Microstructural evolution of h-BN matrix composite ceramics with La-Al-Si-O glass phase during hot-pressed sintering

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Abstract

BN/La-Al-Si-O composite ceramics were fabricated by hot-pressed sintering using h-BN, La_2O_3 , Al_2O_3 and amorphous SiO_2 as the raw materials. The effects of sintering temperature on the microstructural evolution, bulk density, apparent porosity, and mechanical properties of h-BN composite ceramics were investigated. The results indicated that La-Al-Si-O liquid phase was formed during sintering process, which provided an environment for the growth of h-BN grains. With increasing sintering temperature, the cristobalite phase precipitation and h-BN grain growth occurred at the same time, which had the significant influence on the densification and mechanical properties of h-BN composite ceramics. The best mechanical properties of BN/La-Al-Si-O composite ceramics were obtained under sintering temperature of 1700 °C, and the elastic modulus, flexural strength, and fracture toughness were 80.5 GPa, 266.4 MPa and $3.25 \text{ MPa}\cdot\text{m}^{1/2}$, respectively.

1. Introduction

Hexagonal Boron Nitride (h-BN) and its matrix composite ceramics are typical structural-functional ceramics that have been widely used in many fields, such as aerospace, machinery, metallurgy, energy, and electronics [1-7]. Compared with Alumina, Zirconia, Silicon Carbide, Silicon Nitride ceramic which have the high hardness and high strength, h-BN presents the relatively low hardness and good machinable properties, because of its hexagonal layered crystal structure similar to that of graphite [8-11]. Furthermore, h-BN ceramics are difficult to sintering densification, so the low melting point sintering additives and/or second phase are usually added to improve the properties of h-BN composite ceramics [12-16].

There have some researches on the microstructural evolution during sintering and the properties of h-BN ceramics [17-21]. Zhuo Zhang et al. obtained h-BN powders composed of amorphous and nanocrystalline BN by ball milling, and then sintered them under different temperatures and pressures. Higher sintering pressure was more favorable to the preferred orientation growth of the in-plane direction of h-BN grains along the pressure direction, and higher sintering temperature promoted the mass transfer and grain growth. They referred that the structural fluctuation of amorphous BN resulted in the t-BN phase formation during the sintering process, and stacking faults usually existed in the as-grown h-BN grains [22].

For h-BN matrix composite ceramics, there also have some research results which can reveal the microstructures changing mechanisms [23-28]. Bo Niu et al. investigated the effects of raw h-BN particle size on the textured microstructures of BN-MAS (magnesium aluminosilicate) composite ceramics. With the increase of raw h-BN particle size, h-BN grains tended to orientate with the direction perpendicular to the hot pressing direction, while the densification effect of MAS phase on BN-MAS composite ceramics decreased with increasing raw h-BN particle size due to the uneven dispersion of MAS phase [26, 29]. Delong Cai et al. researched the influence of sintering process on the BN-MAS composite ceramics. The sintering pressure had a great influence not only on the mechanical properties of composite ceramics, but

also on the crystallization of MAS and structural order of h-BN. The nucleophilic attack of N on M ($M = \text{Mg}^{2+}$, Al^{3+} and Si^{4+}) and the electrophilic attack of B on O were the crucial factors on the formation of amorphous MAS phase. In addition, chemical bonding was formed between h-BN and MAS and the matrix atoms diffused into the h-BN layer, leading to a strong bonding interface [30-32].

La-Al-Si-O glass phase have been reported on promoting sintering densification and improving the room/elevated-temperature mechanical properties of h-BN matrix composite ceramics [33-37]. But the microstructural evolution during sintering process and its effect on properties of this material systems have not been fully revealed yet, which also has important implications for guiding the composition design and process optimization of composite ceramics.

In this study, BN/La-Al-Si-O composite ceramics were sintered under different temperatures from 1500 °C to 1900 °C, meanwhile the phase composition, nanocrystalline precipitation and grain growth were systematically investigated. The corresponding mechanical properties were tested to reveal the influence of microstructural evolution on the performance of composite ceramics.

2. Materials And Methods

2.1. Materials fabrication

Commercial powders of h-BN (99.5 %, 0.3 μm , Advanced Technology & Materials Co. Ltd., China), hexagonal La_2O_3 (99.9 %, 1.0 μm , Wuxi Meifang industry CO. Ltd., China), rhombohedral Al_2O_3 (> 98 %, 1.5 μm , Showa Denko K.K., Yokohama, Japan), and amorphous SiO_2 (99.9 %, 3.5 μm , Lianyungang Guangyu quartz CO. Ltd., China) were used as the raw materials. The volume ratio of h-BN: (La_2O_3 - Al_2O_3): SiO_2 was 70:10:20, the mole ratio of La_2O_3 to Al_2O_3 was 1:2.

