Rapid Sintering of Ceramics with Gradient Porous Structure by Asymmetric Thermal Radiation

Duan Li^{‡,§} and Zhijian Shen^{‡,§,*,†}

[‡]Berzelii Center EXSELENT on Porous Materials, Stockholm University, S-106 91 Stockholm, Sweden

[§]Department of Materials and Environmental Chemistry, Arrhenius Laboratory, Stockholm University, S-106 91 Stockholm, Sweden

In this study, thermal radiation was employed for sintering silicon carbide foams that achieved a gradient porous structure. The simultaneous use of graphite and carbon fiber reinforced carbon composite (C_f/C) radiators resulted in an axial temperature gradient of $\sim 600^\circ\text{C}$ along the cylindrical sample, as confirmed by both numerical simulation and experimental measurement. By sintering the cylinder top at 1600°C for 5 min, the porous SiC body achieved an axial pore size gradient from $\sim 106 \pm 36\ \mu\text{m}$ to $\sim 250 \pm 84\ \mu\text{m}$ and an open porosity from 41.4 to 79.8 vol%. This work indicates the potential of sintering by intense thermal radiation technique for rapid manufacturing functionally graded materials through asymmetric assembly of thermal radiators.

I. Introduction

SILICON carbide ceramic foams with various pore architectures have received extensive studies during recent years.^{1–13} The unique combination of properties such as good mechanical strength (both at R.T. and high temperature), excellent thermal shock resistance, low thermal expansion coefficient, as well as superior chemical/corrosion resistance enables their potential applications as gas/liquid/particle filters,^{2–5} catalyst support,^{6,7} separation membranes,^{8,9} thermoelectric conversion devices,^{10,11} luminescent materials,¹² solar thermal collectors,¹³ etc.. It is a challenging task to prepare solid silicon carbide foams combining good rigidity and designed porosity because the consolidation of the precursor foams by conventional pressureless sintering requires high sintering temperature and long holding time due to the strong covalent nature of the Si–C bond.^{14,15} In our previous works, intense thermal radiation was utilized for rapid sintering of ceramic materials in a modified spark plasma sintering (SPS) apparatus.^{4,16–19} Strong necks among crystalline grains were formed within only minutes' dwell. In this work, we attempted to rapidly sinter silicon carbide foams with gradient porous structure. To achieve this goal, both graphite and carbon fiber reinforced carbon (C_f/C) composite radiators were simultaneously used to introduce an axially gradient temperature distribution. Sintered SiC foams with a gradient porous structure were achieved by 5 min dwell at 1600°C . Different parts of the sintered samples were taken for further characterizations.

Silicon carbide foams were prepared by a protein-based gel-casting method; see the details in Supporting Information. The obtained cylindrical green bodies have an average size of $\sim \Phi 15\ \text{mm} \times 24\ \text{mm}$ (Diameter $\times$ Height). A finite element method (FEM)-based commercial software package, COMSOL Multiphysics, was employed for simulation. The assumptions and parameters used in the modeling are listed in Supporting Information. Sintering experiments were performed in a modified SPS apparatus (Dr. Sinter 2050; Sumitomo Coal Mining, Tokyo, Japan) under vacuum. The die was heated to 1600°C with a heating rate of $200^\circ\text{C}/\text{min}$ and a dwell time of 5 min. A small mechanical pressure ($\sim 5.6\ \text{kN}$) was applied to ensure a good electric contact and current path. Two radiation thermometers were used to measure temperatures [see Fig. 1(a)]: one is for regulating the sintering program (T_1 , located on the top die surface close to the C_f/C radiator) while the other is to measure the temperature of the bottom radiator (T_2). Different fragments taken from top (close to the C_f/C radiator) to bottom (close to the graphite radiator) of the sintered SiC foam were sampled for further characterizations. The pore morphology was characterized by a field-emission scanning electron microscope (FE-SEM; JSM-7000F, JEOL, Tokyo, Japan). The cell size was measured by using the linear intercept method based on SEM images (ASTM E0112-10). Mercury intrusion porosimetry (Micromeritics AutoPore III 9410; Norcross, Georgia) was used to determine the porosity and pore size distribution. The surface tension and the contact angle of the mercury were set to $0.485\ \text{N/m}$ and 130° , respectively. The open porosity values of bottom and top parts were calculated from the porosimetry results by assuming that the theoretical density of $\text{SiC}-\text{Al}_2\text{O}_3-\text{Y}_2\text{O}_3$ system (mass ratio 1:0.05:0.05) is $3.29\ \text{g}/\text{cm}^3$ according to the mixing rule.

