Journal of the European Ceramic Society xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of the European Ceramic Society

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

Original Article

Effect of technological parameters on densification of reaction bonded Si/SiC ceramics

P.S. Grinchuk[a], M.V. Kiyashko[a,*], H.M. Abuhimd[b], M.S. Alshahrani[b], M.O. Stepkin[a], V.V. Toropov[a], A.A. Khort[a], D.V. Solovei[a], A.V. Akulich[a], M.D. Shashkov[a], M.Yu Liakh[a]

[a] A.V. Luikov Heat and Mass Transfer Institute of the National Academy of Sciences of Belarus, Minsk, 220072, P. Brovki 15, Belarus
[b] National Nanotechnology Research Center King Abdulaziz City for Science and Technology, Riyadh, 11442, P.O. Box 6086, Saudi Arabia

ARTICLE INFO

Keywords:
SiC
Silicon infiltration
Injection molding
Reaction sintering
Porosity

ABSTRACT

Si/SiC composite ceramics was produced by reaction sintering method in process of molten silicon infiltration into porous C/SiC preform fabricated by powder injection molding followed by impregnation with phenolic resin and carbonization. To optimize the ceramics densification process, effect of slurry composition, debinding conditions and the key parameters of all technological stages on the Si/SiC composite characteristics was studied. At the stage of molding the value of solid loading 87.5% was achieved using bimodal SiC powder and paraffin-based binder. It was found that the optimal conditions of fast thermal debinding correspond to the heating rate of 10 °C/min in air. The porous C/SiC ceramic preform carbonized at 1200 °C contained 4% of pyrolytic carbon and ~25% of open pores. The bulk density of Si/SiC ceramics reached 3.04 g/cm^3, silicon carbide content was 83–85 wt.% and residual porosity did not exceed 2%.

1. Introduction

Silicon carbide based ceramics is of considerable interest due to its high mechanical strength, thermal and chemical stability, radiation and thermal shock resistance [1–3]. Porous SiC ceramics is generally used for fabrication of filters and as a catalyst support [4,5]. However, dense silicon carbide ceramics has a wider application field which includes thermal power engineering (heating elements, burner nozzles), aerospace engineering (thermal protection, parts of engine nozzles, satellite optics), electronics and nuclear power engineering [6–9]. For a number of applications, high values of strength and thermal conductivity of SiC ceramics are required [2,10], which can be achieved at maximal density and minimal porosity of ceramics. Thus, one of the most important goals in this area is the production of dense SiC ceramics [7] with the properties close to those of bulk silicon carbide.

There is a number of methods to produce silicon carbide based ceramics with the density close to a theoretical value. Most convenient are methods of reaction bonding, pressure-assisted sintering (hot pressing sintering (HPS), spark plasma sintering (SPS), hot isostatic pressing) and pressureless methods including solid-state sintering and liquid phase sintering (LPS) [6,10–13]. The main advantages of pressure-assisted methods are rapid sintering, possibility of obtaining high density, purity and uniformity of ceramics. However, these methods are typically intended for producing ceramic parts of simple shapes. In case of complex shape fabrication, pressure-assisted methods involve significant challenges since silicon carbide is a hard-to-machine material because of extremely high hardness [8]. For the production of complex shape ceramics, the methods of pressureless sintering are preferable. Due to a strong covalent Si-C bond and low self-diffusion coefficient, silicon carbide ceramics is difficult to densify without external pressure, hence pressureless methods involve sintering additives such as B, C, B_4C, Al, AlN in solid state sintering and Al_2O_3-Y_2O_3 in LPS [7,13]. The latter one is widely used because of a relatively low sintering temperature. However, the process of LPS is accompanied by displacement and rearrangement of SiC particles, which results in volume shrinkage and dissolution of sharp edges [13,14]. Moreover, the use of additives leads to the occurrence of undesirable, in some cases, impurity phases. The reaction bonding method provides a possibility to avoid shrinkage during sintering and hence is preferable for complex shape fabrication, especially for large parts [15].