The weighed powders were mixed with Al_2O_3 balls and ethanol medium for 12 h. The obtained slurry was dried, and then passed through a 100 mesh sieve. The mixed powders were put into a graphite die and cold-compacted uniaxially under 5 MPa pressure. The obtained green compacts were hot press sintered at different temperatures for 1 h under 20 MPa with N_2 atmosphere to maintain the partial pressure of nitrogen and prevent h-BN decomposition. The heating rate was $15\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ and the samples cooled down to room temperature in the furnace spontaneously. According to the phase diagram of La-Al-Si-O system, liquid phase can be formed at about 1700 °C, therefore, the sintering temperatures from 1500 °C to 1900 °C were chosen in this research.

2.2. Materials characterization

Phase compositions were identified by X-ray diffractometer (XRD, D/max- γB CuK α , Rigaku Co., Japan) with a scanning speed of $4\text{ }^\circ\cdot\text{min}^{-1}$. The detailed microstructures were investigated by transmission electron microscope (TEM, Talos F200X, FEI Co., USA), and the concentration of elements was detected by SEM equipped with EDS (EDAX Inc., Mahwah, NJ) detector. The TEM samples were

firstly cut into the small pieces with the thickness of about 0.2 mm, and then polished to about 0.07 mm by 2000# abrasive paper. Ar Ion etching instrument was used to create thin regions to meet the requirement of TEM observation. The bulk densities and apparent porosities of samples were measured by Archimedes law referring to the China national standard GB/T 25995-2010. Flexural strength was measured by three-point bending method using a universal testing machine (Instron-5569, USA), meanwhile Young's modulus was obtained through the stress-strain curve. The sample size was 3 mm × 4 mm × 36 mm with a span of 30 mm and the crosshead speed was 0.5 mm·min⁻¹, the loading direction was perpendicular to sintering pressure direction. Fracture toughness was measured using the single edge notched beam (SENB) method. The sample size was 2 mm × 4 mm × 20 mm with a notch of 2 mm, and the crosshead speed was 0.05 mm·min⁻¹. Fracture morphology was observed using scanning electron microscope (SEM, NanoLab 600i, FEI Co., USA).

3. Results And Discussion

Fig. 1(a) presents the X-ray diffraction patterns of BN/La-Al-Si-O composite ceramics sintered under different temperatures. There were only obvious diffraction peaks corresponding to h-BN phase (JCPDF 34-0421), whereas the diffraction peaks of La₂O₃, Al₂O₃, SiO₂ and their possible reaction products were not found. Considering the total volume content of the adding La-Al-Si-O was about 30 %, which had exceeded the minimum threshold of XRD detection. Thus, we inferred that the amorphous glass phase was formed during hot-pressed sintering process, which was difficult to be characterized by XRD.

Comparing with the peaks of h-BN in different composite ceramics, with the increase of sintering temperature, the relative peak intensity of corresponding (002) lattice plane increased gradually. Graphitizing Index (GI) is an indicator of crystallization degree of graphite and similar crystalline structure materials [38], and it is calculated by the following formula:

$$GI = \frac{\text{Area}(100) + \text{Area}(101)}{\text{Area}(102)} \quad (1)$$

where Area(100), Area(101) and Area(102) denote the integral intensity of the corresponding (hkl) reflex of h-BN. Theoretically, the GI value of ideal h-BN crystal is about 1.6, and a lower GI value is correspond to better crystallization of h-BN grains.

Fig. 1(b) shows the calculated GI values of h-BN grains in composite ceramics. With the increase of sintering temperature, GI values showed a decreasing trend, which basically conformed to the change rule of exponential function. From 1500 °C to 1700 °C, the GI values decreased rapidly from 13.7 to 3.4, while from 1700 °C to 1900 °C, the GI values decreased slowly from 3.4 to 2.4. Sintering temperature had a significant influence on the crystallization growth of h-BN in composite ceramics. Higher sintering

temperature was conducive to heat and mass transfer in liquid phase environment and the better h-BN grains growth during hot-pressed sintering.

