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PREPARATION AND PROPERTIES OF SiAlON CERAMICS BY GEL CASTING AND PRESSURELESS SINTERING

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This study employed a low-toxicity N, N-dimethylacrylamide/N, N-methylene acrylamide (DMAA /MBAM) gel system to near net shape SiAlON ceramics from aqueous slurries with a solid loading of 40 wt.% Si3N4, Al2O3, Y2O3, AlN, and Ce2O3 powder mixtures. The green bodies were sintered by one- and three-step pressureless sintering. Results showed that green bodies had a homogeneous microstructure with a high density of 1,9 g/cm3 and high flexural strength of 28,6 Mpa. Equiaxed α-SiAlON was prepared by one-step pressureless sintering, whereas β-Si4Al2O2N6 with an elongated morphology was fabricated by three-step pressureless sintering. Therefore, a low-temperature heat preservation stage reduces the nucleation rate, which is favorable for the development of elongated β-SiAlON grains.

Key words: SiAlON ceramics, gelcasting, pressureless sintering, microstructure, mechanical properties

INTRODUCTION

SiAlON ceramics are a series of solid solutions with excellent oxidation resistance, high-temperature resistance, and thermal stability. It is widely used in high-temperature metallurgy, materials science, aerospace, military, and other fields [1,2]. The green bodies of SiAlON ceramics are usually made by employing a conventional dry-powder pressing technique. Then, they undergo hot pressing, hot isostatic pressing, discharge plasma sintering, and gas pressure sintering to form a dense, sintered body. However, SiAlON ceramics usually have remarkable hardness and brittleness. These properties are difficult for machines to form SiAlON ceramics into complex shapes of desired size, thereby limiting their further development.

Gel casting methods were disclosed by the American Oak Ridge National Laboratory in the early 1990s. Gel casting is a colloidal molding process that uses organic monomer and solution (non-aqueous or aqueous) to prepare a stable suspension of ceramic powders. Through injection molding, a three-dimensional network structure is formed by cross-linking polymerization between organic substances to form a gel-cured molding. This method effectively eliminates the limitations of dry-powder pressing technique, such as uneven structure, low mechanical properties, and high production cost and has been widely applied in the preparation of green bodies of various ceramics with high strength and accurate size [3,4]. Gel casting technique using acrylamide (AM) as organic monomer is reliable and tested to be appropriate in the preparation of various ceramics. However, AM has been found to be toxic to the nervous system, which is harmful to the human body and environment. AM is also prone to oxygen inhibition during gel curing reaction, which causes skinning and affects the performance of the final product [5]. Therefore, a low-toxic or non-toxic monomer is necessary to replace AM, which has attracted wide attention. In recent years, N, N-dimethylacrylamide (DMAA) has been reported to have similar characteristics to AM but has low toxicity, which is suitable for the preparation of various ceramic materials. Shuang et al. [6] used a low-toxic, water-soluble DMAA gel system to prepare porous Si_3N_4 ceramics, in which the highest flexural strength of the green body that can reach 46,3 MPa. Ibram Ganesh [7] used orthophosphoric acid and dihydrogen aluminum to protect AlN powder from hydrolysis and successfully prepared β-$Si_4Al_2O_2N_6$ ceramics using low-toxicity DMAA gel system. In this study, high-strength ceramic green bodies were prepared by low-toxic and aqueous DMAA and N-methylene acrylamide (MBAM) gel system, and α-SiAlON and β-$Si_4Al_2O_2N_6$ ceramics were prepared through different sintering processes.

EXPERIMENTAL

Raw materials

The green body of SiAlON ceramics was prepared using Si_3N_4 (99,9 % purity, α-$Si_3N_4 \geq 92$ %, $d_{50} < 0,5$ μm, Aladdin Industrial Co., Ltd., China), α-Al_2O_3 (99,9 % purity, Aladdin Industrial Co., Ltd., China), AlN (99,9 % purity, Aladdin Industrial Co., Ltd., China).

