Materials and Design 65 (2015) 12–16

Contents lists available at ScienceDirect

Materials and Design

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

Properties of silicon carbide ceramics from gelcasting and pressureless sintering

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ARTICLE INFO

Article history:
Received 12 August 2013
Accepted 13 August 2014
Available online 23 August 2014

Keywords:
Silicon carbide
Gelcasting
Pressureless sintering
Mechanical properties

ABSTRACT

In this paper, dense silicon carbide ceramics were prepared by aqueous gelcasting and pressureless sintering using dextrin as the carbon source. The influence of carbon content and solid content on the microstructure and mechanical properties of green and as sintered SiC samples was studied. It was shown that the carbon content should be 1 wt% or higher for the fully densification of silicon carbide ceramics. The influence of solid content on the green density and the mechanical properties of SiC ceramics was studied. The optimal solid content with 1 wt% carbon as sintering additives is around 52 vol%. Results showed that dextrin is an effective carbon source for developing SiC ceramics by aqueous gelcasting and pressureless sintering method.

1. Introduction

Silicon carbide ceramics has many excellent properties, such as high strength, high hardness, high resistance to corrosion etc., is considered as one of the promising candidate materials for various applications: such as diesel engines, gas turbines, industrial heat exchangers, high-temperature energy conversion systems [1,2]. However, due to the brittle nature and high hardness, post machining will be difficult and increase the cost of SiC product significantly especially in the fabrication of parts with big size and complex shape.

Gelcasting is a near-net-shape forming method for the preparation of ceramics part with large size and/or complex shape at low cost [3,4]. The gelcasting method involves an in situ polymerization of monomer, such as acrylamide (AM), methacrylamide (MAM) and methacrylic acid (MAA), crosslinker such as MBAM with the addition of initiator. The process has been widely studied in many systems, including $A1_2O_3$ [4–8], Si_3N_4 [9], SiC [10,11], PZT [12], HfB_2 [13], ZrO_2, $BaTiO_3$ etc. However, there are still some problems need to be well resolved. It was found that the monomer polymerization based on free radical reaction has some disadvantages: the oxygen inhibition [14], and some additives inhibition such as carbon [15]. That is the reason why SiC cannot be easily developed by gelcasting, because carbon was usually used as the sintering additives for SiC. The other disadvantage is the uncontrolled gelation during slurry degassing, which causes a failed casting.

Up to now, only few papers reported the gelcasting of silicon carbide with boron and carbon as the sintering additives [12,16–18]. Ganesh Ibram used two kinds of powder, commercial phenolic resin-coated SiC powder (RSC) and pure SiC powder (GSC). It was found that the dispersion of RSC was difficult and only quite low solid content of 37 vol% can be reached. However, the gelcast RSC green samples can be densified by pressureless sintering to about 97.5% TD. While for pure SiC powder, it was easily to prepare high solids loading slurries using sucrose as the carbon source. However, the gelcast green sample cannot be densified by pressureless sintering. Chen YF dispersed both SiC and carbon black together in aqueous slurries and found that carbon had obvious inhibition on the free radical polymerization process. The addition of acetylacetone could help to adjust the idle time for gelation process. The proposed method can be used to prepare porous structure for Si infiltration reaction bonding. As far as we know, the development of dense SiC by gelcasting and pressureless sintering using carbon and boron as the sintering additives is still a challenge.

In the previous study, dextrin was proposed as the sintering additives for the aqueous gelcasting of SiC [19]. The gelcasting process was investigated and parameters relating to the processing was studied and optimized. The green samples showed homogeneous microstructure with high green density.

In the present work, the microstructure and mechanical properties of the SiC samples by gelcasting and pressureless sintering are studied using dextrin as the carbon source. The influence of carbon content and solid loading on the green and as-sintered SiC samples was studied.

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http://dx.doi.org/10.1016/j.matdes.2014.08.034
0261-3069/

Table 1
Raw materials used in gelcasting process.

Raw materials	Abbreviation	Function
Silicon carbide	SiC	Powder
Boron carbide	B_4C	Sintering additives
Dextrin	Dextrin	Carbon (Sintering additives)
Tetramethyl ammonium hydroxide	TMAH	Dispersant
Deionized water	H_2O	Solvent
N,*N*′-Dimethylacrylamide	DMAA	Monomer
N,*N*′-Methylenebisacrylamide	MBAM	Cross linker
2,2′-azobis[2-(2-imidazolin- 2-yl)propane] mixture	AZIP	Initiator

2. Experimental procedure

2.1. Materials and process

The raw materials used in gelcasting process are listed in Table 1. Based on the study in our lab, an initiator system composed of 2,2′-azobis[2-(imidazolin-2-yl) propane]dihydrochloride(AZIP) and other components were used other than the traditional initiator for the well-controlled gelation of the slurries.

Commercially available SiC powder (FCP-15, Saint-Gobain's Silicon Carbide Department, Norway) produced by the Acheson method was used in this study. The average particle size and the specific surface area are 0.58 μm and 15.24 m^2/g respectively. Boron carbide (Mudanjiang Jingangzuan Boron Carbide Co., Ltd.) with the average particle size as 0.93 μm and the specific surface area as 10.78 m^2/g were used as the sintering additives. Dextrin (white powder from maize starch, analytical, Sinopharm Chemical Reagent Co., Ltd. (SCRC)) was used as the carbon source (sintering additives).

