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Ceramics International 36 (2010) 161–165
CERAMICS INTERNATIONAL
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Sintering behavior, microstructure and mechanical properties of silicon carbide ceramics containing different nano-TiN additive

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Received 19 March 2009; received in revised form 1 May 2009; accepted 7 July 2009
Available online 11 August 2009

Abstract

Silicon carbide ceramics with nano-TiN additive were liquid phase sintered at 1950 °C for 15 min and subsequently sintered at 1850 °C for 1 h. The influence of the additive content on the sintering behaviors of silicon carbide ceramics was investigated by analyzing sintering behaviors, phase compositions, microstructure observation and mechanical properties testing. The results show that the addition of nano-TiN particles restrains the densification of silicon carbide ceramic, inhibits the grain growth of ceramic. And the reactions of TiN with SiC and Al_2O_3 to form new phases of TiC and AlN may benefit the silicon carbide ceramics in a certain range of nano-TiN addition. The silicon carbide ceramic with 5 wt.% of nano-TiN possesses high densification, uniform microstructure and superior mechanical properties. The toughening mechanism of nano-TiN on silicon carbide ceramic mainly comes from thermal residual stresses, crack deflection and crack bridging.

Keywords: A. Sintering; C. Mechanical property; Ceramics; Microstructure

1. Introduction

Silicon carbide (SiC) ceramic is a kind of structural material with excellent properties such as high strength, high hardness, resistance to extreme temperature, corrosion and abrasion [1]. Liquid phase sintering is an innovative approach to sinter SiC to theoretical density with incorporated oxides as sintering additives [2–5]. These oxides are added to improve the sintering and fracture toughness of SiC materials. Study of silicon carbide ceramics with additives of yttria/alumina mixture has become a hotspot of SiC materials research. The oxide phase greatly lowered the sintering temperature and improved the fracture toughness of the materials due to the in situ formed yttrium aluminum garnet (YAG) phase. At present, the study on the further enhancement of the strength and fracture toughness of silicon carbide ceramics has become a growing interest.

TiN is a structural material with high hardness and high wear resistance, and is similar to SiC. By introducing TiN nanoparticles into SiC matrix, the SiC/nano-TiN composite ceramics can be prepared and the strength and fracture toughness can be improved by nanoparticle reinforcing and toughening mechanism. This work investigated the influence of the nano-TiN addition on the sintering behavior, microstructure and mechanical properties of silicon carbide ceramics.

2. Experimental

2.1. Preparation process

The starting materials used in this experiment were α-SiC powder (particle size of 0.5–1 μm) as matrix, Al_2O_3 and Y_2O_3 mixed powders (analytical regents) as sintering additives and TiN nanoparticles (the average particle size of 20 nm, analytical regents) as reinforcement phase. The $SiC/TiN_{(np)}$ composite powders with 10 wt.% Al_2O_3 and Y_2O_3 mixture at a molar ratio of Y:Al = 3:5, the stoichiometry of $Y_3Al_5O_{12}$ (YAG), were prepared by aqueous spray drying technique [6]. Table 1 presents the compositions of the samples in this study and the theoretical densities are also listed in this table. The composite nanopowders in a carbon steel die were uniaxially pressed at 100 MPa to form rectangular specimens and subsequently compacted

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doi:10.1016/j.ceramint.2009.07.013

Table 1
Compositions of different samples in the experiments.

Sample	Nano-TiN (wt.%)	SiC (wt.%)	Al_2O_3 (wt.%)	Y_2O_3 (wt.%)	Theory density (g/cm^3)
NT-0	0	90	4.3	5.7	3.31
NT-5	5	85	4.3	5.7	3.377
NT-10	10	80	4.3	5.7	3.451
NT-15	15	75	4.3	5.7	3.529

in a cold isostatic press at 250 MPa. These green bodies were liquid phase sintered in a vacuum furnace at 1950 °C for 15 min and subsequently at 1850 °C for 1 h. The sintered specimens were finished by machining before testing.

