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Microstructure, mechanical properties and sintering model of B_4C nozzle with micro holes by powder injection molding

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ABSTRACT

Powder injection molding was adopted to prepare B_4C matrix composites with the additions of silicon carbide and zirconia. The B_4C nozzles with micro holes were well replicated from the mold, then successfully debound and sintered. The sintering characteristics, microstructures and mechanical properties of the B_4C matrix composites materials were investigated. The results show that the additions of SiC and ZrO_2 and increase of sintering temperature are in favor of the densification of the B_4C matrix composites materials. In addition, the X-ray analysis shows that the sintered composites are composed of B_4C, SiC and ZrB_2 phases. The morphologies of ZrB_2 and SiC phases change from nearly equiaxed to plate-like grains with increasing the sintering temperature. The fracture strength and hardness value of composites sintered at 2240 °C reach to 305.9 MPa and 3201 HV, respectively. The sintering model between the linear shrinkage and relative density was also established, predicting the sintering density and revising the measured density by the Archimedes and other methods. The calculated and measured results correspond well with each other.

1. Introduction

Because of their excellent properties such as ultrahigh hardness, low density, high neutron absorption cross section and good chemical and mechanical stability, boron carbide (B_4C) micro holes have good potential applications in micro-electromechanical systems (MEMS) serving as channels or nozzles to connect two micro-features[1–3]. Up to now, B_4C ceramics have been used for high temperature thermoelectric conversion, lightweight personal armor, blasting nozzles, control rods in nuclear reactors and fibers for reinforced ceramic composites [4–6]. However, industrial applications for complex shaped B_4C components, especially for microcomponents or irregular parts with micro hole-arrays are limited, because of the poor machinability of B_4C ceramics and higher manufacturing cost. As its advantages of lower cost, shape complexity, mass production, good tolerance and mechanical properties, powder injection molding (PIM) is an appropriate technique for manufacturing of complex parts with micro holes using ceramic or metal powders [7–9]. PIM has four processing steps: firstly, fabrication starts by compounding a thermoplastic binder and powder mixture, referred to as the feedstock, then, followed by injection molding, debinding and sintering. Every step has important effects on the eventually forming quality of parts which cannot be eliminated in the subsequent process. Some researchers have been focused on the effects of PIM process on the forming and property of SiC,ZrO_2 and WC materials [10–12]. However, literature on PIM of B_4C and relevant research data are less and still need to be further strengthened. In addition, B_4C has high melting point, low self diffusion coefficient, high vapor pressure and predominantly covalent bonds which need high sintering temperatures for densification [13]. Sintering with additives might be a feasible method to decrease the sintering temperature. Various sintering additives have been tested to improve the densification rate and mechanical properties of B_4C, such as C, Al, ZrO_2 and Al_2O_3 [14–17]. However, so far there have been rare reports on the effect of multivariate additive systems on the sintering characteristics of B_4C ceramics.

Therefore, the purpose of this study is to investigate the fabrication of B_4C nozzle with micro holes by PIM. The effects of $SiC-ZrO_2$ multivariate additive system on the sintering process of B_4C matrix composites were studied. The phase composition, microstructures, mechanical properties and sintering model between the linear shrinkage and relative density of B_4C matrix composites were also discussed.

2. Experimental procedures

In the present study, commercially available B_4C powders (mean particle size is 1.2 μm, Mudanjiang Abrasive and Grinding Tools Co, China) were used. SEM micrograph (Fig. 1) of the powder depicts a wide particle size distribution which helps to retain shape during debinding process. In order to make the powders mixing uniformly and eliminated the agglomeration of the applied powders,B_4C

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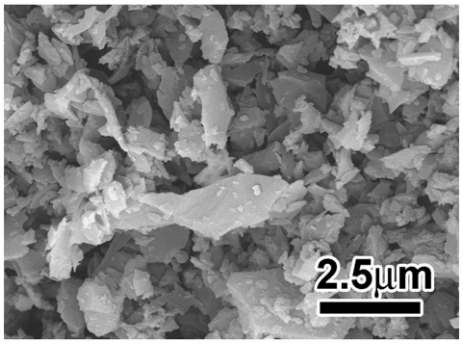

Fig. 1. SEM micrograph of the B_4C powder.

(80 wt.%), SiC (mean particle size is 0.45 μm, 5 wt.%) and ZrO_2 (mean particle size is 0.2 μm, 15 wt.%) powders were mixed in a planetary ball mill in ethanol for 12 h at a speed of 400 r/min. ZrO_2 balls and polypropylene container were used. After mixing, the slurry was dried. The softly agglomerated powders were then crushed and sieved through a 100 mesh sieve. The milled powder mixtures (55 vol.%) were compounded with a multi-component wax-based binder system (paraffin wax, polypropylene and stearic acid) in a double star mixer. After compounding, the feedstock was granulated by single-screw extrusion machine for several times and then molded by a 5-ton Babyplast6/10 micro injection molding machine. A set of suitable injection molding parameters was used, as shown in Table 1. In order to prevent the oxidation of B_4C, molded green samples were debound at 1150 °C in flowing Ar. Finally, the samples were pressureless sintered at 1900 °C, 1950 °C, 2000 °C, 2050 °C, 2100 °C, 2160 °C and 2240 °C for 2 h in flowing Ar, respectively.