The model for both simulation and experiment is described in Fig. 1. The modified SPS system consisted of four parts: two inconel electrodes connected with water-cooling plates ($\Phi 120 \times 90$), six symmetrically located graphite spacers ($\Phi 150 \times 20$, $\Phi 120 \times 20$ & $\Phi 100 \times 20$), two asymmetrical radiators (top: C_f/C , $\Phi 45 \times 18$; bottom: graphite, $\Phi 60 \times 15$), and one hollow graphite die with a cylindrical sample centered inside [see Fig. 1(a)]. Graphite felts were used at different positions: surrounding the outer wall of the die (to reduce heat loss by radiation to the environment), surrounding the inner wall of the die (to insulate the radiation between the inner wall of the die and the sample, $\sim 8\ \text{mm}$ from the top), and under the sample (for supporting the sample and minimize the conductive heat transfer from the graphite radiator to the sample), respectively. The amount of Joule heat (Q_{Joule}) and the net heat gain (Q) of the radiators during sintering can be calculated using the equations:

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*Member, The American Ceramic Society

†Author to whom correspondence should be addressed. email: shen@mmk.su.se

Fig. 1. (a) Schematic details of the stationary model with a fixed geometry used for simulation and (b) the image of the core part during sintering (Unit: mm).

$$Q_{\text{Joule}} = I_{\text{eq}}^2 R t \quad (1)$$

$$Q = \gamma_{\text{p,m}} \Delta T \quad (2)$$

where I_{eq} is the equivalent electric current, R is the electric resistance, t is the time, $\gamma_{\text{p,m}}$ is the specific heat at constant pressure, and ΔT is the temperature increase. When sintering equilibrium is reached, $Q_{\text{Joule}} \approx Q$; from Eq. (1) and (2) a new Eq. (3) can be obtained:

$$\Delta T = \frac{R}{\gamma_{\text{p,m}}} I_{\text{eq}}^2 t \quad (3)$$

As $I_{\text{eq}}(C_f/C) = I_{\text{eq}}(\text{graphite})$, $R(C_f/C) > R(\text{graphite})$, and $\gamma_{\text{p,m}}(C_f/C) < \gamma_{\text{p,m}}(\text{graphite})$, the temperature increase in C_f/C radiator (ΔT) is larger than that of the graphite radiator. It means that at any time the C_f/C radiator would be “hotter” than the graphite radiator and a temperature gradient is generated axially between the two radiators. In the image during sintering, the C_f/C radiator is much brighter (hotter) than the graphite radiator, see Fig. 1(b). The strong brightness contrast proves the occurring large temperature difference.

To evaluate the temperature distributions within the asymmetric heated samples, an FEM simulation was performed using a stationary model (without considering the dwell time) at $T_1 = 1600^\circ\text{C}$ and the results are summarized in Fig. 2. It can be observed that the temperature distribution over the radiators and die is asymmetric [see Fig. 2(a)], and different from the previous models.¹⁹ The maximum temperature of the C_f/C radiator is about 1600°C , while that of the graphite radiator is below 800°C . Heating of the radiators gave out thermal radiation with different intensities in direct proportion to the fourth power of the temperature, thus the amount of energy emission at high temperature is considerable.²⁰ With radiative heat transfer from the radiators, the maximum temperatures of different parts of the sample are 1328°C (top) and 610°C (bottom), respectively [see Fig. 2(b)]. The temperature decrease axially from the top to the bottom along the sample is near linear, as revealed by the line graph in Fig. 2(c). All the simulation results predict the formation of a large temperature gradient in both radiators and the sample.