2.2. Properties and microstructure measurement

The shrinkages, weight loss and the densities of the sintered samples were measured by vernier caliper, electronic balance and Archimedes displacement method, respectively, and the theoretical density was calculated according to the rule of mixtures. Phase identification was performed by the X-ray diffraction (XRD) method on a Rigaku D/max-RA X-ray diffractometer using nickel filtered CuKα radiation in the range of $2\theta = 10–80^\circ$ with a scanning speed of 2° per min. The morphology, element content of the sintered samples were observed by scanning electron microscopy (SEM, Model: HITACHI S-4800) with Genesis 4000 EDAX spectral analysis. Flexural strength was measured by three-point bending tests with a 30 mm span at a cross-head speed of 0.5 mm/min. Hardness was determined by Rockwell hardness testers. The fracture toughness was calculated by the length of the cracks originating from the edges of the indentation marks, using the equation described by Niihara et al. [7]:

$$K_{\mathrm{Ic}} = 0.018H\sqrt{a}\left(\frac{E}{H}\right)^{0.4} \times \left(\frac{c}{a} - 1\right)^{-0.5} \qquad (1)$$

where K_{Ic} is the fracture toughness of the materials, H the Vickers hardness, E the Young's modulus (for silicon carbide a value of 400 GPa was assumed), c the crack length and a the half indentation diameter.

Table 2
Sintering properties of silicon carbide ceramics containing different nano-TiN additive.

Sample	Shrinkage (%)	Weight loss (%)	Volume density (g/cm^3)	Relative density (%)
NT-0	14.5	1.0	3.17	95.8
NT-5	16.3	2.90	3.31	98.0
NT-10	19.17	6.0	3.34	96.8
NT-15	18.47	8.48	3.35	95.0

3. Results

3.1. Sintering properties

The sintering properties (shrinkage, weight loss and density) of the samples as the functions of the nano-TiN content were resumed in Table 2. After LPS all samples reached final relative densities higher than 95% t.d. and shrinkages more than 14%. With increasing addition of nano-TiN, the shrinkage increases, reaching the highest at 10 wt.% nano-TiN, and then decreases; but the weight loss increases monotonically. The relative density of the specimens reaches the highest at 5 wt.% nano-TiN, and then decreases with the continuous increase of nano-TiN.

Due to high specific surface area of added nano-TiN, the green body may have more micropores among SiC particles, resulting in a large shrinkage during the sintering process. However, nano-TiN particle inhabits grain boundary movement by pinning effect, which restrains the densification of silicon carbide ceramics. On the other hand, nano-TiN can react with Al_2O_3 and SiC to form a large number of volatile compounds (such as CO and SiO), which leads to a large weight loss. It is the reason why the sintering properties of the samples become worse with much more nano-TiN additives.

3.2. Phase compositions

Fig. 1 shows the XRD patterns for silicon carbide ceramics with different nano-TiN contents. The major phase of sintered specimens was α-SiC (6H or 4H) and the minor phase was YAG, with the existence of some new phases such as TiC, TiN and AlN. It can also be seen in the figure that the diffraction peaks of TiC overlap with TiN, and their main peaks (near 36°, 60° and 72°)

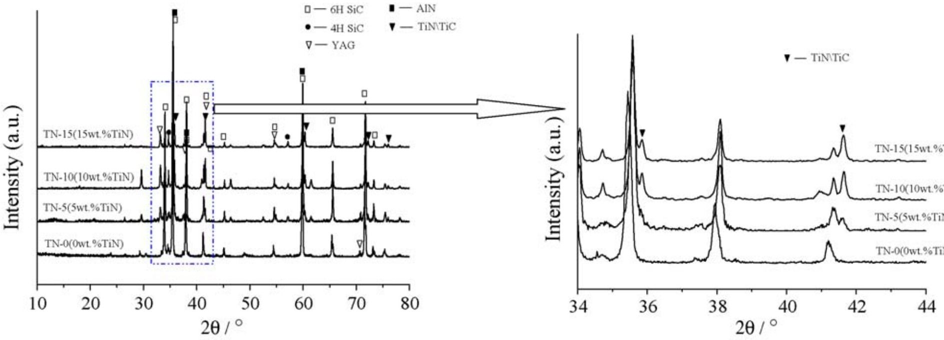


Fig. 1. X-ray diffraction patterns for silicon carbide ceramics containing different nano-TiN additive.

