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Fabrication and properties of dense silicon carbide ceramic via gel-casting and gas silicon infiltration

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ABSTRACT

The dense Silicon Carbide (SiC) ceramics are fabricated by means of gel-casting and gas silicon infiltration (GSI) using carbon black and α-SiC as raw materials. We have successfully introduced a new initiator AIBA which is very suitable to aqueous gel-casting system containing carbon black, overcoming the problems posed by the conventionally used initiator. We have investigated the influences of the monomer acrylamide (AM) content, the ratio of the monomer to crosslinking agent AM/MBAM content, the particle size distribution and the solid content on the mechanical and structural properties of samples. The result show that, the linear shrinkage of the green body can be reduced to 1.0% and its bending strength can reach 59.2 MPa at the optimized gel-casting process that has an AM content of 25 wt%, an AM to MBAM ratio of 12, a SiC particle distribution of 3/2 and a solid content of 60 vol%. After the GSI process, the bending strength and elastic modulus of the final products from such green bodies can reach 245 MPa and 220 GPa respectively. The study highlights that the combined application of the gel-casting and the GSI processes can produce high-quality silicon carbide ceramics that are suitable in the space optical applications.

1. Introduction

Optical system plays a crucial role in the space collecting information. As a key component in such optical systems, the space mirror has drawn intensive attentions of researchers. The candidate materials for space mirrors need to possess a high flexural strength, a high elastic modulus (>200 GPa), as well as a dense structure without any holes, etc. Currently, the silicon carbide (SiC) is considered as an ideal material for space mirrors due to a combination of its desirable properties for space systems, such as high mechanical properties, good optical performance, corrosion resistance, etc [1–4]. There are a wide variety of methods to make SiC materials among which the gas silicon infiltration (GSI) is the most promising process due to its short preparation period, low sintering temperature, minimum sintering shrinkage and low cost. In a typical GSI process, the gaseous silicon reacts with carbon to form β-SiC at a temperature range of 1500–1700 °C with the existence of carbon black [5,6].

Prior to the GSI process, a carbon green body with an appropriate porosity need to be prepared. In the current study, we select the gel-casting method to make such green carbon bodies due to its advantages such as to make green bodies with near-net-shape, high strength, high quality, and high density, etc. Currently, a commonly used aqueous gel-casting system includes acrylamide (AM) as the monomer, N,N′-Methylenebisacrylamide (MBAM) as the crosslinking agent and ammonium persulphate (APS) as the initiator [7–14]. Unfortunately, the addition of carbon black to this system exerts a detrimental effect on the gelation. The carbon black is well known of composing of layered hexagonal graphite microcrystalline, which has a strong capturing effect on the radical $\cdot SO_4^-$ released by the initiator APS. In addition, this effect can in turn promote the release of the radicals according to Le Chatelier's principle. Hence the gelation reaction cannot be controlled, i.e. the gelation time tends to be less than 5 min. Moreover, the gelation acceleration effect becomes more apparent with higher carbon contents. Clearly, such uncontrollable gelation processes cannot satisfy the requirement of the casting process, which should have a gelation time ideally more than 30 min. In order to address this problem, Chen et al. added acetylacetone (Acac) into the slurry so as to slow down the gelation reaction, however, Acac did not work when the carbon content was over 15 wt%. In another attempt, Zhang et al. used dextrin instead of carbon black, but the sintering temperature became too high, i.e. around 2200 °C [15–18], which becomes inappropriate.

In this study, the direct initiative is to address the initiator issue. We select a new initiator 2,2′-Azobis (2-methylpropionamidine)

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dihydrochloride (AIBA) to replace APS and investigate the influence of factors such as the AM/MBAM content, particle size distribution and solid content on the gel-casting process. The following findings are unveiled. Firstly, the carbon black has much weaker capability to capture radicals released by AIBA. Secondly, the concentration of initiators AIBA and the reaction temperature control the decomposition of AIBA. Hence, the gelation reaction can be controlled at ease, suggesting AIBA is appropriate as an initiator gel-casting system that contains carbon.

2. Experimental

2.1. Gel-casting process

The green body was fabricated by gel-casting. Firstly, AM and MBAM (Chinese Medicine Chemical Reagent Co., Ltd.) were dissolved in deionized water to form a solution. Secondly, the carbon black (N550, 35 m^2/g, China United Rubber (Group) Company) and SiC powders (Qingzhou Shandong fine powder Co., Ltd) were added to the above solution to form slurry, with the addition of PVP (polyvinyl pyrrolidone, Chinese Medicine Chemical Reagent Co., Ltd.) and TMAH (Tetramethylammonium hydroxide, Chinese Medicine Chemical Reagent Co., Ltd.) as the dispersants of C and SiC respectively. Subsequently, the above slurry is subjected to 8 h ball-mixing and 30 min vacuum-degassing, AIBA (Shanghai Aladdin Bio-chem Technology Co., Ltd.) was added to the slurry. Afterwards, the slurry was poured to the mould that is 60 mm in diameter and 10 mm in height and the gelation reaction took place. Finally, the green body was dried to constant weight at room temperature.