Sintering experiments for rapid consolidation were conducted using the simulated model. The real temperatures (T_1 and T_2) were measured during the entire sintering process with 5 min dwell time. The result in Fig. S1 suggested that $\Delta T (= T_1 - T_2)$ was increased rapidly with temperature rise to 1600°C and started to decline during the prolonged dwell time. Although the real temperature difference between the sample top and bottom parts is difficult to measure, it can be still estimated to be $\sim 600^\circ\text{C}$ based on the ΔT values.

The morphology and pore properties from the top and bottom parts of the sample after sintering were evaluated, see the results in Figs. 3 and 4. A series of pore morphology images in Figs. 3(a)–(d) indicate that all parts kept the macroporous structure. However, measurement of the pore cell size revealed significant differences from the top to bottom: $106 \pm 36 \mu\text{m}$ [Fig. 3(a)], $122 \pm 32 \mu\text{m}$ [Fig. 3(b)], $169 \pm 41 \mu\text{m}$ [Fig. 3(c)] and $250 \pm 84 \mu\text{m}$ [Fig. 3(d)]. The porous structure with the pore size gradient resulted from the temperature differences that were generated by different thermal radiation intensities and is in accordance with the simulation results. It can be also seen that the struts of the top parts [Figs. 3(a) and (b)] are more rigid than the bottom parts [Figs. 3(c) and (d)]. The reason is that with a dwell at 1600°C , the real temperature of the top part is sufficiently high for neck formations between SiC grains under the liquid-phase sintering condition. In contrast, nonsintering occurred for the bottom part at a much lower temperature ($\sim 1000^\circ\text{C}$). Further, the pore size distribution profile of top and bottom parts determined by mercury porosimetry is illustrated in Fig. 4. For the bottom part, the open porosity is 79.8 vol% and two populations of pores were detected: larger pores with dimensions 10–100 μm (related to the cell windows and occasional macrodefects) and smaller pores with sizes ranging 0.1–1 μm (related to the residual porosity). In comparison, the top part which was better sintered possessed less open porosity (41.4 vol%). It also displayed a narrower pore size distribution within the 10–100 μm range and almost eliminated 0.1–1 μm porosity (due to sintering). All observations have proved that asymmetric radiation conditions favored the formation of gradient structures characterized by different open porosity levels, pore sizes, and their size distribution.

II. Conclusions

In conclusion, an asymmetric intense thermal radiation approach was employed for rapid sintering of porous SiC green bodies resulting in solid foams with the axially gradient porous structure. By using both C_f/C composites and graphite as radiators, radiative heat transfer was generated asymmetrically. The resulting temperature gradient from the

Fig. 2. Simulation results depicting the gradient temperature distribution of the stationary model at $T_1 = 1600^\circ\text{C}$: (a) overall system (max.: 1600°C), (b) the radiation surfaces of the sample (1328°C – 610°C), as well as the (c) temperature change in the cylinder center along the axial direction from top to bottom.

Fig. 3. A series of SEM images of taken from top to bottom of the silicon carbide foam sintered at $T_1 = 1600^\circ\text{C}$ with 5 min dwell. The inset is the optical image of the sintered bulk sample.

top to the bottom part of the sample was estimated to be $\sim 600^\circ\text{C}$ at the sintering temperature, as revealed by both simulation and experimental results. The sintered SiC foam possessed both an axial pore size gradient (from

$\sim 250 \pm 84 \mu\text{m}$ down to $\sim 106 \pm 36 \mu\text{m}$) and decreased open porosity (from 79.8 to 41.4 vol%). The findings demonstrated that this sintering approach is efficient for rapid fabricating of functionally graded materials.

Fig. 4. The measured pore size distribution of specimens collected at the top and bottom parts of the sintered silicon carbide foam.

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Supporting Information

Additional Supporting Information may be found in the online version of this article:

Data S1. The experimental data for T1-T2 & T1 evolution during sintering to 1600°C with 5 min dwell (T in °C).

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