Journal of the European Ceramic Society 7 (1991) 243–247

Hot Isostatic Pressing of Presintered Silicon Carbide Ceramics

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(Received 17 September 1990; revised version received 7 November 1990; accepted 13 November 1990)

Abstract

The influence of encapsulation free post-hipping on the density, strength and Weibull modulus of pressureless sintered α-SiC ceramics was studied. The SiC was doped with B_4C and C (solid-state sintered) or with B_4C, C and Al_2O_3 (liquid-phase sintered). Density could be increased when the open porosity in the presintered compact was less than 0·6%, i.e. above 92% of the fractional density. Strength increased with post-hipping temperature from 1850 to 2000°C by 18%. Prolongation of the time resulted in a pronounced increase in the Weibull modulus from 7·2 before up to 18·3 after post-hipping for 120 min at 1850°C.

Drucklos gesintertes α-SiC wurde ohne Kapselung einer Nach-HIP-Behandlung unterzogen. Für dieses Material wurde die Dichte, die Festigkeit und der Weibull-Modul bestimmt. Das SiC wurde entweder mit B_4C und C (Festkörpersintern) oder mit B_4C, C und Al_2O_3 (Flüssigphasensintern) dotiert. Die Dichte konnte dann gesteigert werden, wenn die offene Porosität im vorgesintern Preßling kleiner als 0·6% bzw. über 92% th.Dichte lag. Die Festigkeit nahm mit zunehmender Nach-HIP-Temperatur von 1850 bis 2000°C um 18% zu. Eine Verlängerung der HIP-Zeit führte zu einem deutlichen Anstieg des Weibull-Moduls von ursprünglich 7·2 auf 18·3 nach einer 120 min Nach-HIP-Behandlung bei 1850°C.

On a étudié l'influence du pressage isostatique à chaud sans encapsulage consécutif au frittage naturel (post-hipping) sur la densité, la résistance mécanique et le module de Weibull d'échantillons de α-SiC. Le SiC était dopé par B_4C et C (frittage en phase solide) ou par B_4C, C et Al_2O_3 (frittage en phase liquide). On observe un gain de densité lorsque la porosité ouverte de l'échantillon pré-fritté est inférieure à 0·6%, c'est à dire lorsque sa densité est supérieure à 92% de la densité théoretique. La résistance mécanique croît de 18% lorsque la température de post-hipping passe de 1850 à 2000°C. Un prolongement du temps de maintien entraîne une nette amélioration du module de Weibull: celui-ci, qui a une valeur initiale de 7·2 atteint 18·3 lors d'un traitement de post-hipping de 120 min à 1850°C.

1 Introduction

Silicon carbide has been identified as a promising candidate for high-temperature applications because of its unique combination of properties, such as excellent high-temperature strength and creep resistance, good corrosion and oxidation resistance and low specific weight.[1] Due to the highly covalent character of the silicon–carbon bond (>85% according to Pauling), however, sintering additives like B, Al, C, or their compounds Al_4C_3, B_4C, AlB_2 are required to accelerate diffusion-controlled sintering and to achieve nearly theoretical density.[2–4] Pressureless sintering and hot pressing are still the major fabrication technologies for structural parts.[5] While long sintering times and high temperatures promote the formation of a

Journal of the European Ceramic Society 0955-2219/91/$3.50

coarse and uneven microstructure in pressureless sintered materials, only simple shaped parts can be produced by hot pressing.[6] The development of hot isostatic pressing (HIP) technology, however, makes the reduction of sintering time and temperature possible so that complex parts may be densified without abnormal grain growth. Thus, hot isostatic pressing allows near net shape forming and the resulting microstructure is characterized by a fine grain size resulting in improved strength with reduced scattering.