Generally, reaction bonding method accompanied by infiltration of a liquid or gaseous reactant into a porous ceramic preform is relatively easy to scale and allows production of complex shaped ceramic elements by machining prior to the densification stage [9,16–18]. As for silicon carbide based ceramics, free carbon containing porous SiC-matrix can be mechanically machined and then densified by siliconizing

* Corresponding author.
E-mail address: manilmsteen@tut.by (M.V. Kiyashko).

https://doi.org/10.1016/j.jeurceramsoc.2018.07.014
Received 12 March 2018; Received in revised form 6 July 2018; Accepted 11 July 2018

process. During high temperature siliconizing, chemical reaction occurs between free carbon inside the preform and the infiltrated molten silicon. Secondary silicon carbide formed during the reaction grows inside the pores and binds together the SiC particles of the preform. The rest of pores are filled with excess silicon. One of the most important things in the fabrication of such two-phase Si/SiC composite is to obtain silicon carbide based ceramics with maximal density and maximal amount of the silicon carbide phase.

The resultant content of silicon carbide in Si/SiC ceramics and, correspondingly, its bulk density, is strongly affected by the processing conditions on every stage, starting from the preparation of raw materials. Powder injection molding (PIM) is a well known and efficient method for fabrication of ceramic articles [19]. At the stage of the initial workpiece forming it is important to increase the amount of silicon carbide powder in a molded preform and to keep the content of binder as low as possible. On the other hand, the amount of binder should be enough to completely wet solid particles and to provide moldability, so there is a critical value of solid loading that depends mainly on the composition of slurry. For the preparation of low-viscosity slurry with elevated critical solid loading, low molecular weight organic compounds (beeswax, paraffin wax, etc.) are used as the base of the binder in combination with surfactants (typically stearic and palmitic acids) and optional thickening agents [19–21]. Along with the binder composition, characteristics of the SiC powder are important in the slurry preparation. Powders with controlled bimodal and even trimodal size distribution are used in PIM to increase the powder packing density and related properties [22,23].

At the next stage of the Si/SiC ceramics preparation, the organic binder should be carefully removed without the formation of any kind of defects to obtain a porous SiC matrix for following introduction of carbon into the pore space. In some cases, for example, in gel-casting methods, solid carbon is introduced directly into the workpiece at the molding stage by admixing to slurry [16,24]. This method significantly simplifies all the technological process but increases the slurry's viscosity, leads to reduction of solid loading and, correspondingly, to a decrease in the amount of silicon carbide in the final ceramics. To improve the properties of silicon carbide based ceramics, it is preferable to introduce carbon after the debinding stage by impregnation of porous SiC matrix with a phenolic resin with subsequent pyrolysis. Such a way enables one to introduce carbon uniformly throughout the volume and to improve mechanical properties of C/SiC preform [3]. Phenolic resins are widely used due to a high carbon-yielding ratio and the porous structure of carbon formed after pyrolysis, which is important for the subsequent siliconizing stage [25,26].

For efficient silicon infiltration into the pore space during siliconizing and the formation of a high silicon/carbon contact surface area, it is crucial to provide high open porosity of the C/SiC preform. Low open porosity can limit silicon penetration into carbon-containing pores thus leading to a high content of residual carbon and high porosity of the final ceramics. At the siliconizing stage either silicon vapor infiltration [16] or molten silicon infiltration [25,26] can be performed. Siliconizing in a melt allows simultaneous reaction sintering and filling the remaining pores with silicon, and therefore requires less time.

The present work is concentrated on the densification of reaction-bonded Si/SiC ceramics produced by a multistage process which includes the stages of injection molding, thermal debinding, phenolic resin impregnation, pyrolysis and, finally, siliconizing of the C/SiC preform. The objective of this study is to optimize key technological parameters and conditions at every production stage in order to achieve a high density of reaction bonded Si/SiC ceramics.