2.2. Gelcasting and sintering

The formulation for gelcasting slurries was shown in Table 1. The gelcasting process is described in the following. Initially, SiC powder was dispersed in a premix solution, which had been prepared by dissolving defined amount of dextrin in de-ionized water, followed by the addition of 12 wt% ,N-dimethyl acrylamide (DMAA) and N, N′-methylenebisacrylamide (MBAM) in a 13:1 ratio. 0.6 wt% tetramethyl ammonium hydroxide(TMAH) with respect to the SiC powder was used as the dispersant [8,20]. After milling, initiator system was added and the well dispersed slurries were degassed in order to eliminate the air bubbles trapped. Afterward, the slurries were cast into the aluminum molds, which were then allowed to set in water bath at 45–60 °C for 50–60 min in order to gel the system. The gelled green bodies were de-molded and dried under controlled humidity conditions (in the temperature and relative humidity range of 20–35 °C and 80–90% respectively) to avoid cracking and non-uniform shrinkage due to rapid drying. The green blocks were heated to 600 °C at a heating rate of 1.0 °C/min and held several times at 320 °C, 400 °C and 430 °C respectively to burn out the monomers and other volatiles, followed by pressureless sintering at 2200 °C for 1 h in Ar atmosphere for densification purpose. The shrinkage of SiC during sintering was observed in situ and calculated using a thermo optical measuring system (TOM-AC, Fraunhofer Institut Silicatforschung ISC, Germany).

Rheological measurements were performed on a Rheolab QC (Anton Paar, Austria). Measurements were carried out at 25 °C.

2.3. Characterization of gelcasting green bodies and as-sintered samples

The density of green pieces was determined by Hg intrusion porosimetry using a Micromeritics ASAP2010 porosimeter. Bulk densities of as-sintered samples were determined by Archimedes' method. Flexural strength was measured by three-point bending with a span of 30 mm and a cross-head speed of 0.5 mm/min, using Instron 5566 universal testing machine, according to the Chinese Standard GB/T 6569-2006 [21]. The size of the samples was normally 3 mm × 4 mm × 36 mm. Fracture toughness (*KIc*) were measured at room temperature by the Vickers diamond indentation method and evaluated by the equations given by Evans and Charles [22]. Fracture toughness was determined using Microstructures of SiC samples were investigated by field emission scanning electron microscopy (JSM-6700F, Jeol, Japan). The grain size of the samples was characterized by scanning electron microscopy (SEM; Magellan 400, FEI, Eindhoven, The Netherlands) equipped with electron backscatter diffraction (EBSD).

3. Results and discussion

In this work, dextrin was selected as the carbon source to avoid the dispersion problem between SiC and C and the polymerization-inhibition effect of carbon. The carbon content in the slurries was calculated according to the TG-DTA data of dextrin (24.3 wt% C would leave after pyrolysis). As the addition of dextrin in water have obvious influence on the solid content of SiC slurries, it is better to reduce the dextrin content as long as the SiC ceramics can be densified. In order to determine the influence of carbon content on the sintering behavior of gelcast SiC samples, 50 vol% SiC slurries with different dextrin content (corresponding to the carbon content in the range of 0.5–1.5 wt%) were prepared for gelcasting. It was found that at low carbon content (<1 wt%), SiC samples cannot be well densified after sintering at 2200 °C with 1 h holding, Fig. 1. The oxygen content of as received powder was 1.35 wt% as determined through the chemical analysis. According to the following reaction, the least carbon content needed for the complete removal of surface silica layer is 0.81 wt%.

$$3C + SiO_2 \rightarrow 2CO + SiC \quad (1)$$

Therefore, the C content should be higher than 0.81 wt% for the well densification of silicon carbide ceramics. This is in accordance with the fact that the density increased greatly as the C content increased up to 1 wt% or higher. Bocker also reported the similar trend for die-pressed SiC samples using polyphenylene as the carbon source. However, the carbon content of 1.5 wt% was required for the well densification of SiC [23]. With less C content, it is also possible to obtain well densified SiC ceramics by increasing the temperature up to 2280 °C or higher, possibly after the completely removal of the residual surface silica. However, the grain size increased greatly at high temperature and the mechanical properties decreased correspondingly, which is not favorable for the sintering of SiC. As shown in Fig. 1, the bending strength of the samples also showed the similar trend as the density. This might be due to the presence of pores in the samples.

The shrinkage of SiC samples with different C content was characterized through the TOM-AC equipment. Results are shown in Fig. 2. The shrinkage of SiC began at about 1400 °C and a considerable linear shrinkage rate appeared around the temperature of 1950 °C. This can be related to the removal of surface SiO_2 layer of SiC particles due to the reaction between carbon and SiO_2. The shrinkage was almost finished at about 2200 °C. A comparison of two samples with different C content showed that there was no big difference incurred with the increase of carbon from 1 wt% to 1.5 wt%. In this study, based on the result above, 1 wt% carbon was selected for the preparation of the SiC slurries for reducing the dextrin content. The sintering condition is 2200 °C with 1 h holding in Ar atmosphere.