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Sintering and microstructure of silicon carbide ceramic with $Y_3Al_5O_{12}$ added by sol-gel method*

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Abstract: Silicon carbide (SiC) ceramic with YAG ($Y_3Al_5O_{12}$) additive added by sol-gel method was liquid-phase sintered at different sintering temperatures, and the sintering mechanism and microstructural characteristics of resulting silicon carbide ceramics were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and elemental distribution of surface (EDS). YAG (yttrium aluminum garnet) phase formed before the sintering and its uniform distribution in the SiC/YAG composite powder decreased the sintering temperature and improved the densification of SiC ceramic. The suitable sintering temperature was 1860 °C with the specimen sintered at this temperature having superior sintering and mechanical properties, smaller crystal size and fewer microstructure defects. Three characteristics of improved toughness of SiC ceramic with YAG added by sol-gel method were microstructural densification, main-crack deflection and crystal ‘bridging’.

Key words: Silicon carbide, Ceramic, Yttrium aluminum garnet (YAG), Sol-gel
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INTRODUCTION

Sintering and properties of SiC materials with incorporated oxides had been widely studied (Lee and Kim, 2003; Izhevsikyi and Genova, 2001; Jensen and Luecke, 2000; Liden and Carlstrom, 1995; Ye and Pujar, 1999; Kim and Kim, 2000; Biswas and Rixecker, 2001; van Dijen and Mayer, 1996). 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 (Samanta and Dhargupta, 2001; Zhang and Ru, 2002; Zhou and Hirao, 2003; She and Ueno, 1999a; 1999b; Huang and Jia, 2003) has become a hotspot of SiC materials research. The oxide phase greatly decreased the sintering temperature and improved the fracture toughness of the materials due to the formation of an in situ YAG (yttrium aluminum garnet) phase. At present yttria/alumina mixture is added into SiC powder by mechanical mixing method. It is difficult to achieve the homogeneity of their distribution, which affects the sintering, properties and microstructure of SiC materials. Wet chemical method is an effective approach for adding the oxides into the SiC powder, and can achieve uniformity of YAG phase in the SiC composite. Liden and Carlstrom (1995) studied the homogeneous distribution of Al_2O_3 (2 wt%) and Y_2O_3 (1 wt%) sols in liquid-phase sintered silicon carbide by an electron probe microanalyzer, with the addition of sols yielding a more homogeneous microstructure for green compacts. Zhang and Ru (2002) studied the YAG phase added by chemical co-precipitation to prepare the SiC/YAG composite ceramics, but which did not enhance the sintering properties of SiC materials. We adopted sol-gel method to add the YAG additive into SiC powder to obtain SiC sealing material with superior properties and manipulable microstructure. The preparation and characteristics of SiC/YAG composite powder will be

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presented elsewhere. The aim of the present work was to study the effects of sintering temperature on the sintering and microstructure of SiC ceramic with YAG additive added by sol-gel method, to study the sintering behavior and mechanism of reinforcing SiC materials.

EXPERIMENTAL

The starting materials used in this experiment were α-SiC powder (with average particle size of 0.75 μm), $Al(NO_3)_3{\cdot}9H_2O$, $Y(NO_3)_3{\cdot}6H_2O$ and $(CH_2)_6N_4$. $Al(NO_3)_3{\cdot}9H_2O$ and $Y(NO_3)_3{\cdot}6H_2O$ were mixed homogeneously according to the stoichiometry of 10 wt% YAG (Y:Al=3:5). $(CH_2)_6N_4$ as catalytic agent was added into the above two aqueous solutions, and the mixed solution was stirred for a short time at the room temperature and yielded some sol which became transparent when heated to 50 °C in water-bath box. Ultra-fine SiC powder was added into the sol, and with the continuous stirring and gelating for some time and adjustment of pH value, the SiC/sol transformed into SiC/gel, which was then dried in air at 80 °C for 24 h and calcined at 900 °C for 2 h respectively to obtain the SiC/YAG composite powder after grinding and sieving through a 200-mesh screen. The composite powders were uniaxially pressed at 100 MPa in a carbon steel die into rectangular specimens. Subsequently, these green bodies were compacted at 250 MPa in a cold isostatic press, and then sintered in a vacuum pressureless-sintering furnace. 1860 °C, 1950 °C and 2000 °C were chosen as the sintering temperatures, and the holding time was 45 min. After finishing by machining, the specimens were prepared.