2. Experimental

The main stages of preparation of reaction-bonded Si/SiC ceramics are schematically shown in Fig. 1.

Two commercially available fractions of silicon carbide powder were used as raw materials: coarse M50 grade with characteristic grain size of 50 μm and fine M5 grade with grain size of 5 μm (Volzhsky Abrasive Works, Russia). Silicon carbide powder and thermoplastic binder on the base of paraffin wax and beeswax were mixed for 6 h and casted into the mold. All the specimens were disk-shaped with a diameter of 200 mm and thickness of 10 mm. The ratio of coarse and fine silicon carbide fractions, beeswax content in the binder, feedstock temperature and extruding pressure were varied for the optimization of the molding process.

Thermal debinding was carried out in air or in nitrogen atmosphere. In all cases, the specimens were submerged in a kaolin powder backfill previously calcined at 1000 °C in air. Heating parameters were varied in a wide range to obtain a maximal degree of binder removal without any kind of defects. Heating rate, temperature and time of debinding were varied in the ranges of 0.3–10 °C/min, 100–900 °C and 2–10 h, respectively.

Resolic resin-based Bakelite lacquer LBS-1 (plant named after Y. M. Sverdlov, Russia) was used for impregnation of debonded porous SiC matrix. The impregnation process was carried out at 40 °C to decrease the lacquer viscosity. The specimen was placed into the impregnation tank, which was then evacuated by a vacuum pump to residual pressure 1000 Pa and held for one hour at this condition. After that the Bakelite lacquer was delivered into the tank to a level that provides complete coverage of the specimen, and the residual volume was filled with nitrogen under excess pressure of 0.3–0.6 MPa. Nitrogen was used to avoid premature gelation of the resin in case of contact with atmospheric oxygen. The holding time was varied from 3.5 to 6 h.

After the impregnation stage the specimen was placed into an aerated drying cabinet, where impregnated phenolic resin was cured at 120 °C for 4 h. The subsequent carbonization was carried out by pyrolysis in two steps. The first pyrolysis step, accompanied by intensive gasification, was carried out in a nitrogen flow under ambient pressure at 700 °C for 2 h. The second, high-temperature step was performed in a vacuum furnace (VacETO, Russia) at the temperature of 1200 °C and pressure of 0.13 Pa for 2 h.

The same vacuum furnace was used for the final siliconizing stage, which was performed at the temperature of 1800 °C and pressure of 0.13 Pa for 4 h. The specimen was placed horizontally into a graphite crucible and covered with a uniform layer of electronic grade silicon powder (Semiconductor Plant, Ukraine), which was melted while heating up and penetrated into the porous structure of C/SiC preform. As the result of siliconizing the surface of the specimen became rough and non-uniform, so mechanical polishing was used to remove the residual silicon and provide appropriate conditions for further study of the ceramics. Fig. 2 displays the external appearance of specimens at the end of each preparation stage.

All the volumetric and mass changes were monitored in the process of specimen preparation. Generally, the volume was measured by the Archimedes method of water displacement, but in the case of undesirable water contact it was calculated from a geometrical model, which was obtained using optical 3D scanner HP David SLS-3. The accuracy of mass measurements was 0.3%. The relative error in the volume measurements was 0.3% for the Archimedes method and 1.5% in case of 3D model-based calculations. Similar measurements were performed to determine the bulk density of the binder, the phenolic resin after curing and the residue after curing and pyrolysis (in two stages, at 700 °C and 1200 °C) of the resin.

Open porosity of the ceramic specimens was measured at each preparation stage by the water absorption method. For these measurements, dry specimens were held in distilled water at 80 °C for 4 h inside an ultrasonic bath operated in pulse degassing mode. The open porosity was determined as the volume of absorbed water divided by the full volume of the specimen including pores.

Thermogravimetry analysis (TG) of Bakelite lacquer was performed by the NETZSCH STA449 F3 thermal analyzer from room temperature up to 950 °C in nitrogen atmosphere. Morphology, microstructure and