Starting from the porous green compact a gas-tight container has to be used to transmit the gas pressure to the compact.[7] Various encapsulation techniques exist to encapsulate the compact with refractory metals or glasses. Without encapsulation the compacts have to be presintered to close open porosity followed by post-hipping. Alternatively, a combined multistep process called sinter–hip may be applied.[8] Due to the reduction of residual porosity and grain size density, the strength and Weibull modulus of SiC were found to be significantly improved by hot isostatic pressing.[9,10]

The object of the present work is to point out the effects of post-hipping on the microstructure formation of presintered silicon carbide. Density, fracture strength and Weibull modulus are evaluated for two different silicon carbide materials doped with boron carbide, carbon and alumina, respectively.

2 Experimental Procedure

An α-SiC powder with a specific surface area of 20 m^2/g and a mean grain size of approximately 1 μm was used (Grade 7, Wu-Xi Grinding Wheel Works, China). The composition of the SiC powder in wt% was Si (total) 68·45, Si (free) 0·87, C (total) 29·12, C (free) 1·04, O (total) 1·27, Al_2O_3 0·22 and Fe_2O_3 0·12. Two different samples were prepared: SiC(I) contains 96·4 wt% α-SiC, 0·6 wt% B_4C, and 3 wt% C; SiC(II) additionally contains 0·6 wt% Al_2O_3 balanced by slightly lower α-SiC content of 95·8 wt%. The mean grain size was 1 and 3 μm for Al_2O_3 and B_4C, respectively. The powder blends were mixed with ethanol in a polyethylene ball mill for 48 h, dried and finally sieved through a 100-mesh screen. Rectangular specimens of 45 mm × 8 mm × 6 mm were uniaxially pressed in a carbon steel die at a pressure of 3 MPa and subsequently cold isostatically pressed at 200 MPa. Density of the green compact achieved 1·93–1·99 g/cm^3 which corresponds to 60–62% of the theoretical density (3·21 g/cm^3) of SiC.

The specimens were sintered in a carbon resistance furnace under pure argon atmosphere at 2100°C for 60 min. After sintering modulus of rupture (MOR) test bars (36 mm × 4 mm × 3 mm) were prepared by diamond cutting and grinding. The bars were post-hipped with argon under 180 MPa. Sample I was given a 60 min soak at a temperature of 1850, 1900 or 2000°C, whereas sample II was post-hipped for 30, 60 and 120 min at 1850°C.

The density ρ of the presintered or post-hipped sample was determined according to the Archimedean principle in distilled water at 25°C:

$$\rho = \frac{m_3 \rho_w}{m_2 - m_1} \tag{1}$$

where ρ_w is the density of water and m_1, m_2 and m_3 are the weights of the sample in water, in air after removing water only from the sample surface, and in air after drying the sample in an oven at 120°C for 6 h, respectively. The volume fraction of open porosity accessible to water penetration, P_0, was calculated directly from the density measurements according to

$$P_o = \frac{m_2 - m_3}{m_2 - m_1} \tag{2}$$

The modulus of rupture of the diamond-ground specimens was measured by three-point bending tests with a 30 mm span at a crosshead speed of 0·5 mm/min. The microstructure of the polished and subsequently etched (Murakami agent) as well as the fractured surfaces was analysed by SEM. Crystalline inclusions in the sintered SiC were identified by XRD.

3 Results and Discussion

3.1 Density and porosity

Figure 1 shows the effect of post-hipping for 60 min at 2000°C under 180 MPa on the density of the

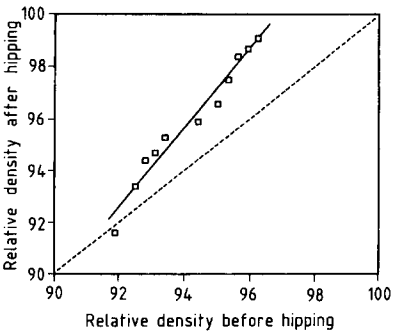


Fig. 1. Effect of post-hipping on density of pressureless-sintered SiC(I).