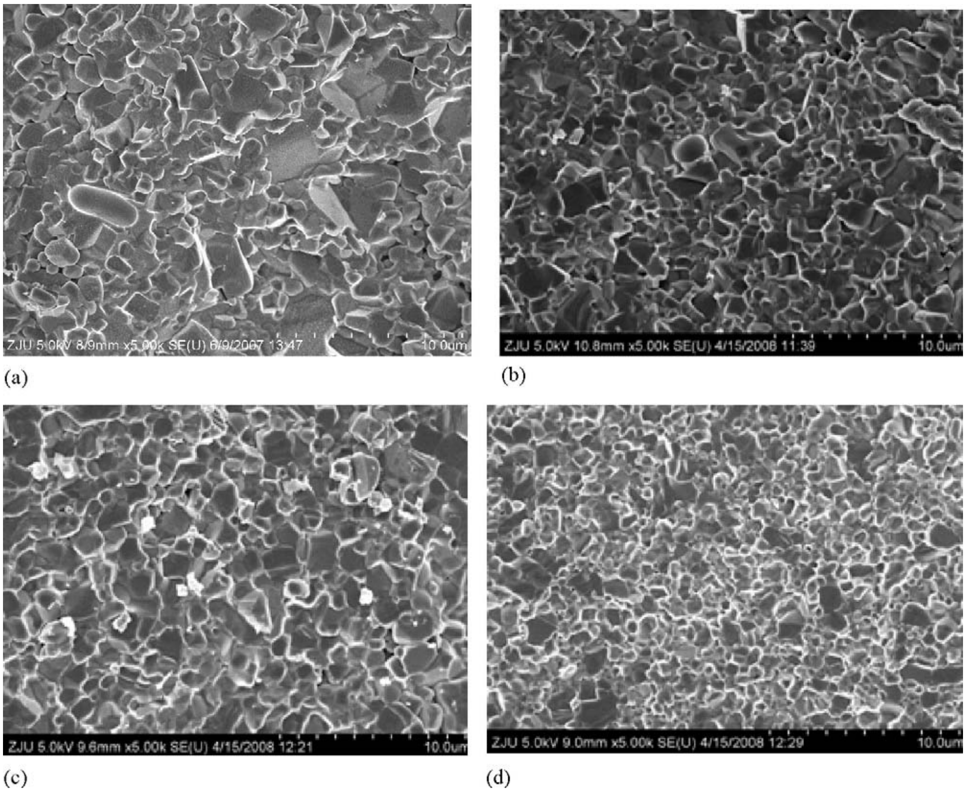


Fig. 2. SEM of fracture surface of silicon carbide ceramics containing different nano-TiN additive. (a) 0 wt.% TiN; (b) 5 wt.% TiN; (c) 10 wt.% TiN; (d) 15 wt.% TiN.

separate with the main peaks of SiC. The intensity of their peaks increases with the increase of nano-TiN content, as obviously shown in the enlarged pattern at 34–42° of 2θ. This means that TiN reacts with the matrix to form TiC and AlN indeed, which is in agreement with the results of sintering properties.

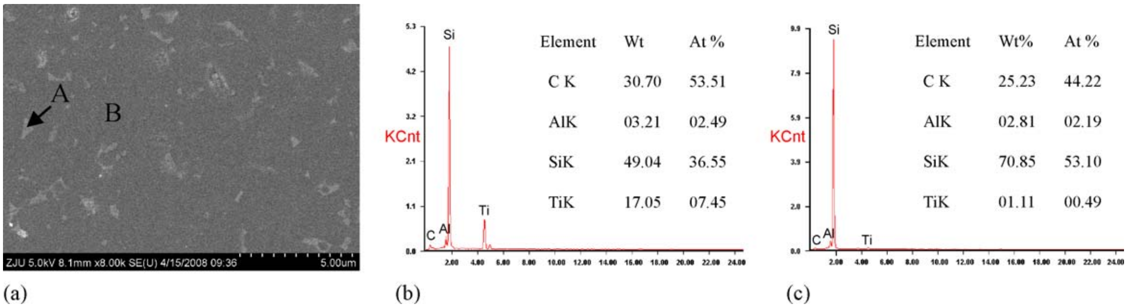
3.3. Microstructure

Fig. 2 shows the microstructure of the fracture surface of samples with different nano-TiN content, respectively. It is observed that the grains of silicon carbide ceramics have a uniform size distribution, and the size decreases with the increase in nano-TiN content. The grain of the sample with 15 wt.% nano-TiN is about 0.5 μm, and approximately the particle size (0.5–1 μm) of the starting SiC powder, which indicates the SiC grains almost do not grow during the sintering process. This implies that the nano-TiN can restrain the growth of SiC grains. The reason is that when nano-TiN content is small, TiN particles exit with intragranular and grain boundary structure. When the content of nano-TiN increases to 15 wt.%, TiN particles mainly distribute at the grain boundary among SiC particles, which retards the abnormal grain growth of SiC particles and leads to the fine-grained structure of silicon carbide ceramics.