In Fig. 2(a-c), TEM characterization was used to investigate the detail microstructures of BN/La-Al-Si-O composite ceramics hot press sintered under 1500 °C, 1700 °C, 1900 °C, and the corresponding element distributions of B, N, O, Al, Si, La were shown in Fig. 2(d). The h-BN grains showed typical lamellar morphology and were uniformly dispersed in the all composite ceramics. La-Al-Si-O glass phase filled in the space between h-BN grains and had a good combination with h-BN grains, and there were few obvious interfacial cracks. It could be obviously observed that the grain size of h-BN became bigger with increasing sintering temperature, which was because the liquid phase had better heat and mass transfer effect at higher temperature, promoting the growth of h-BN grains.

Some pores were observed in the sample sintered at 1500 °C, this was due to the relatively low fluidity of the liquid phase at this sintering temperature, which could not fully fill the gaps between the h-BN grains. While in the sample sintered at 1900 °C, a small number of pores were also found, this was because the grown h-BN grains overlapped each other to form closed pores, which could not be filled by liquid phase. By contrast, no obvious pores were found in the sample sintered at 1700 °C, indicating this sintering temperature was favorable for obtaining composite ceramics with the high relative density.

Interface microstructures between h-BN grains and La-Al-Si-O phase of composite ceramics sintered under different temperatures are presented in Fig. 3(a-c), and the corresponding elemental line scanning profiles from h-BN zone to La-Al-Si-O zone are shown in Fig. 3(d-f). No defects such as crack could be observed at the phase boundary, indicating a good wettability between La-Al-Si-O glass phase and h-BN grains. The changes of elemental contents were continuous, La, Al, Si and O content of glass phase increased, whereas B and N content of h-BN phase decreased gradually along the arrow direction. Comparing with three samples, when the sintering temperature increased from 1500 °C to 1900 °C, the width of the diffusion zone at the two phases interface increased from about 38 nm to more than 55 nm, indicating higher sintering temperature were more beneficial to the element diffusion in the phase interface region during hot-pressed sintering process. In Fig. 3(g), high-resolution transmission electron microscopy (HRTEM) results exhibited the detailed interface zone formed by atom diffusion between La-Al-Si-O glass phase and h-BN phase, which showed a gradual transition from order to disorder arrangement. On the whole, continuous, defect-free and interdiffusion grain boundary was beneficial to provide the good interface bonding and better performance of composite ceramics.

Precipitation nanocrystalline was also found in La-Al-Si-O glass phase, and with the increase of sintering temperature, the size of these precipitated grains showed a gradual increasing trend, as shown in Fig. 4(a-c). High sintering temperature was more likely to form precipitation phase with bigger size. Through selecting electron diffraction analysis as shown in Fig. 4(d), the precipitated phase was identified as cristobalite, which meant the precipitated cristobalite phase and La-Al-Si-O glass phase were coexisted in the composite ceramics. This phenomenon was also reported in the similar multiple oxide system, such

as $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$, $\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$, $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$, inhomogeneous nucleation in glass phase is the main reason for the formation of cristobalite nanocrystals [39,40].

Fig. 5 shows the bulk densities and apparent porosities of BN/La-Al-Si-O composite ceramics sintered under different temperatures. With the increase of sintering temperature, bulk density of h-BN composite ceramics first increased and then decreased, whereas apparent porosity exhibited the opposite tendency. The composite ceramic sintered at 1700 °C had the highest bulk density and the lowest apparent porosity. With the increase of sintering temperature, the liquid phase had better fluidity and wettability, and could well fill into the voids formed by the overlap of h-BN grains, which contributed to the improvement of densification. However, with the further increase of sintering temperature, h-BN grains had obvious growth, which led to the larger pores in the mutual framework by the large h-BN grains, resulting in the decrease of bulk density. Furthermore, some liquid phase was extruded during hot-pressed sintering at 1900 °C because the good fluidity of La-Al-Si-O glass phase at high temperature. Therefore, the glass phase content in the composition of this sample is less than that of other samples, leading to lower density and higher porosity.

Fig. 6 shows mechanical properties of BN/La-Al-Si-O composite ceramics sintered under different temperatures, including flexural strength, elastic modulus, and fracture toughness. With the increase of sintering temperature, the mechanical properties presented a small increase and followed by a rapid decrease, which was consistent with the tendency of bulk density. The best mechanical properties of BN/La-Al-Si-O composite ceramics were obtained under sintering temperature of 1700 °C, and the elastic modulus, flexural strength, and fracture toughness were 80.5 ± 0.7 GPa, 266.4 ± 10.1 MPa and 3.25 ± 0.05 MPa·m^{1/2}, respectively.

