Materials Science & Engineering A 607 (2014) 38–43

Contents lists available at ScienceDirect

Materials Science & Engineering A

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

Anisotropic mechanical properties and fracture mechanisms of textured h-BN composite ceramics

Xiaoming Duan*, Meirong Wang, Dechang Jia, Nan Jing, Zhiliang Wu, Zhihua Yang, Zhuo Tian, Shengjin Wang, Peigang He, Yujin Wang, Yu Zhou

Institute for Advanced Ceramics, Harbin Institute of Technology, P.O. Box 433, Harbin 150001, China

ARTICLE INFO

Article history:
Received 20 January 2014
Received in revised form
16 March 2014
Accepted 30 March 2014
Available online 5 April 2014

Keywords:
Hexagonal boron nitride
Texture
Anisotropy
Mechanical properties
Fracture mechanisms

ABSTRACT

The hexagonal boron nitride (h-BN) grain shows typical lamellar structures, so textured materials can be achieved by arranging h-BN grains along the same direction. In this work, textured h-BN composite ceramics with the *c*-axis orientation arranged along pressure direction were manufactured by hot-press sintering using mullite as the sintering additive. The results show that sintering pressure is an important factor that affects not only the density and the textured degrees of composite ceramics, but also the mechanical properties. Based on the textured microstructure features, the composite ceramics show the obviously anisotropically characterized mechanical properties, such as elastic modulus, flexural strength and fracture toughness, together with various fracture mechanisms.

1. Introduction

The hexagonal boron nitride (h-BN) has a lamellar structure which is similar to that of graphite. B and N atoms in the layer are combined with strong covalent bonding, while the layers are bonded by weak Van der Waals forces, which allow the layers to slide against each other easily. The special crystal structure and bonding characteristics bring h-BN unique performances, such as comparative chemical and thermal inertness, excellent electrical insulation properties and good manufacturability [1–10].

Materials with textured microstructures have obvious anisotropic properties, and may achieve better properties beyond the isotropic homogeneous materials. So this kind of material has played an important role in various application fields [11–14]. Theoretically, the textured h-BN ceramic can be formed due to the lamellar structure of h-BN grain. Once the *c*-axis of h-BN grains can be arranged along the same direction, textured h-BN bulk ceramic with laminated microstructures can be fabricated. Then its mechanical property, thermal property, and electrical property will be anisotropic, which offers a unique opportunity to optimize the performance of materials [15–20]. But in practice, there are several problems which must be resolved. Firstly, the grain shape of h-BN should be controlled. Only the ideal crystal state h-BN grains with high aspect ratio sheet geometry are the candidate materials that can be aligned to form textured structures. Secondly, the preparation methods of making grains preferential alignment must be chosen carefully, and the effect mechanisms should be discovered. Finally, h-BN ceramic is hard to sintering because of both its valance bonds combination and microstructure characteristics. Based on the above reasons, the sintering procedures should be widely investigated to make more desirable materials.

In this work, we used the hot-press sintering method to manufacture textured h-BN composite ceramics, and effects of sintering pressures on the texture degrees, and their mechanical properties were investigated. Furthermore, mullite was used as the sintering additive to glue and constrain h-BN grains, which benefited the sintering. Meanwhile, texture characteristics were investigated, along with mechanical properties along different loading directions. Finally, the fracture surfaces were observed by SEM to explore the fracture mechanisms.

2. Materials and methods

The raw materials are h-BN powders (15 μm in diameter and 0.3 μm in thickness, purity > 99%) and mullite powders (average particle size is 3.2 μm, purity > 98%), and mass ratio of h-BN to mullite is 8:2. The powders were mixed with α-Al_2O_3 balls for 24 h with ethanol as milling medium and then dried. Finally, the as-dried powder mixtures were put into graphite die and hot-press sintered at 1900 °C for 60 min in 1 atm N_2 atmosphere. Different

* Corresponding author. Tel.: +86 451 86418792; fax: +86 451 86414291.
E-mail address: dxmhit@126.com (X. Duan).

http://dx.doi.org/10.1016/j.msea.2014.03.132
0921-5093/

sintering pressures were applied, i.e., 10 MPa, 20 MPa and 30 MPa, and the corresponding samples were denoted as h-BN10, h-BN20 and h-BN30, respectively.

The densities of composite ceramics were calculated by the results of mass divided by volume using rules shape samples. The crystallographic orientation and phase compositions were evaluated by XRD (Rigaku Co., Tokyo, Japan, Cu Ka radiation) on both top surface and side surface of the sintered samples with a scanning rate of 4°/min. Anisotropy mechanical properties including elastic modulus, flexural strength and fracture toughness were measured along three different directions. Flexural strength was measured on bar specimens with dimensions of 3 mm × 4 mm × 36 mm using a three-point bend fixture with a span of 30 mm and a cross-head speed of 0.5 mm/min. Fracture toughness measurement was performed on single-edge-notched beams (2 mm × 4 mm × 20 mm) with a span of 16 mm at a cross-head speed of 0.05 mm/min, and a half-thickness notch was made using a 0.1 mm thick diamond wafer blade. Microstructures of polished surfaces of sintered ceramics and fracture surfaces were observed by scanning electron microscopy (SEM, FEI Sirion) after being sprayed with a gold film.

3. Results and discussions

3.1. Phase compositions and texture characteristics

In order to facilitate distinction, the sample surfaces parallel (//) and perpendicular (⊥) to h-BN layers' arrangement direction are denoted as // direction and ⊥ direction, respectively. Fig. 1 (a) shows the XRD patterns along two different directions of the samples sintered under different pressures. The relative intensities of mullite peaks are relatively low because of two reasons: one is the relative contents of mullite in the composites is low, and another reason is the degree of crystallization of mullite grains is also lower than that of h-BN grains, leading to a relatively low diffraction intensity. Hence, the peaks of h-BN are displayed obviously, while the peaks of mullite are not displayed clearly.

