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Investigation of compaction and sintering behavior of SiC powder after ultra-fine treatment*

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Abstract: Silicon carbide ceramics were prepared with SiC powder treated by the fluidized bed opposed jet mill as raw materials, and the effects of the ultra-fine treatment mechanism on the compaction and sintering behavior of SiC ceramics were investigated. The results showed that the compacts had higher density and microstructure homogeneity when the sintering temperature of the compact was decreased; and that the surface microstructure, densification and mechanical properties of the sintered body could be ameliorated obviously.

Key words: SiC ceramic, Ultra-fine treatment, Compaction efficiency, Sintering behavior
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INTRODUCTION

In powder compaction, the characteristics of the powder affect the compaction behavior and the quality of the pressed green body and its relative density, porosity, pore size distribution, sintering and the consequent microstructure of the final sintered body. Superfine powder is prerequisite for preparing high performance ceramic materials (Liu, 1996; Lange *et al*., 1983; Lange, 1989). At present, most of the chemosynthesis methods are not suitable for preparing industrial superfine powder. Ultra-fine treatment of materials is essential and has become a new developing direction (Vaßen *et al*., 1995; 1996).

As a high-temperature structural material, silicon carbon (SiC) ceramics offer many advantages and have promising applications (She and Ueno, 1999; Biswas and Rixecker, 2001; Giuseppe and Giancarlo, 2001). Industrial SiC powders usually have large particle size, wide particle-size distribution, obvious agglomeration, etc. Industrial SiC powder must be treated in order to reduce the particle size and get uniform particle size distribution.

This paper reports ultra-fine treatment of industrial SiC powder by fluidized bed opposed jet mill. The compaction and sintering behavior of ultra-fine treated powder and the microstructures and mechanical properties of sintered SiC ceramics made from the ultra-fine treated powder were investigated.

EXPERIMENT DETAILS

Industrial SiC powder (provided by Zhejiang Dongxin Seal Limited Company, Wenzhou, China) was ultra-fine treated on the QLM-80K fluidized

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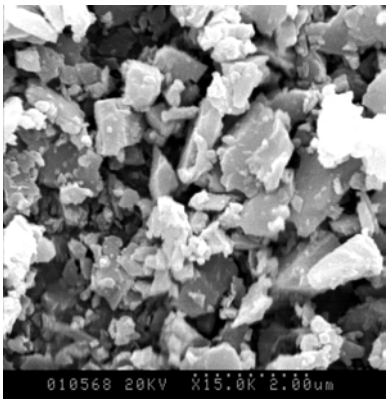
bed opposed jet mill (Zhejiang Shangyu Heli Powder Limited Company, Shangyu, China). The crushing pressure was 0.6 MPa, the sorter frequency was 40 Hz and the milling was performed one time for each batch of powder. The average particle sizes of the powders before and after treatment (Fig.1) were 3.01 μm and 0.75 μm, respectively.

The treated SiC powder (90 wt%) and the additives (B, C) were mixed in ethanol using high-purity α-SiC milling media. After drying in air at 70 °C, the powder mixture was uniaxially compacted to green bodies at 250 MPa. Pressureless sintering was conducted in a vacuum furnace at sintering temperature of 2000~2200 °C for 1~2 h. After the sintering, the samples were finished by machining.

The actual density and porosity were measured through the conventional water-displacement method.



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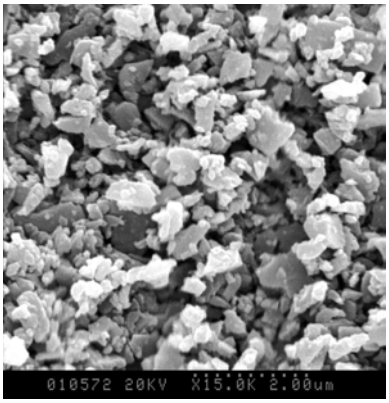


(b)

Fig.1 SEM micrographs of the SiC powders
(a) before treatment; (b) after treatment

The surface morphologies of the sintered bodies were observed by scanning electron microscopes (SEM Cambridge Stereoscan-600 and HITACHI S-570). The hardness and fracture toughness were measured by the Vickers indentor with 10 kg load. The flexural strength was measured by three-point bending tests with span of 30 mm and the cross-head speed of 1 mm/min.