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Y_2O_3 (99.99 % purity, HC Starck), and Ce_2O_3 (99,99 % purity, Aladdin Industrial Co., Ltd., China) as raw materials. DMAA was used as monomer, and MBAM (Aladdin Industrial Co., Ltd., China) was used as crosslinker. Ammonium polyacrylate (Aladdin Industrial Co., Ltd., China), ammonium persulfate (self-prepared), N, N, N', N'-Tetramethylethylene -diamine (TEMED), and DF-801 were used as dispersant, initiator, catalyst, and defoamer, respectively.

Experimental procedure

Figure 1 shows the manufacturing process of SiAlON ceramics by gel casting and pressureless sintering. First, the premix solution was prepared by dissolving the monomer, crosslinker (DMAA+MBAM=12,4 wt.%), and dispersant in water. Then Si_3N_4, α-Al_2O_3, AlN, Y_2O_3 and Ce_2O_3 powders were added to the premixed solution with a solid loading of 40 wt.%. The slurries were ball milled for 9 h in a planetary mill. The catalyst and initiator (2,0 wt.%) were added to the slurries. Subsequently, they were casted into a designed mold and were de-molded after curing at 25 °C for 24 h.

The thermogravimetric-differential scanning calorimete (TG-DSC) curves of SiAlON green body under Ar atmosphere was shown in in Figure 2. It can be seen from Figure 2 that the main temperature range of mass loss was 250 – 450 °C, and the polymer pyrolysis mainly occurred at 230 – 280 °C and 350 – 400 °C. Therefore, to prevent cracks and deformation of the green body, the green bodies were heated to 300 °C for 6 h and 450 °C for 6 h and then to 600 °C for 4 h at a heating rate of 2,5 °C/min to pyrolyze the volatiles. Finally, the degreased green bodies were sintered by one- and three-step pressureless sintering. The one-step pressureless sintering process was that the green body was sintered to 1 650 °C for 1 h with a heating rate of 10 °C/min. The three-step pressureless sintering process was that the green body was sintered to 1 350 °C and 1 450 °C for 30 min and then to 1 650 °C for 1 h with a heating rate of 10 °C/min.