Phase identification was performed by the X-ray diffraction (XRD) method on an XJ10-60 X-ray diffractometer using nickel filtered Cu K_α radiation in the range of 2θ=10°~80° at scanning rate of 2° per minute. The morphology and element content of the sintered samples were observed by scanning electron microscopy (SEM, Model: FEI SIRION) and Genesis 4000 EDAX spectral analysis. Densities of the sintered specimens were measured by a conventional water displacement method. The theoretical density was calculated according to the rule of mixtures. Flexural strength was measured by three-point bending tests with a 30 mm span at a cross-head speed of 0.5 mm/min. Fracture toughness was determined by using the single edge notch beam (SENB) method with a notch width of 0.25 mm and a support span of 20 mm.

RESULTS AND ANALYSIS

The morphology of SiC/YAG composite powder by sol-gel method is shown in Fig.1. Note that the gray larger particle (around 1 μm) is considered to be SiC. There is a white fine particle (0.1~0.5 μm) on the surface of the SiC particle. The white fine particle is attributed to be YAG according to EDS analysis (Fig.2). The distribution of elemental yttrium, aluminum and magnesium in the composite powders is more homogeneous, which is caused by the gel network structure on the surface of the SiC particle. The uniform distribution of YAG in the SiC powder is conductive to the decrease of the sintering temperature and sintering time and enhances the sintering properties of the SiC composite.

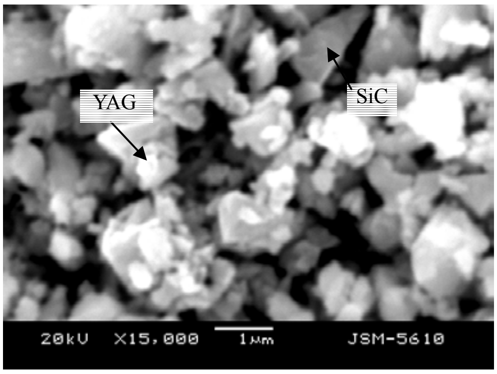
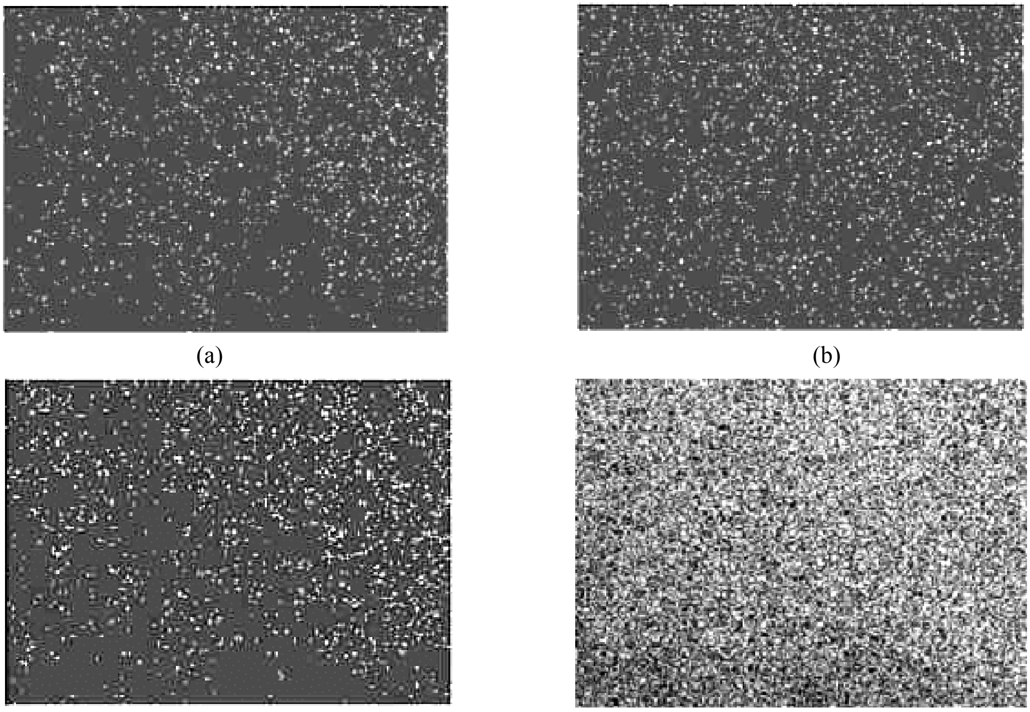