The bulk densities of the samples were measured by the Archimedes method with an immersion medium of deionized water. The mass changes of samples sintered at different temperatures were tested by an electronic balance namely sartorius BS124S. The phase compositions of samples at different stages were tested by X-ray diffraction analysis (XRD). XRD experiments were performed at room temperature with a D/max-rB X-ray diffractometer using Cu Kα radiation (λ = 0.15418 nm). The fracture surfaces morphology of the sintered specimens were observed by the S-3400 scanning electron microscopy (SEM), while the microstructures of sintered samples were detected by using backscattered electron (BSE). Three-point bending (TPB) samples with 30 mm span length (total length = 36 mm), 4 mm width and 3 mm thickness were acquired by injection molding and then polished into the ideal samples. Bending tests were performed by the Instron5569 universal testing machine and the reported flexure strength was the average of three measurements. Vickers' hardness of the sintered samples was measured with a hardness tester using an applied load of 500 N for 15 s.

3. Results and discussion

3.1. Sintering characteristics

The B_4C nozzles were successfully manufactured by powder injection molding. Fig. 2. shows the molded, sintered samples and the local

Table 1
Injection molding parameters of B_4C matrix composites.

Injection molding parameters	Value
Injection pressure (MPa)	120
Closing force (kN)	45
Injection rate (cm^3/s)	5
Cooling time (s)	10
Mold temperature (°C)	50
Plastic temperature(°C)	180

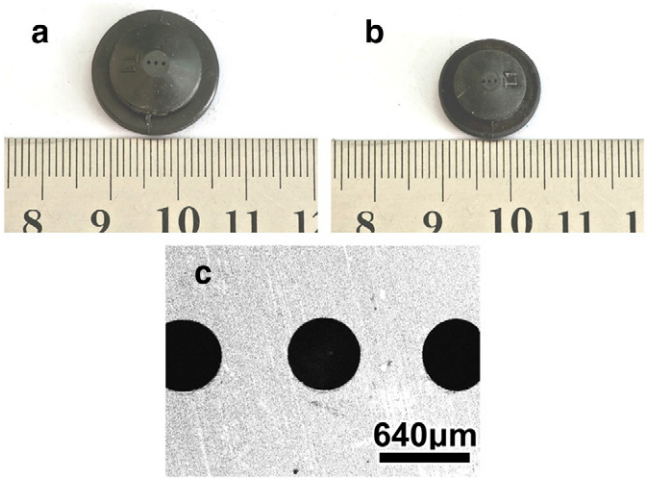

Fig. 2. Photographs of molded (a), sintered (b) and local view of small hole of B_4C nozzle.

view of micro holes, respectively. As can be seen, B_4C nozzles are well replicated from the mold. Excellent roundness was acquired for micro holes. The diameter of micro holes after sintering is 450 μm with a standard deviation under 1.5%. Compared with the molded samples, the linear shrinkage of the debound sample is slight (less than 1%). However, all sintered samples shrink obviously comparing with molded and debound samples. The linear shrinkage is confirmed by:

$$\Delta L = (L_m - L_s)/L_m \quad (1)$$

where ΔL, L_m and L_s are the linear shrinkage, the length of molded samples and the length of sintered samples. And the relative density is defined as:

$$\Delta\rho = (\rho_s/\rho_0) \times 100\% \quad (2)$$

where $\Delta\rho$—the relative density, ρ_s—the density of sintered samples measured by Archimedes method, and ρ_0—the theoretical density of mixed powders. The relative density and linear shrinkage of sintered samples increase consistently with increasing the sintering temperature (Fig. 3). The relative density and linear shrinkage of samples sintering at 1900 °C are only 65.3% and 5.21% which increase to 95.1% and 18.6% when the sintered temperature reaches to 2240 °C. This indicates that the additions of SiC and ZrO_2 and the increase of sintering temperature are advantageous for the improvement of density which is compared with as-sintered pure B_4C ceramics [18].

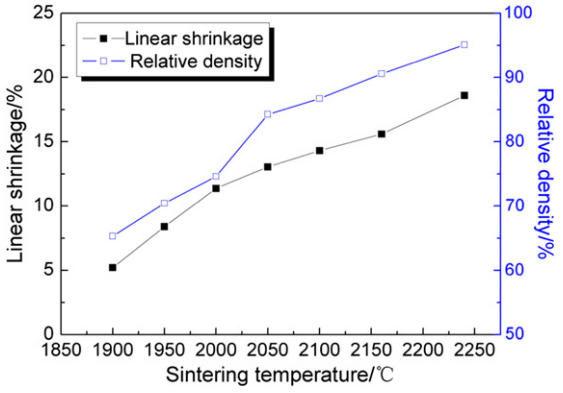

Fig. 3. Relative density and linear shrinkage of B_4C samples sintered at different temperatures.