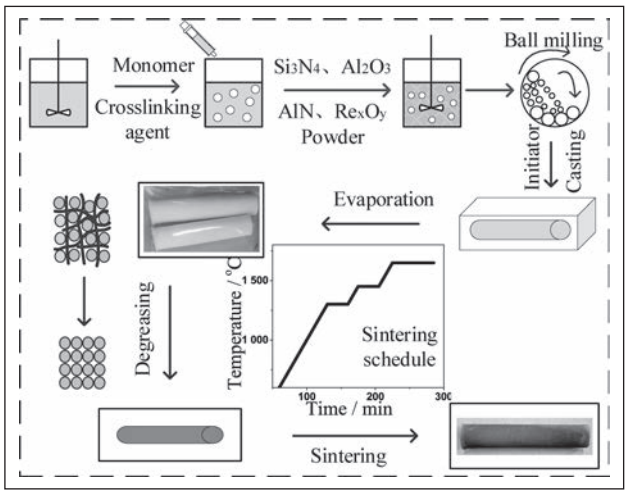

Figure 1 Flow diagram for preparation of SiAlON ceramics

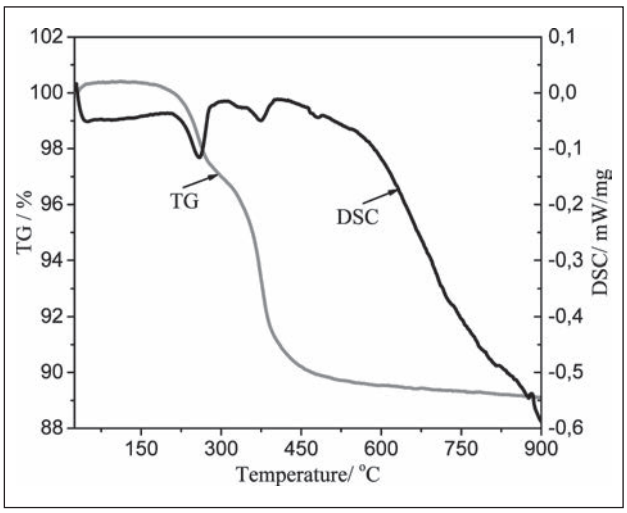

Figure 2 TG-DSC curves of SiAlON green body under Ar atmosphere

Characterization

The phase composition was identified using X-ray diffraction (XRD, Rigaku SmartLab, Japan) with Cu radiation at 40 kV and 50 mA at a scan rate of 4 °/min to record the diffraction patterns. The flexural strength of the green bodies was examined via the three-point bending method using a universal testing machine (PWS-E100, Jinan Times Test Gold Testing Machine Co., Ltd., China) with a sample dimension of 3 mm × 4 mm × 40 mm. The span and crosshead speed were 30 mm and 0,5 mm/min, respectively. The microstructures of the green and sintered bodies were observed under a scanning electron microscope (SEM, Inspect F50, FEI, USA) along with the energy-dispersive X-ray spectroscopy (EDS, Octane Super, EDAX, USA). The density was measured according to Archimedes' principle in deionized water. Fracture toughness of sintered bodies was determined by the single-edge notched beam method with dimensions of 2 mm × 4 mm × 20 mm (span was 16 mm, kerf width was 0,25 mm, and depth was 1,6 – 2,4 mm). Vickers hardness was tested by a Vickers diamond indenter (HV-50). The standard procedure was to apply a load of 10 kg for 15 s.

RESULTS AND DISCUSSION

Properties of green body

Figure 3 shows the microstructure of green body with a solid loading of 40 wt.% (DMAA+MBAM=12,4 wt.%). The particles are tightly bound to the three-di-

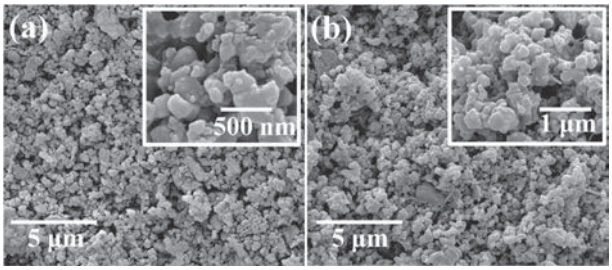

Figure 3 SEM micrographs of the green body (a) surface, (b) fracture surface

mensional gel network, and no evident particle agglomeration exists, as shown in Figure 3. The green body has a homogeneous microstructure, excellent properties, flexural strength of 28,6 Mpa, and density of 1,9 g/cm^3.

Properties of sintered bodies

Composition

The degreased green bodies were sintered by one- and three-step pressureless sintering. The effect of sintering process on the composition, microstructure, and mechanical properties of sintered bodies were investigated. Figure 4 shows the XRD patterns of SiAlON ceramics sintered at different conditions. For the sample sintered at 1 650 °C for 1 h, the main phase is α-SiAlON, and no other phase is detected (Figure 4(a)). The intensity of (210) crystal plane is the largest, followed by the diffraction peaks of the (102) and (201) crystal planes. As shown in Figure 4(b), only β-$Si_4Al_2O_2N_6$ exists in the sample sintered by three-step pressureless sintering (1 350 °C and 1 450 °C for 30 min and then to 1 650 °C for 1 h). The intensity of (101) crystal plane is the largest, followed by the diffraction peaks of the (210) and (200) crystal planes.