Fig.1 SEM photo of SiC/YAG composite powder

The sintering and mechanical properties of the final SiC sintered body are given in Table 1. Note that all the sintering and mechanical properties of the SiC sample sintered at 1860 °C are higher than those of the samples sintered at 1950 °C and 2000 °C. Compared with those of the sintered SiC with YAG additives added by mechanical mixture method (Jensen and Luecke, 2000; She and Ueno, 1999b; van Dijen and Mayer, 1996), the sintering temperature of the sintered SiC with additives added by sol-gel method is lower than 100~200 °C and the properties are much superior, thus indicating that YAG additives added by sol-gel method can decrease the sintering temperature



(a) (b) (c) (d)

Fig.2 EDS (elemental distribution of surface) of SiC/YAG composite powder. (a) Al; (b) Y; (c) O; (d) Si

Table 1 Properties and crystalline phases of the composites

Samples	Bulk density (g/cm^3)	Relative density (%)	Fracture toughness ($MPa \cdot m^{1/2}$)	Bending strength (MPa)	Crystalline phases	
					Major	Secondary
Sintered at 1860 °C	3.19	96.1	5.7	486	6H-SiC	YAG
Sintered at 1950 °C	3.11	93.7	4.9	437	6H-SiC	YAG
Sintered at 2000 °C	3.01	89.2	3.3	356	6H-SiC	YAG

of the SiC composite and enhance the sintering and mechanical properties of the final SiC ceramics.

Crystalline analysis (Fig.3) on the sintered samples by XRD revealed that the major phase of the sintered specimens was α-SiC (6H) and the secondary phase was YAG, with no existence of Al_2O_3 or Y_2O_3 phases. This means that the YAG phase was formed during the preparation of SiC/YAG powder by sol-gel method. The YAG phase decreased with increase of sintring temperature, which indicates that YAG reacts with SiC and volatilizes at a higher temperature.

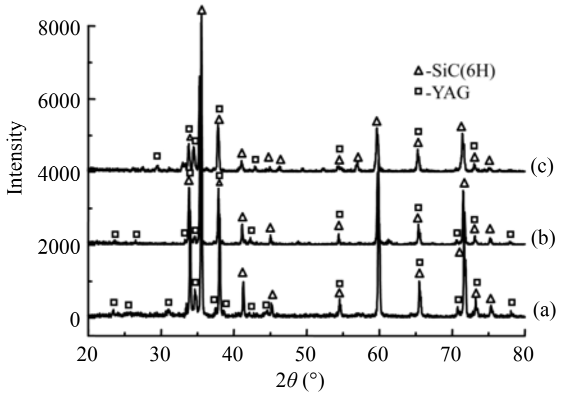
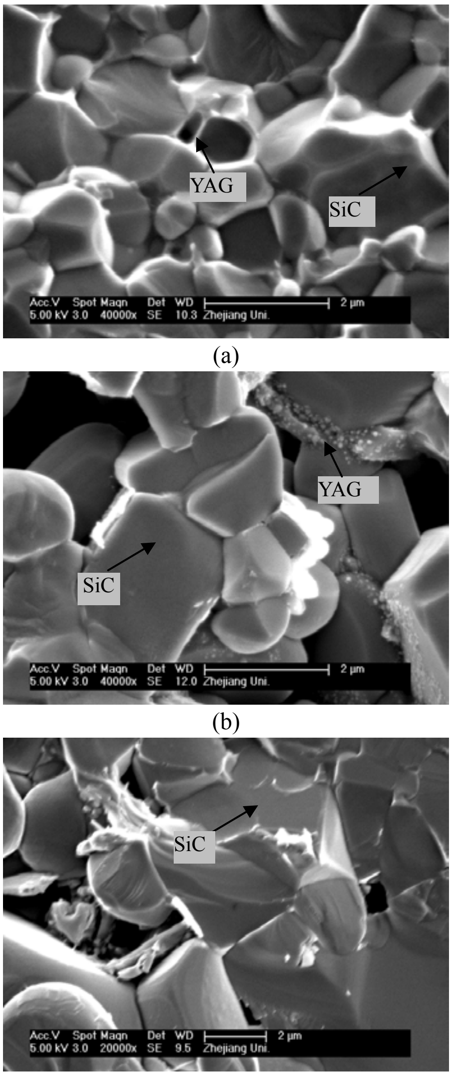


Fig.3 XRD patterns of the specimens sintered at 1860 °C (a), 1950 °C (b) and 2000 °C (c)