presintered sample I. For presintered samples with a fractional density less than approximately 92% no increase of density could be obtained, whereas for samples above 98% full density is achieved by post-hipping. Between 92 and 98% an increasing fraction of closed porosity in the presintered microstructure promotes a linear density increase with fractional density of the presintered material. While in the low-density region porosity P decreases according to the increase of the fractional sintered density ρ_s/ρ_{th}

$$P = 1 - \frac{\rho_s}{\rho_{th}} \tag{3}$$

in the post-hipping sensitive density interval above $\rho_s/\rho_{th} \approx 0{\cdot}92$ the total porosity may be separated into a decreasing open, P_o, and an increasing closed fraction, P_c,

$$P_o = 1 - \frac{\rho_h}{\rho_{th}} \qquad P_c = \frac{\rho_h}{\rho_{th}} - \frac{\rho_s}{\rho_{th}} \tag{4}$$

where ρ_s and ρ_h are the densities of the presintered and the post-hipped compacts, respectively, and ρ_{th} denotes the theoretical density of silicon carbide (3·21 g/cm^3). Figure 2 shows the differences in porosity distribution in the presintered sample I. Table 1a lists the fractional density, open porosity and MOR for sample I which was post-hipped at different temperatures. With increasing temperature the final density as well as the open porosity increase slightly.[11] For sample II, the density was notably increased from 91·2 to 96·3% by post-hipping under 200 MPa at 1850°C for 60 min (Table 1b). Though the density of the presintered sample II was only 91·2%, a very small fraction of open porosity of 0·6% was found. From XRD analysis traces of mullite ($Al_2O_3 . SiO_2$) were identified, suggesting that during sintering a small amount of aluminium silicate liquid was formed by reaction of the Al_2O_3 with the SiO_2 present on the SiC-particle surface. Thus the intergranular liquid phase and the small fraction of open porosity may have supported the densification during post-hipping.

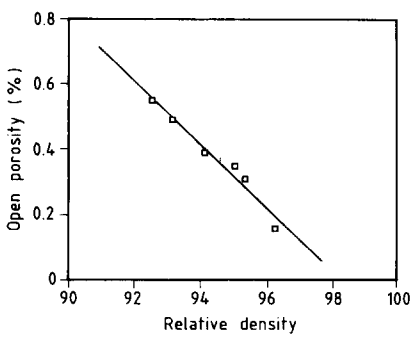


Fig. 2. Open porosity versus fractional density for pressureless-sintered SiC(I).

Table 1a. Open porosity, relative density and room-temperature strength of SiC(I) at different hipping temperature for 60 min

Condition	*Before hipping*	*After hipping*		
		1850°C	*1900°C*	*2000°C*
Open porosity, %	0·46	0·46	0·50	0·50
Relative density, %	93·1	93·8	93·8	95
Bending strength, MPa	326 ± 44	349 ± 47	382 ± 45	386 ± 50
Strength increase, %	—	7·1	17·2	18·4

Table 1b. Open porosity, relative density and room-temperature strength of SiC(II) at 1850°C for various times

Condition	*Before hipping*	*After hipping*		
		30 min	*60 min*	*120 min*
Open porosity, %	0·47	0·47	0·47	0·48
Relative density, %	91·2	92·8	96·3	96·1
Bending strength, MPa	354 ± 44	366 ± 48	396 ± 53	384 ± 51
Strength increase, %	—	3·4	11·9	8·5

The small increase in open porosity found after post-hipping indicates that post-hipping was incapable of healing or closing the open pores. SEM observation of the polished surfaces of post-hipped SiC ceramics revealed that subsurface pores had collapsed to form craters (some craters are a local depression in the surface, others puncture) as schematically shown in Fig. 3.[12] The collapsing of subsurface pores resulted in a slight increase of open porosity. Moreover, Tables 1a and 1b indicate that the density of both presintered samples I and II was increased although the open porosity was not