RESULTS AND ANALYSIS

The moulding properties of the SiC powder green body before and after treatment is given in Table 1 showing that the water absorption and apparent porosity of the SiC green body after treatment are evidently less than those before treatment; and that the bulk density of the SiC green body after treatment is obviously higher than that before treatment. The morphology of the green body's fracture surface before treatment is coarse, with many large pores, agglomerates and holes, whereas the fracture surface after treatment is smooth with little porosity and has uniform particle sizes, as shown in Fig.2. It is certainly helpful for sintering that the compact has high density, few pores, and uniform pore size distribution. Ultra-fine treatment of the powder is beneficial for increasing the compact efficiency of SiC powder.

Table 1 Moulding properties of SiC compact

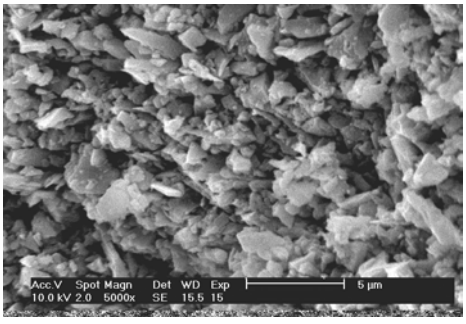
Characteristics	Before treatment	After treatment
Water absorption (%)	24.0	18.02
Apparent porosity (%)	45	33.56
Bulk density (g/cm^3)	1.57	1.76
Relative density (%)	49.5	55.5

The sintering of the compacts made before and after the treatment was conducted at the same sintering temperature. The micrograph (Fig.3b) of the sintered SiC body made from the treated powder reveals that there exist an "oversintering" phenomenon with larger crystal size and low relative density (83.5%). The treated powder compact was tiptop sintered at temperature decreasing by 50~100 °C, under which condition the densificat-

ion of the sintered body increased obviously. This proved that reduction in the number of powder particles and homogenization of particle size decreased with sintering temperature. Fig.3a and Fig.4 show that the surface of the SiC sintered body after treatment had fewer and smaller voids or pores than those before treatment and confirms that the powder particle size and the microstructure homogeneity of the compacts decreased with sintering temperature.

The sintering properties of the final SiC sintered body before and after treatment are given in Table 2 showing obviously that the water absorption and apparent porosity of the final SiC sintered body after treatment were less than those before treatment; and that the density, hardness, toughness and strength were all higher than those before treatment.

The existence of some micropores on the fracture surface of the SiC ceramics (Fig.5) is considered to be related to the rate of pores removal. During sintering, the rate of crystal boundary migration is quicker than that of pores removal. If there is not enough time for some pores to be remo-



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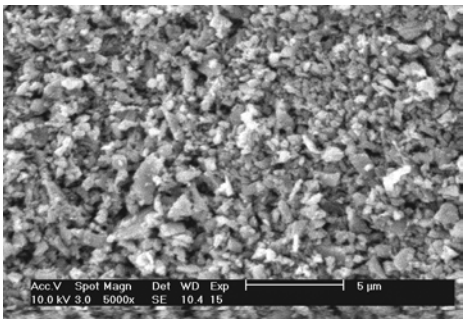
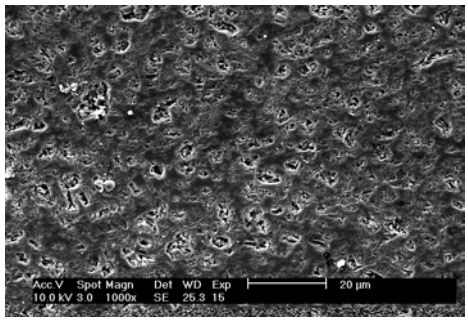


(b)

Fig.2 SEM micrographs of green body with the powder
(a) before treatment; (b) after treatment

Table 2 Properties of SiC sintered body

Characteristics	Before treatment	After treatment
Water absorption (%)	0.15	0.07
Apparent porosity (%)	0.21	0.05
Bulk density (g/cm^3)	3.05	3.12
Relative density (%)	95.31	97.5
Hardness (GPa)	20.5	26.0
Fracture toughness (MPa·m$^{1/2}$)	3.1	3.8
Bending strength (MPa)	353	420