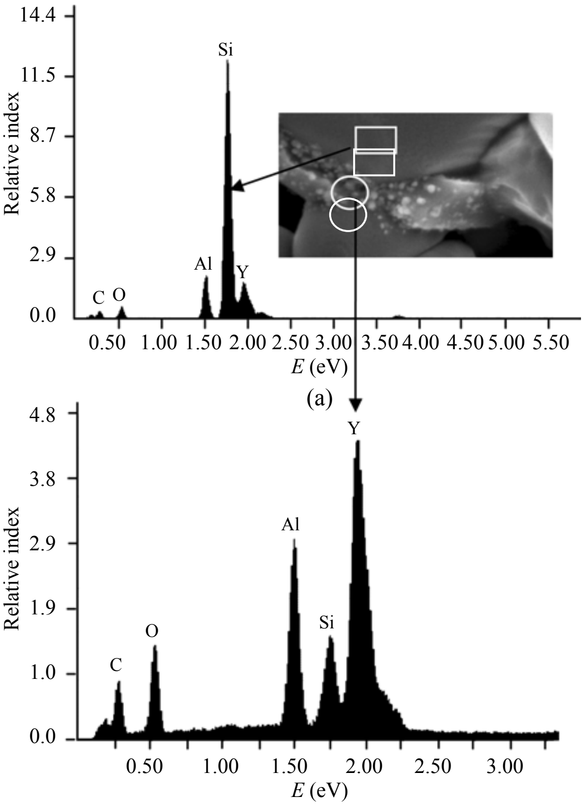
Fig.4 shows the fracture structure of SiC ceramic sintered at 1860 °C, 1950 °C and 2000 °C. Note that the crystal size of the ceramics is much larger than that of the powder (0.83 μm of the average size), which is 0.5~5 μm, and that the crystals show columnar shape with complete crystallization. As also seen in Fig.4, compared with those sintered at 1950 °C and 2000 °C (Fig.4b), the fracture surface of the SiC ceramics sintered at 1860 °C (Fig.4a) has higher densification, smaller crystal size (0.5–2.5 μm) and fewer microstructure defects. The fracture modes of the ceramics sintered at 1860 °C is mostly intergranular, and the fracture modes at 1950 °C and 2000 °C are predominantly trans-granular. The microstructure of the specimen sintered at 1860 °C exhibits obvious ‘drawing’ characteristic of crystal particles, with the films (50 nm thickness) remaining on the grain boundary. EDS (Fig.5) showed that grains (column particles) consist of Si-Y-Al-O, which indicates that SiC grains have core/rim structure where the rim contains smaller amounts of dissolved Y, Al and O; and the secondary phase consists of Y-Al-O-Si, which indicates that YAG phase exists in the intergranular boundary and contains SiC smaller grains.

This implies that YAG phase has a ‘weak’ wetting on the surface of SiC grains and that SiC grains with smaller and/or rounded sections will be under dissolution effects in the liquid-phase sintering. The YAG phase becomes thin or messy points and disappears in some triple pockets at 1950 °C and 2000 °C, as shown from Figs.4b and 4c.



(a)
(b)
(c)

Fig.4 SEM photos of fracture surface of the specimens sintered at 1860 °C (a), 1950 °C (b) and 2000 °C (c)



(a)
(b)

Fig.5 EDS of grain (a) and grain boundary (b) of specimen sintered at 1950 °C

DISCUSSIONS

According to the sintering mechanism of liquid-phase sintering, the sintering of ceramics is related to the particle size of the raw materials, additive and its distribution, and sintering procedure. The effect of additive on the sintering of ceramic relates to its content and uniformity. The distribution of additive with the same content is very important for the sintering. Some researchers maintained that the uniform liquid phase is beneficial for decreasing the sintering temperature and improving the densification during the sintering procedure (Liden and Carlstrom,1995; She and Ueno, 1999a; Biswas and Rixecker, 2001; Huang and Jia, 2003). In this study, the SiC/YAG composite powder was prepared by sol-gel method. After hydrolysis and polymerization, the inorganic salts formed the sol, which after a short time was transformed into the gel with network structure and enwrapped on the SiC particles. After drying and heat treatment, the YAG phase (nanometer size) was uniformly distributed in the SiC/YAG composite powder, thus ensuring the homogeneity of the YAG liquid phase during sintering period and improving liquid-phase sintering of SiC ceramic. Compared with the mechanical mixing method, YAG added by sol-gel method formed in advance and resolved the problem of inhomogeneity of phase distribution during the sintering period.