2.2. Gas silicon infiltration process

Dense Si/SiC ceramics were prepared by the GSI method. The above-obtained green body was buried in the silicon powders in a furnace and then heated up to 1500 °C in 5 h in the argon atmosphere to turn the solid Si to liquid phase. Subsequently the furnace was fired to 1700 °C in 1 h in vacuum and dwelled at this temperature for 2 h, during which the liquid Si turned to gaseous phase and the silicon and carbon reaction took place.

2.3. Samples characterization

Differential scanning calorimetry (DSC/DTA-TG, Netzsch STA 449 F3 Jupiter) was used to analyze the gelation reaction and to calculate the reaction heat. The Al_2O_3 serves as the reference material, with the heating rate as 10 °C/min and the dwelling time as 60 min.

The mechanical properties are evaluated by the three-point bending test. The samples were cut and polished to 40 mm in length, 4 mm in width and 3 mm in thickness. The length and width directions were parallel to warp and weft directions, respectively. During the three-point bending test, the ratio of span to height was kept as 15 and the crosshead speed was 0.5 mm/min. The flexural strength σ_b and elastic modulus E_b are calculated according to Eqs. (1) and (2) respectively.

$$\sigma_b = \frac{3PL}{2bh^2} \tag{1}$$

$$E_b = \frac{L^3}{4bh^3}\cdot\frac{\Delta P}{\Delta f} \tag{2}$$

where P is the maximum load, L is the span, b is the specimen width, h is the specimen thickness, and $\Delta P/\Delta f$ is the slope of the linear portion of the load-displacement curve.

The microstructures of the specimens before and after sintering were examined by the scanning electron microscopy (SEM, FEI Quanta-200).

The phase and composition of the samples were identified by the X-ray diffraction (XRD, D8 Advance), with the Cu-kα radiation. The samples were scanned from 10 to 80°, with 0.01° as the step length and holding 1 s at each step. The chemical compositions of the samples were analyzed by the X-ray photoelectron spectroscopy (XPS, Escalab 250Xi), using 12 kV Al-Kα as the exciting light source, with a power of 72 W and a resolution of 0.5 eV. Prior to the test, samples were subjected to the sputtering Ar^+ for 10 min so as to reduce the surface contamination.

3. Results and discussion

3.1. Preparation of high solid content slurry

Fig. 1(a) shows the effect of the monomer AM content in water on the viscosity of the slurry. As shown, the viscosity of the slurry increases dramatically with the increase of the AM content, which can be attributed to the following reasons. Firstly, with the addition of the monomer AM, the volume of the solution expands. For instance, the addition of each gram monomers gives 0.92 ml solution volume expansion. By contrast, as we keep the solid content constant, the content of deionized water in the slurry decreases with the increase of the AM content. Secondly, with the addition of the monomer AM, the organic molecules interaction become more violent, which can undoubtedly lead to the increase of the viscosity.

Fig. 1(b) shows the effect of particle size distribution on the viscosity of slurry. The viscosity of the slurry initially decreases and then increases, with the F240/F1200 ratio at 3/2 reaching the lowest value. According to Andreason classical close packing theory, the content of particles with different sizes can be calculated by Eq. (3),

$$U(D) = \left(\frac{D}{D_{max}}\right)^m \tag{3}$$

where D_{max} is the diameter of the maximum particle, U(D) is the mass fraction of the particles that have a diameter of D, and m refers to the model parameter. Based on the simulation results, when m=0.37, the void fraction of the model reaches the minimum. In this study, in order to prepare high solid content slurry, we employed two kinds of SiC powders with different particle sizes: the coarse ones (refereed as F240) with an average diameter of 43 μm and the fine ones (referred as F1200) with an average diameter of 3.8 μm. Accordingly, Eq. (3) gives a U(D) value of 0.41 with D_{max}=43, D=3.8, m=0.37. That is to say, when F240/F1200=3/2, SiC powders come to the most compact stack state, and it can be considered that coarse powders are closely packed, fine particles are filled in the space homogeneously. In this case, there is no particle aggregation of only F240 or F1200, and it is generally known that particle aggregation can cause the increase of viscosity. As is shown in Fig. 1(c), when F240/F1200=3/2, the viscosity of slurry come to a minimum.

Fig. 1(c) demonstrates the effect of solid content on the viscosity of the slurry. As seen, the viscosity increases steadily with the increase of the solid content. It is well known that the slurry becomes too viscous to be used in the gel-casting process when the viscosity of the slurry exceeds 1.5 Pa s. On the other hand, pores will appear in the green body when the solid content is less than 55 vol%. Considering the above two factors, the solid content of

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