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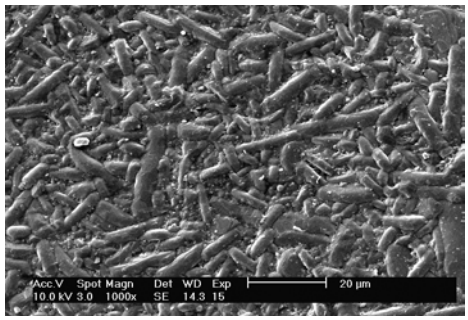


(b)

Fig.3 SEM micrographs of surface of SiC ceramic at same sintering temperature
(a) before treatment; (b) after treatment

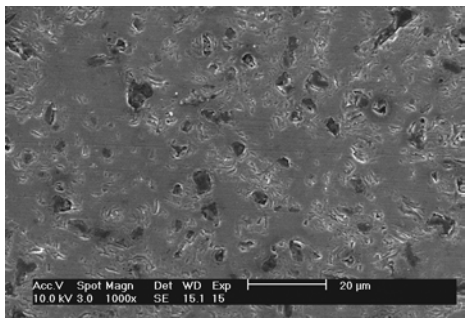
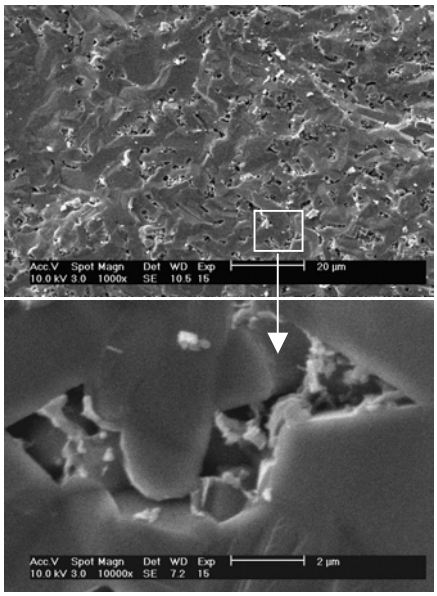


Fig.4 SEM micrograph of surface of SiC ceramic after treatment at lower sintering temperature

ved, the pores are closed in the solution to form micropores, which is one of the main reasons that the sintering body cannot reach complete densification. The crystal size of the ceramics is larger than the particle size of the powder, which is 2~5 μm. Fig.5b shows that the fracture surface of the SiC ceramics made from the powder after treatment was smoother than that before treatment (Fig.5a); and that the size and quantity of micropores were smaller and less than those before treatment. The ceramic fracture mode before treatment was of along-granular and trans-granular character, while the fracture mode after treatment was predominantly trans-granular.



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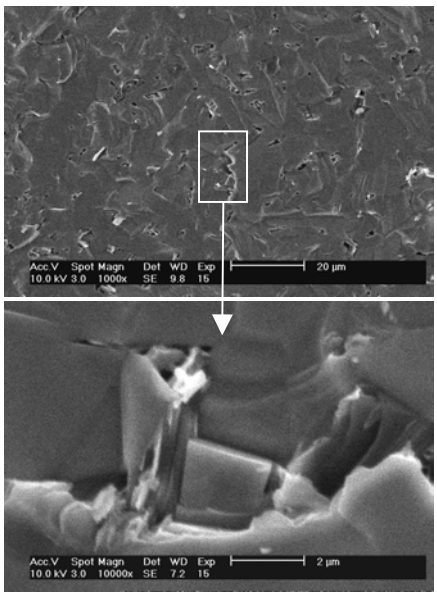

(b)

Fig.5 SEM of fracture surface of SiC sintering body
(a) before treatment; (b) after treatment

DISCUSSION

Sintering is aimed at densifying the powder or compacts and affects the properties and microstructure of the sintered body or ceramics. At the initial stage of the sintering, the crystalline particles reset and contact each other as described by Eq.(1) and the diffusion promotes the local balance of the network between crystalline boundary and pores.