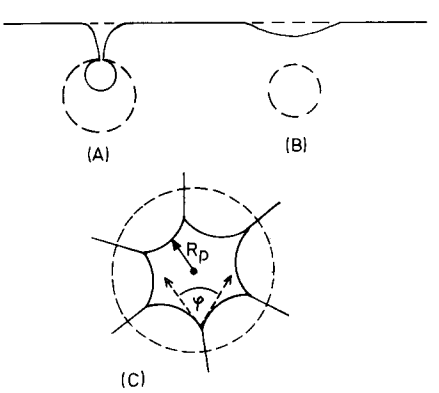


Fig. 3. Scheme of post-hipped pore structure showing (A) punctures associated with near surface pores, (B) surface dippling and (C) residual pores.

reduced after post-hipping. This evidence supported the conclusion that post-hipping can eliminate some residual closed pores in the sintered ceramic. From the fractured surfaces given in Fig. 4 it may be concluded that small pores can be eliminated but large voids can only be reduced in size.

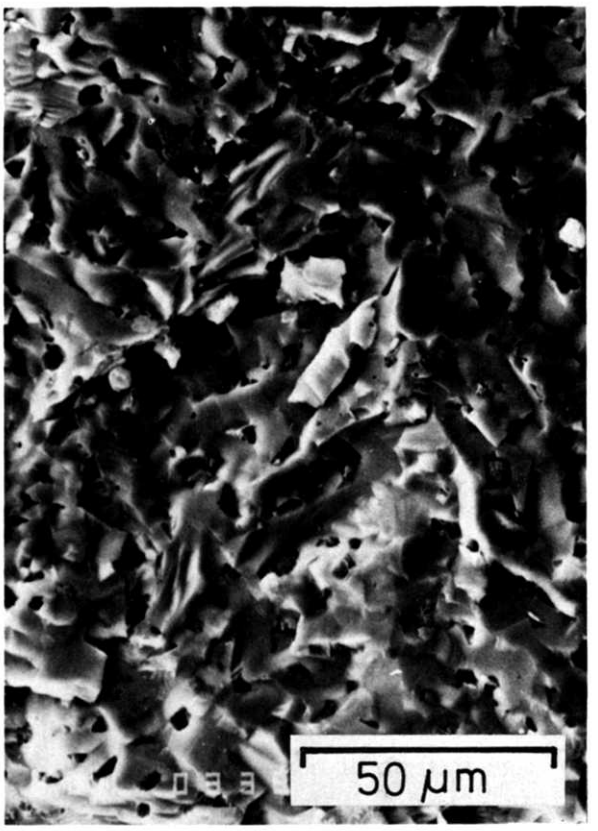
For thermodynamically stable pores (e.g. pores with a size/pore coordination larger than a critical pore size/pore coordination number[13] the equilibrium pore radius R_p is the minimum attainable pore radius which changes with applied HIP pressure σ_a as[12]

$$R_p = \frac{\cos(\phi/2 + \pi/2)}{(\sigma_a/\gamma_s + 2/D\cos(\phi/2))} \quad (5)$$

where ϕ is the dihedral angle and γ_s the surface energy at the pore curvature in a material of mean grain diameter D. Using $\gamma_s \approx 1850\ \mathrm{mJ/m^2}$ for pure SiC at 1430°C,[14] an R_p value of less than 10 nm is calculated from eqn (5) for the applied HIP pressure at $\phi = 2\pi/3$. In the case of the Al_2O_3-containing SiC(II), γ_s will be significantly smaller (for Al_2O_3 at 1850°C $\gamma_s \approx 900\ \mathrm{mJ/m^2}$,[14] which results in an equivalent reduction of R_p due to the dominance of the factor σ_a/γ_s in eqn (5). Thus the higher density increment of SiC(II) over SiC(I) observed upon hipping may be explained by a smaller residual pore size, as was confirmed by SEM examination of fractured surfaces. Only pores of subcritical radius/pore coordination number ($n_c \approx 2\pi/(\pi - \phi)$) may be eliminated whereas larger pores will only be reduced in size. This is the reason why the theoretical density can not be obtained even by post-hipping.[15] Extended grain growth, however, decreases the pore coordination number so that further elimination of pores may occur at higher temperatures or longer soaking time.[13]