The diffraction intensities of (002) plane of h-BN phase on the // direction are much higher than that of (100) plane on // direction. However, the diffraction intensities of (002) plane on the ⊥ direction are lower than that of (100) plane on ⊥ direction. The results show that the hot-press sintered h-BN composite ceramics have significant orientation and the *c*-axis of h-BN grains tend to orientate with the direction parallel to the pressure direction.

Sintering pressure plays an important role in the sintering process, so its effects on texture characteristics of h-BN composite ceramics are considered. The orientation degrees of the textured h-BN composite ceramics can be quantified by the Index of Orientation Preference (IOP) values, which are calculated by the following formula:

$$IOP = \begin{cases} \frac{(I_{100}/I_{002})_{perp}}{(I'_{100}/I'_{002})_{par}}, & \text{when} \quad (I_{100}/I_{002})_{perp} > (I'_{100}/I'_{002})_{par} \\ -\frac{(I'_{100}/I'_{002})_{par}}{(I_{100}/I_{002})_{perp}}, & \text{when} \quad (I_{100}/I_{002})_{perp} < (I'_{100}/I'_{002})_{par} \end{cases} \quad (1)$$

where I_{hkl} and I'_{hkl} in the formula are the intensities of corresponding diffraction lines at // direction and ⊥ direction, respectively [17,21]. If IOP $= \pm 1$, the grains are randomly arranged in composites. A value of IOP > 1 means the *c*-axis of h-BN lattice prefers to orient perpendicular to the pressure direction. On the other hand, an IOP < -1 indicates the *c*-axis prefers to orient parallel to the pressure direction. The larger IOP value, the more h-BN grains with the *c*-axis oriented perpendicular to the pressure direction will be formed.

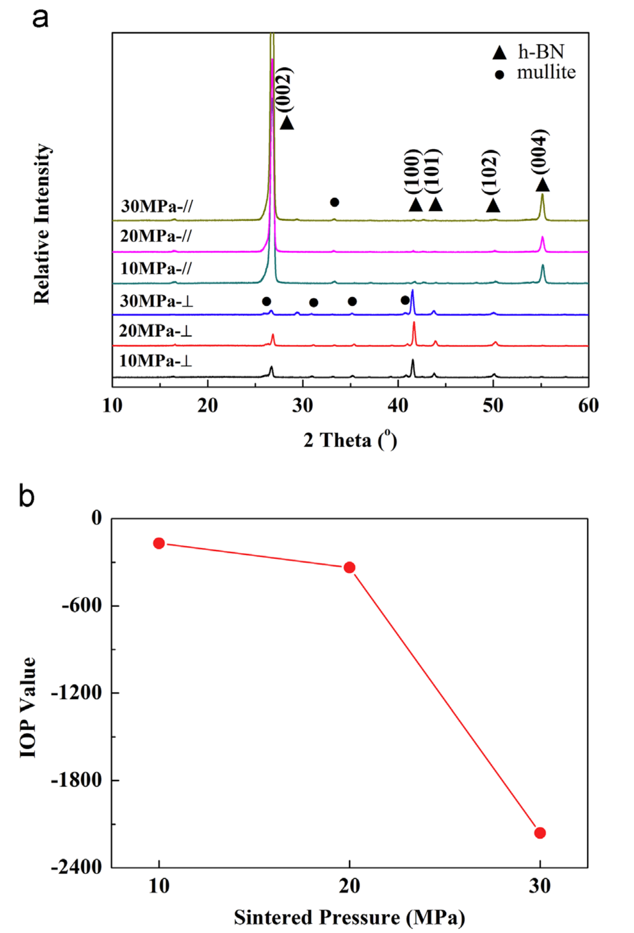

Fig. 1. XRD patterns of sample surfaces parallel (//) and perpendicular (⊥) to h-BN layers' arrangement direction. (a) XRD patterns of hot-press sintered sample with the pressures of 10 MPa, 20 MPa, 30 MPa; (b) the relationship of IOP values and sintered pressures.

The calculated IOP values of textured h-BN composite ceramics with different sintering pressures are shown in Fig. 1(b). All IOP values are less than -1, which means the *c*-axis of the crystal prefers to orient parallel to the pressure direction. The IOP values significantly decrease when the sintering pressures increase from 10 MPa to 30 MPa, implying that the higher sintering pressure can facilitate more h-BN grains' rearrangement and enhance the degrees of preferred orientation.

The densities of textured h-BN composite ceramics sintered under different pressures are measured and shown in Fig. 2. With the increase in sintering pressures from 10 MPa to 30 MPa, the densities of composite ceramics also rise from 2.00 g/cm^3 to 2.17 g/cm^3. Therefore, higher sintering pressure can help to obtain denser materials. Since the h-BN grains are lamellar which tend to overlap each other and form the pores, h-BN composites with high relative density and few pores are difficult to prepare. In our work, the sintering additive is mullite ($3Al_2O_3 \cdot 2SiO_2$), which is one of the most prominent ceramic materials [22–26]. The melting point of mullite is about 1810 °C, which was 90 °C lower than the sintering temperature of composite ceramics of 1900 °C. So the mullite will form in liquid phase which can effectively contribute to grains' rearrangement and diffusion during the sintering process. Under the high temperature environment, higher sintering pressures make the grains tend to be oriented (shown as the XRD results of Fig. 1) which will reduce the occurrence of pores and increase the density. The increasing of sintering pressures can make more mullite fill in the pores, resulting in higher density. Furthermore, high pressures can make the grains combine more closely and help