo [12,13], whose work is noted for both its high quality and enormous quantity. In order to improve anisotropy of properties, the fabrication of textured ceramics with grains of highly oriented microstructures such as hexagonal Si_3N_4 and BN is another effective method to obtain good combination of properties, such as good fracture toughness and thermal shock resistance because layered materials show significant anisotropy of properties [12–14] and many of these studies draw inspiration from O. Zgalat–Lozynskyy [15–17], whose work is noted for first sinterforging under SPS and texturing under this process. The templated grain growth [18], hot–forging [19] and strong magnetic field alignment [20] are frequently used to fabricate textured ceramics. Like these textured Si_3N_4 and BN ceramics with hexagonal grains, the anisotropic grain growth of TiB_2 with hexagonal *P*6/*mmm* AlB_2 may occur during sintering. Up to now, however, there have been only a few reports on the anisotropic growth of TiB_2–based structural ceramics, and even fewer reports focusing on the ability of microstructure tailoring to produce textured structures of TiB_2–based ceramics.

In the present work, the powder mixtures of TiB_2 plus 2.0mol.% carbon black with trace La_2O_3 and Al_2O_3 are used to fabricate textured TiB_2 ceramic by hot–pressing at 1800 °C, and then the TiB_2 ceramic is hot–forged. The purpose of this paper is to report on the novel fabrication method and initial investigation of textured TiB_2 ceramic. Furthermore, the formation mechanism and mechanical properties of textured TiB_2 ceramic is discussed in detail.

2. Experimental procedure

Commercially available TiB_2 with a mean size of about 3 μm and carbon black with a mean size of about 20 nm were purchased from Alfa Aesar Co., Ltd., USA. Their reported purity was more than 99.0% and The content of oxygen element in the raw TiB_2 powder is 0.08 at %. The additives Al_2O_3 with an average size of 0.5 μm (Aladdin ShangHai, China, purity 99.95%) and La_2O_3 with an average size of 0.5 μm (Aladdin ShangHai, China, purity 99.90%) were used as raw materials and the molar ratio of Al_2O_3 to La_2O_3 was 1:1 [21]. The SEM pictures of TiB_2 (A), La_2O_3 (B) and Al_2O_3 powders are shown in Fig. 1. The powder mixture of TiB_2 plus 2.0mol.% carbon black plus 0.2mol.% oxides (it is labeled as TiB_2 with oxides) was ball mixed for 8 h in a polyethylene bottle using TiO_2 balls and ethanol as the grinding media. After mixing, the slurry was dried in a rotary evaporator and screened. The resulting powder mixtures were hot–pressed by resistance heating in argon flow with a heating rate of 15 °C/min up to 1500 °C and applied a uniaxial load of 30 MPa, and then hot–pressed with a heating rate of 10 °C/min up to 1800 °C and soaked at 1800 °C for 60min, finally cooled down naturally. The hot–forging procedure is as follows: the hot–pressed specimen was heated by resistance heating with a heating rate of 15 °C/min up to 1500 °C and then heating with a heating rate of 10 °C/min up to 1800 °C and soaked at 1800 °C for 60min in argon flow. When the temperature of furnace reached 1800 °C, the pressure cycle is adopted: after the pressure was applied and rose to 40 MPa and held for 2 min, the pressure is unloaded and then the pressure was again loaded. In order to investigate the effect of the mixture of Al_2O_3 and La_2O_3 and the hot–forging on textured structures, the powder mixture of TiB_2–2.0mol.%carbon black without mixtures of Al_2O_3 and La_2O_3 (it is labeled as TiB_2 without oxides) was hot–pressed, and the hot–pressing and hot–forging procedures are the same as described above. Flexural strength of the samples before and after the water quenching was tested in three–point bending on 3 mm by 4 mm by 36 mm bars, using a 30 mm span and a crosshead speed of 0.5 mm min^{-1}. Each specimen was ground and polished with diamond slurries down to a 1 μm finish. The edges of all the specimens were chamfered to minimize the effect of stress concentration due to machining flaws. Fracture toughness (K_{IC}) was determined by a single–edge notched beam test with a 16 mm span and a crosshead speed of 0.05 mm min^{-1} using 2 mm by 4 mm by 22 mm test bars, on the same jig used for the flexural strength. All specimens were machined with the tensile surface parallel to the hot-pressing direction and at least six specimens were tested for each experimental condition and all specimens were from same billet. Hardness (Hv 1.0) was measured by Vickers' indentation with a 9.8 N load applied for 15 s on polished sections. Twenty measurements were made at different locations of each pellet. The microstructural features of the specimen were observed by scanning electron microscopy (SEM, FEI Sirion, Holland). The phase composition was determined by X–ray diffraction (XRD; Rigaku, Dmax–rb, CuKα = 1.5418 Å). The bulk density of the specimens was measured by the Archimedes method.

3. Results and discussion

Fig. 2A shows the micrograph of polished surface of the hot–-pressed TiB_2 ceramic with oxides. The obvious holes are observed in the polished surface and the relative density of the hot–pressed TiB_2 with oxides was determined to be 92.3% by dividing the bulk density by the theoretical density, as listed in Table 1. In general, the relative density of TiB_2 ceramic was about 80% after TiB_2 powder was sintered at 1800 °C in other works. In the present work, the relative density of the hot–pressed TiB_2 ceramic with oxides was 92.3% due to the addition of carbon black [7]. Grain coarsening in nonoxides ceramics, including diborides, is promoted by oxygen present as oxide impurities on the particle surfaces [7]. It was recognized that the main impurities on the surface of TiB_2 particles were TiO_2 and B_2O_3. In addition, the impurity TiO_2 was inevitably introduced into powder mixtures during ball milling [7,8]. At elevated temperature, the carbon black reacted with TiO_2 and B_2O_3 by the classic carbothermal reduction reaction, which was used to synthesize TiB_2 commercially:

$$TiO_2 + B_2O_3(l) + 5C = TiB_2 + 5CO(g)\ \Delta G = -1231.4\ \text{kJ/mol}\ (1800\ ^\circ\text{C},\ 5\text{Pa}) \quad (1)$$

In the present work, a high vacuum (pressure of 5 Pa) was maintained during hot–pressing. CO gas was readily removed by the vacuum, which was thermodynamically favorable to reaction (1). TiO_2 and B_2O_3 on the surface of TiB_2 were converted to very fine TiB_2 particles and CO gas. The elevated temperature resulted in the evaporation of B_2O_3 liquid at 1450 °C under high vacuum [7,8],