Fracture morphology of BN/La-Al-Si-O composite ceramics sintered under different temperatures are shown in Fig. 7(a-e). Digital Micrograph software was used to measure the grain size of h-BN at the representative region, the average grain size was calculated from about 30 measured h-BN grains. The grain size increased significantly with increasing sintering temperature, and the statistically average values are listed in Fig. 7(f). As the sintering temperature changed from 1500 °C to 1900 °C, the average size of h-BN grains increased from 0.35 μm to 2.5 μm.

From the above results, we comprehensively analyzed the influence of sintering temperature on the mechanical properties of BN/La-Al-Si-O composite ceramics, which mainly included the following two points: (1) High sintering temperature facilitated heat transfer and atom diffusion in liquid phase, which were beneficial to liquid phase pore filling to increase the relative density and improve the mechanical properties; (2) The grain sizes of h-BN increased rapidly with the increase of sintering temperature, and when h-BN grains grew to larger size, the porosity of composite ceramics became higher, resulting in an adverse effect on the densifying process and mechanical properties.

The microstructural evolution process of BN/La-Al-Si-O composite ceramics during hot-pressed sintering can be illustrated as Fig. 8. Firstly, the four raw powders were uniformly mixed and heated gradually in

the graphite mold (Fig. 8(a)); When the sintering temperature increased, La-Al-Si-O liquid phase was formed and h-BN grains were uniformly distributed in the liquid phase environment (Fig. 8(b)); With the further increase of sintering temperature, the heat and mass transfer ability of the liquid phase was enhanced, and the h-BN grains began to grow significantly (Fig. 8(c)); At the case of sintering temperature increasing or holding time extending, the grain size of h-BN further grew. At the same time, the cristobalite phase nanocrystalline was also precipitated in the liquid phase (Fig. 8(d)). These microstructural evolution mechanisms of BN/La-Al-Si-O composite ceramics are consistent with Fig.2, Fig.3 and Fig.4 shown above.

4. Conclusions

The BN/La-Al-Si-O composite ceramics were hot press sintered under different temperatures to reveal the microstructural evolution mechanisms. Ternary La-Al-Si-O liquid phase was formed during the sintering process, which had a good wettability with h-BN grains and could effectively fill the pores to improve the densification of composite ceramics. Higher sintering temperature contributed to the growth and crystallization of h-BN grains through better heat transfer and atomic diffusion in liquid phase environment. Furthermore, cristobalite nanocrystals were precipitated from the liquid phase and also grow gradually with the increase of sintering temperature. The BN/La-Al-Si-O composite ceramics sintered under 1700 °C exhibited the best mechanical properties, which was attributed to the mutual influence of liquid phase environment, h-BN grain size and precipitated phase.

Declarations

Acknowledgments

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Figures

Figure 1

XRD patterns (a) and crystallization graphitization index (b) of BN/La-Al-Si-O composite ceramics.

Figure 2

Microstructures of BN/La-Al-Si-O composite ceramics sintered under different temperatures: (a) 1500 °C; (b) 1700 °C; (c) 1900 °C; (d) B, N, O, Al, Si and La element distribution corresponding to (c).

Figure 3

Interface microstructures between h-BN grains and La-Al-Si-O glass phase of composite ceramics sintered under different temperatures: (a) 1500 °C; (b) 1700 °C; (c) 1900 °C; (d), (e), (f) elemental line scanning corresponding to line A, B, C; (g) HRTEM corresponding to interface of /La-Al-Si-O glass phase and h-BN grain in (c).

Figure 4

Nanocrystalline precipitation microstructures in La-Al-Si-O phase of composite ceramics sintered under different temperatures: (a) 1500 °C; (b) 1700 °C; (c) 1900 °C; (d) diffraction patterns of amorphous phase and cristobalite nanocrystalline.

Figure 5

Bulk densities and apparent porosities of BN/La-Al-Si-O composite ceramics.

Figure 6

Mechanical properties of BN-La₂O₃-Al₂O₃-SiO₂ composite ceramics.

Figure 7

Fracture morphology of BN/La-Al-Si-O composite ceramics sintered under different temperature: (a) 1500 °C; (b) 1600 °C; (c) 1700 °C; (d) 1800 °C; (e) 1900 °C; (f) statistics of average grain size.

Figure 8

Microstructural evolution mechanism diagrams of BN/La-Al-Si-O composite ceramics: (a) mixed raw powders; (b) La-Al-Si-O liquid phase formed; (c) h-BN grain growth; (d) cristobalite nanocrystalline precipitation