Fig. 3 shows the microstructure and EDS results of the polished surface of the sample with 5 wt.% nano-TiN. It is also visible that the white grains are TiN or TiC (light-colored region) and the size is 0.5–1.0 μm near the one of SiC grain (Fig. 2), which indicates that the nano-TiN particles aggregate and grow during the sintering process.

3.4. Mechanical properties

The mechanical properties of the silicon carbide ceramics with nano-TiN are given in Table 3. It is noted that the bending strength and fracture toughness of the sample increase with the



Element	Wt	At %
C K	30.70	53.51
AlK	03.21	02.49
SiK	49.04	36.55
TiK	17.05	07.45

Element	Wt%	At %
C K	25.23	44.22
AlK	02.81	02.19
SiK	70.85	53.10
TiK	01.11	00.49

Fig. 3. SEM and EDS of polished surface of silicon carbide ceramics with 5 wt.% nano-TiN. (a) SEM; (b) light-colored region (A point); (c) dark region (B point).

Table 3
Mechanical properties of silicon carbide ceramics containing different nano-TiN additive.

Sample	Bending strength (MPa)	Hardness (HRA)	Fracture toughness (MPa $m^{1/2}$)
NT-0	472.0	91.1	5.20
NT-5	686.80	92.0	7.04
NT-10	511.72	92.8	6.57
NT-15	482.56	92.2	6.44

increase of nano-TiN, reach the highest at 5 wt.% nano-TiN, and get lowered gradually for the samples with 10 and 15 wt.% nano-TiN, but the hardness reaches highest at 10 wt.%, and decreases to the middle at 15 wt.% nano-TiN. The bending strength and fracture toughness of sintered body mainly depend on the density and grain size of ceramics. Though the grain size of sintered body decreases with nano-TiN additions, the relative density becomes obviously lower with much porosity, which results in the lower bending strength and fracture toughness. The size of TiN/TiC enhancement grains increases with nano-TiN additions, and the toughening mechanism of TiN/TiC grains becomes worse. The nano-TiN can react with the matrix to form TiC, and new phase TiC has a higher hardness than TiN, it is the reason why the hardness of sintered body with 10 and 15 wt.% nano-TiN is higher than the one with 5 wt.% nano-TiN. As above mentioned, the silicon carbide ceramic with 5 wt.% nano-TiN has a high densification, uniform microstructure and superior mechanical properties, its bending strength, hardness and fracture toughness are 686.8 MPa, 92 HRA and 7.04 MPa $m^{1/2}$, respectively, and the bending strength is higher than that of hot isostatically pressed silicon carbide ceramic and near the one of silicon carbide ceramic by hot pressing. This implies that the addition of nano-TiN is an effective approach to improve the performance of silicon carbide ceramics.

4. Discusses

As reported elsewhere, the following reactions occur in silicon carbide ceramics with YAG as sintering additives at high temperature [8]:

$$SiC(s) + Al_2O_3(s) = SiO(g) + Al_2O(g) + CO(g) \qquad (2)$$

$$SiC(s) + 2Y_2O_3(s) = SiO(g) + 4YO(g) + CO(g) \qquad (3)$$

Under the condition of adding high active nano-TiN and vacuum environment, the possible and important reactions are shown as follows:

$$4TiN(s) + 7SiC(s) + 4Al_2O_3(s) = 4TiC(s) + 4AlN(s) + 7SiO(g) + 2Al_2O(g) + 3CO(g) \qquad (4)$$

$$TiN(s) + 2SiC(s) + 3Y_2O_3(s) = TiC(s) + AlN(s) + 2SiO(g) + 6YO(g) + CO(g) \qquad (5)$$

Reactions (4) and (5) show that TiN can react with SiC and Al_2O_3 to form new solid phases TiC and AlN, as proved by XRD analysis. TiC has higher hardness and melting point temperature than TiN, and can enhance the strength and high-temperature properties of silicon carbide ceramics. AlN can combine with SiC to form solid solutions, and improve the sintering behavior and mechanical properties of silicon carbide ceramics [9]. Obviously, these prove that these suitable reactions taking place between nano-TiN, SiC and Al_2O_3 benefit silicon carbide ceramics. However, if too much nano-TiN reacts with SiC and Al_2O_3, the escape of gaseous species (SiO, Al_2O, YO, and CO) during sintering may result in the formation of much ‘‘new’’ pores, a decreased density, and worse mechanical properties, as certificated by this experimental.