3.2 Strength

The effect of post-hipping (180 MPa, 2000°C, 60 min) on the strength distribution of sample I according to Weibull statistics[16] is shown in Fig. 5. While a substantial increase of mean fracture stress by 18% after post-hipping was found, no positive effect on the Weibull modulus is seen. The scatter in strength is attributed to a scatter in pre-existing flaw sizes which is based on the weakest link theory that the fracture is controlled by the weakest defect of all the defects present in the system. Thus post-hipping of sample I is suggested only to result in a mean reduction of defect size, whereas defect size distribution remains unchanged. Other strength-limiting defects such as coarse grains, inclusions and second-phase particles will not be influenced in size by post-hipping.



(a)

(b)

Fig. 4. SEM micrograph of the fracture surface of sintered SiC(II); (a) before post-hipping and (b) after post-hipping.

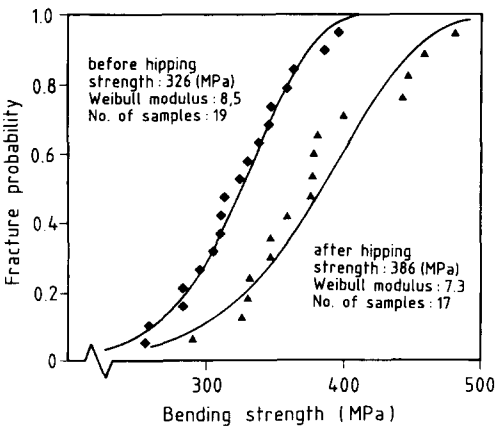


Fig. 5. Effect of post-hipping on strength distribution of pressureless-sintered SiC(I) before and after post-hipping.

While post-hipping of sample I at 2000°C resulted in an increase of mean strength by 18% over the presintered specimen, no influence on strength was observed at 1850°C (Table 2). Prolonged post-hipping time, however, brought a substantial increase in the Weibull modulus from 7·2 for the presintered to 18·3 for the specimen post-hipped for 120 min at 1850°C. A reduction of strength scatter may be attributed to diffusion-controlled elimination of small-sized pores due to grain growth during prolonged post-hipping, resulting in a reduced defect size distribution.

4 Conclusions

Post-hipping of presintered SiC resulted in a density increase with increased fraction of closed porosity, e.g. above approximately 92% of the fractional presintered density. While sample I is supposed to densify via a solid-state sintering process, a small amount of liquid phase is present in sample II. At the same presintered density the fraction of open porosity is less in the liquid-phase sintered material as indicated by the higher density increment upon post-hipping. The strength increased with post-hipping temperature from 1850 to 2000°C by 18% and exhibited a maximum at 60 min soaking time at 1850°C. Prolongation of post-hipping time also resulted in a pronounced increase in the Weibull modulus from 7·2 before up to 18·3 after post-hipping for 120 min at 1850°C.

Table 2. Effects of post-hipping on strength and Weibull modulus of sintered SiC(I) with lower density (at 1850°C)

Condition	*Before hipping*	*After hipping*		
		30 min	*60 min*	*120 min*
Relative density, %	87·2	87·5	86·9	86·9
Bending strength, MPa	299 ± 44	296 ± 33	297 ± 29	295 ± 21
Weibull modulus	7·2	9·3	10·4	18·3

Acknowledgement

Financial support from the German Science Foundation (DFG) and the Natural National Science Foundation of China (NNSFC) is gratefully acknowledged.

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