$$\cos(\theta/2) = \gamma_b/2\gamma_s \tag{1}$$

The sintering conditions of diffusion is described by Eq.(2)

$$\gamma_b/\gamma_s < \sqrt{3} \tag{2}$$

wherein θ is the crossing angle of pore surface and boundary, γ_b is crystalline boundary energy, γ_s is surface energy. During the middle stage of the sintering, the transferring of all crystal particles ceases; the substance inside the crystal transfers surfaceward through diffusion of the crystal lattice or boundary to shrink the compacts, narrow the pore channels and form close pores. At the later stage of the sintering, the crystalline particles grow, and the pressure in pores increases to stop the shrinking. During the three sintering stages, without outside force, the sintering potential energy $\overline{\Delta u}$ is described by Eq.(3).

$$\overline{\Delta u} = \phi\varphi\frac{\gamma_s\partial A_s + \gamma_b\partial A_b}{\partial V} < 0 \tag{3}$$

wherein ϕ is efficiency factor, φ is atom-volume, A_s is whole pore surface area, A_b is whole crystal boundary area, V is powder volume.

According to the above sintering theory, the

ultra-fine treatment of powder affect the properties and microstructure of SiC ceramics as described below.

1) Increasing the sintering potential energy and decreasing the sintering temperature. After ultra-fine treatment, the surface area and surface energy increase with decrease of particle size. When additives (B, C) are added, a part of B and SiC forms solid solution to decrease crystal boundary energy, and the reaction between C and SiO_2 eliminate SiO_2 film on the SiC surface and increase the surface energy. It can accelerate $\gamma_b/\gamma_s < \sqrt{3}$ and increase sintering potential energy ($\overline{\Delta u}$) to heighten the thermodynamic impetus of densification. The relationship between particle size (G) and sintering temperature (T) is described by Eq.(4).

$$\ln G = const - E/(4kT) \tag{4}$$

wherein E is diffusion activation energy, k is constant. Therefore, the particle size can decrease with sintering temperature.

2) Increasing sintering density and strength. The relationship between sintering density and sintering time (t) is expressed as follows:

$$\ln\frac{1-\rho}{1-\rho_0} = Kt \tag{5}$$

wherein ρ_0, ρ are initial density and density at time t respectively, K is densification rate. Densely populated pores with large pore diameters increase the diffusion distance between particles on the one hand, and reduce the sintering motive force for pore shrinking on the other hand. After ultra-fine treatment of the powder, the particle size decreases, the agglomeration is eliminated and the particle-size distribution becomes narrow and uniform; the green body has high densification and no obvious density gradient; the diffusion distance and the sintering time are shortened from ρ_0 to ρ.

Combined with crystal size and porosity, the strength can be expressed as:

$$\sigma = (\sigma_0 + k_1 d^{-1/2})\, e^{-np} \tag{6}$$

wherein σ is true strength, σ_0 is strength with no micropores, k_1 and n are constants, d is crystal size, and p is porosity. Eq.(6) shows that the strength increases with decrease of crystal size and porosity. In this experiment, on the one hand, the crystal size and porosity of SiC sintered body after treatment decreased, and the strength increased; on the other hand, some micropores existing in the ceramic can absorb distortion, resist expansion of crack, and strengthen the mechanical properties of the sintered body (Fig.5 and Table 2).

3) Decreasing microstructure defects and obtaining ideal microstructures. According to pore shrinking thermodynamics, the pores in ceramics cannot shrink in the sintering procedure if the pore size is larger than a critical value. At the later sintering stage, the pore and crystal boundary cannot transfer together; the transfer rate of crystal boundary is higher than the removal rate of the pores; the pores are enwrapped in the crystal particles, and become various shaped porosities. Due to particle size and agglomeration, some pore sizes of green body without ultra-fine treatment are larger than the critical value, and the pores cannot be removed and leave the crystal particle; the pore-size distribution and density distribution are not uniform, the sintering rate in the high density area is rapid; smaller pores are removed preferentially. However, the sintering rate in the low density area is slow, the grown crystal particle cannot pack into the larger pores, some pores still cannot be removed in the later stage and can form microstructure defects with large porosity and abnormal crystal. After ultra-fine treatment, the microstructure defects can be removed and the ideal microstructure is attained.

CONCLUSION

SiC powder was ultra-fine treated by fluidized bed opposed jet mill, and the effect of ultra-fine treatment on the compaction and the sintering behavior of SiC ceramic were investigated. The results showed that the compacts had relatively high density and microstructure homogeneity; the sin-

tering temperature of the compact decreased; the surface microstructure, densification and mechanical properties of the sintered body can be ameliorated obviously by proper control of the sintering temperature.

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