Microstructure and mechanical properties

Figures 5 and 6 show the SEM micrographs and grain size distribution of SiAlON ceramics sintered under different conditions. From the figures, the microstructure of the sample sintered by one-step sintering exhibits equiaxed α-SiAlON morphology with an aver-

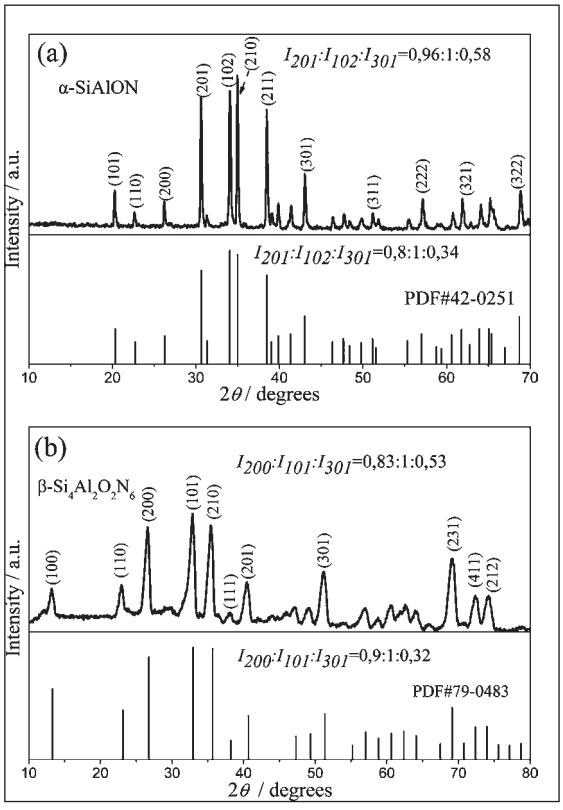

Figure 4 XRD patterns of SiAlON ceramics sintered at different conditions (a) one-step, (b) three-step

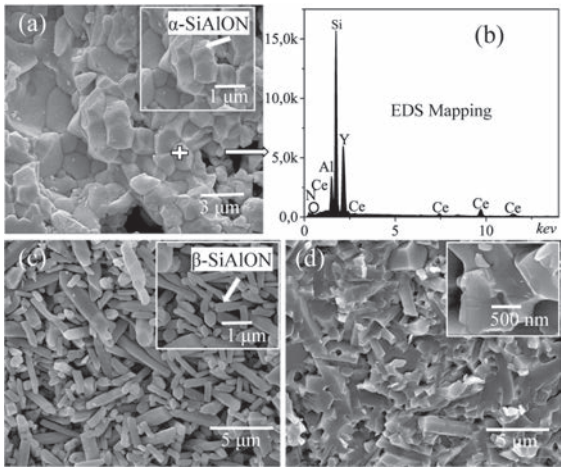

Figure 5 SEM micrographs of SiAlON ceramics sintered at different conditions (a) one-step sintering, (b) EDS mapping of (a), (c) and (d) corrosion and fracture surfaces of sample sintered by three-step sintering