The present toughening mechanisms of silicon carbide ceramics include thermal residual stresses, crack deflection, crack bridging and stress-induced cracking [10–12]. In this experimental, nano-TiN enhanced silicon carbide ceramic can be proved by the following toughening mechanisms:

(1) Thermal residual stresses and crack deflection. The thermal expansion coefficients of TiN ($9.35 \times 10^{-6}\ K^{-1}$) and TiC ($7.4 \times 10^{-6}\ K^{-1}$) are different from that of SiC crystal ($4.0 \times 10^{-6}\ K^{-1}$), which leads to the thermal residual stress field. The SiC matrix around the second phase particles will generate a radial compressive stress (σ_r) and a tangential tensile stress (σ_t). They will propel the main-crack to deflect and prolong its route expansion, which increases the fracture toughness of the SiC materials, as shown in Fig. 4.

(2) Crack bridging. In Fig. 5, the light-colored region belongs to TiC/TiN crystal, and dark region belongs to SiC crystal. When the main-crack meets TiC/TiN crystal, it directly traverses the first TiC/TiN crystal to form transgranular fracture, due to high stress intensity of the crack. Subsequently, the main-crack deflects to the grain boundary between TiC/TiN and SiC crystal to form intergranular fracture. Thereafter, the main-crack generates the deflection of more than 90° and traverses TiC/TiN crystal again due to high grains-boundary bond strength, which forms the interlocking phenomena. On the other hand, the main-crack becomes thinning obviously, indicating that the crack bridge produces a force closure for two crack surface, which restrains the expansion of crack to enhance toughness fracture of silicon carbide ceramics.

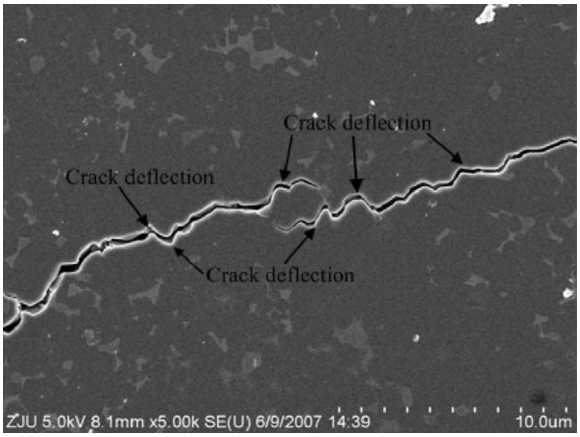


Fig. 4. Crack deflection of silicon carbide ceramic with 5 wt.% nano-TiN.

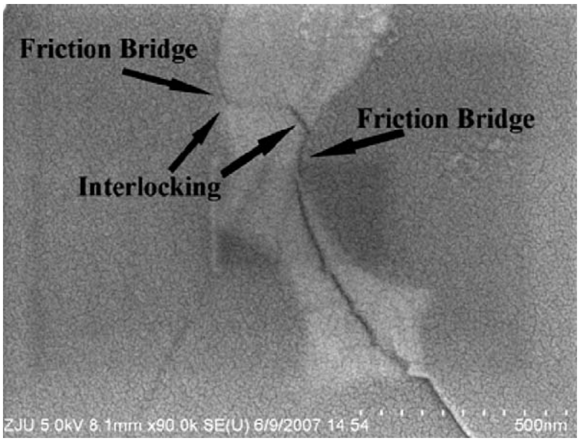


Fig. 5. Crack bridging of silicon carbide ceramic with 5 wt.% nano-TiN.

5. Conclusions

Silicon carbide ceramics with 0–15 wt.% nano-TiN additives can be sintered by two stage sintering including 1950 °C for 15 min and subsequently 1850 °C for 1 h. The effects of nano-TiN content on the densification and properties of the silicon carbide ceramics can be analysed by microstructure observation and mechanical property testing. The nano-TiN particles restrained the densification of silicon carbide ceramic and inhibited the grain growth of silicon carbide ceramic. TiN reacted with SiC and Al_2O_3 to form new phases of TiC, AlN and some volatile phases. The reactions may benefit the silicon carbide ceramics in a certain range of nano-TiN addition, otherwise deteriorate them. The high densification, uniform microstructure and superior mechanical properties could be obtained for the sample containing 5 wt.% of nano-TiN additives. The toughening mechanisms of silicon carbide ceramics by nano-TiN were thermal residual stresses, crack deflection and crack bridging.

Acknowledgements

This work is supported by the Research Fund for the Doctoral Program of Higher Education (20070335017) and the High Science & Technique Key Project of Ministry of Education of China.

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