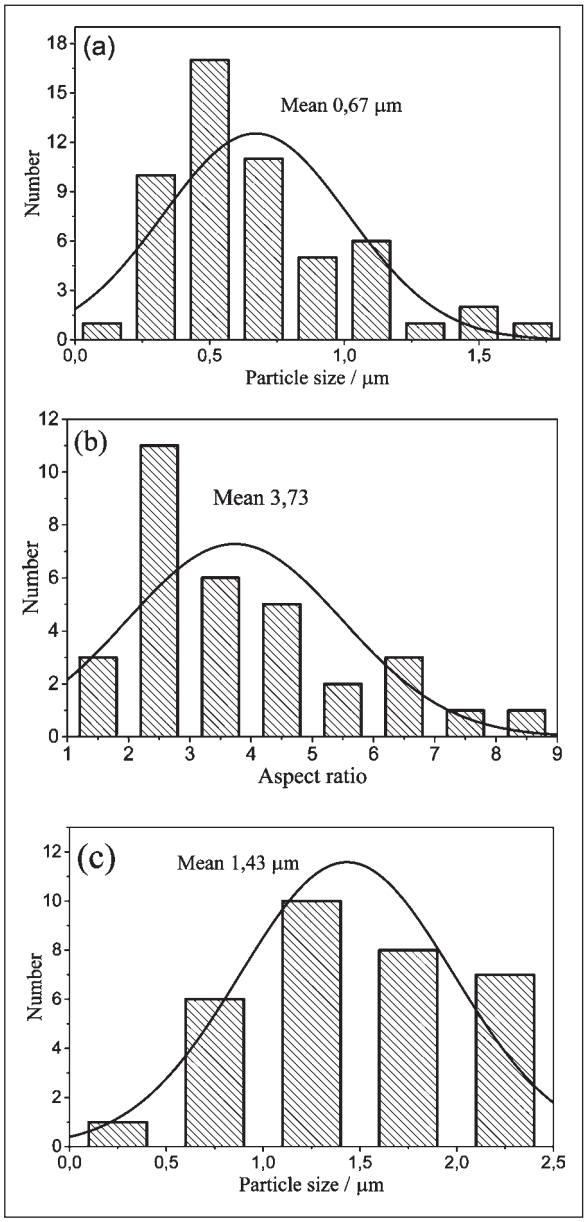

Figure 6 Grain size distribution of SiAlON ceramics sintered at different conditions (a) grain size distribution of Figure 4(a), (b) and (c) grain size distribution of Figure 4(c)

Table 1 **Mechanical properties of sintered bodies**

Samples	Sintering methods	HV / GPa	K_{Ic} / MPa·m$^{1/2}$
1#	One step	17,3	5,6
2#	Three-step	15,8	6,1

age grain size of 0,67 μm. The sintered body exhibits high Vickers hardness of 17,3 GPa and relatively low fracture toughness of 5,6 MPa·m$^{1/2}$ (Table 1), whereas the microstructure of the sample sintered by three-step sintering has an elongated β-SiAlON morphology. This condition is due to the reduced nucleation rate caused by low-temperature insulation stage, and only a small amount of nucleation is formed at the beginning. These crystal nuclei grow in a preferred orientation along the direction of the lowest energy and develop into elongated grains. This process indicates that low-temperature insulation provides sufficient growth space for the crystal nucleus to facilitate the formation of whisker-like β-SiAlON grains. The average grain length is 1,43 μm, and the average aspect ratio is 3,73. As shown in Table 1, the β-SiAlON ceramic prepared by three-step pressureless sintering has a high fracture toughness of 6,1 MPa·m$^{1/2}$ and relatively low Vickers hardness of 15,8 GPa.

CONCLUSIONS

A low-toxicity DMAA/MBAM gel system was employed to near net shape SiAlON ceramics from aqueous slurries with a solid loading of 40 wt.% Si_3N_4, Al_2O_3, Y_2O_3, AlN, and Ce_2O_3 powder mixtures. The green bodies were sintered by one- and three-step pressureless sintering. The major conclusions are as follows:

(1) The green bodies had a homogeneous microstructure with high density of 1,9 g/cm^3 and flexural strength of 28,6 Mpa.

(2) The equiaxed α-SiAlON was prepared by one-step pressureless sintering to 1 650 °C with holding time of 1 h. The α-SiAlON ceramic exhibited high Vickers hardness of 17,3 GPa and relatively low fracture toughness of 5,6 MPa·m$^{1/2}$.

(3) β-$Si_4Al_2O_2N_6$ with an elongated morphology was fabricated through three-step pressureless sintering (1 350 °C and 1 450 °C holding for 30 min and 1 650 °C holding for 1 h). It had high fracture toughness of 6,1 MPa·m$^{1/2}$ and relatively low Vickers hardness of 15,8 GPa.

Acknowledgements

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Note: The professional translator for the English language is Jing Li, Changsha, China.