The sintering temperature affects the sintering properties and microstructure of SiC ceramic. At a high temperature, the content of liquid phase increases to improve the densification, while possibly leading to the over-growth of crystal, the volatilization of YAG phase and the reaction of SiC with other oxides. At a low temperature, the content of liquid phase is not enough for the required densification of SiC ceramics. The lowest eutectic temperature in the Al_2O_3-Y_2O_3 system is 1760 °C (YAG), the presence of surface silica on the SiC starting powder particles clearly reduces the eutectic temperatures. In this study, with YAG phase formed before the sintering procedure, the sintering temperatures of 1950 °C and 2000 °C were higher by 200 °C and 240 °C than the liquid phase temperature of YAG (1760 °C) respectively, which attains rapid densification rate. Results in the reaction of SiC with other oxides and rapid growth of SiC grains are shown in Figs.3 and 4. This confirmed that SiC ceramic with YAG added by sol-gel method had over-sintering phenomenon above 1950 °C. The specimen sintered at 1860 °C possessed high densification, small crystal size and ideal microstructure, indicating that the liquid phase content met the requirement of densification and that the crystal did not grow too much at the temperature. Therefore, 1860 °C was more suitable sintering temperature for SiC/YAG composite powder.

One of the approaches to enhance the strength and improve the toughness of the ceramic is obtaining fine, dense, uniform and pure crystal structure. Since YAG liquid phase existed from the beginning, it provided easy paths for fine SiC grains to slide and grow, which was enhance by the constant interdiffusion between films and grains. Once YAG crystal formed and the interdiffusion was complete, they slowed and blocked further grain sliding and over-growing, centralized in the intergranular boundary and triple points and led to the eventual microstructure. Three characteristics of improved toughness of SiC ceramic with YAG added by sol-gel method were as follows:

1. Microstructural densification: Combined with its crystal size and porosity, the strength of ceramics can be expressed as (Brook, 1999):

$$\sigma=(\sigma_0+k_1d^{-1/2})\mathrm{e}^{-np} \tag{1}$$

where σ is true strength; σ_0 is strength with no micropore; k_1 and n are constants; d is crystal size and p is porosity. As seen in Eq.(1), the strength increases with the decrease of crystal size and porosity. In this work, the specimen sintered at 1860 °C had ideal microstructural densification with a fine crystal size and few pores, which improved the strength and fracture toughness. According to the fracture mechanism, the finer the crystal particle, the larger the proportion of grain boundary and the longer the expanding route of crack; furthermore, the finer the crystal particle, the smaller the initial crack size and the higher the critical stress. They increased the fracture toughness of materials, which was why the mechanical properties of the specimen sintered at 1860 °C were better than those sintered above 1950 °C.

2. Main-crack deflection: The thermal expansion and elasticity of YAG crystal were different from those of SiC crystal, which led to the microcracks (grey arrow pointing) during the cooling, as shown in Fig.6. The production of microcracks dissipates the forcing energy of main-cracks expansion, inducing the passivation of cusp of main-crack; on the other hand, there occurs volume expansion with microcracks forming, which results in the remaining strain after the disappearance of stress. They compel the main-crack to deflect and prolong its route expansion, thus increasing the fracture toughness of the SiC materials. In the intergranular mode of fracture, the main-cracks deflect along the crystal. This also prolongs the route of main-crack expansion, thus increasing the fracture toughness.

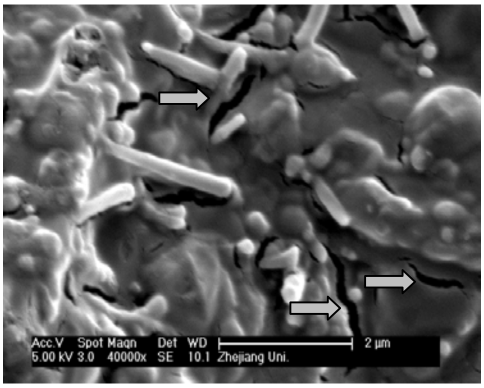


Fig.6 Microcracks of surface of no-polished specimen sintered at 1860 °C

3. Crystal 'bridging': Grain boundary and triple pockets of SiC crystals contain the YAG crystal (phase) and played a role of 'bridging' of the YAG crystals and SiC crystals and enhanced the fracture toughness of SiC ceramic.

CONCLUSION

1. Silicon carbide ceramic with YAG additive added by sol-gel method was liquid-phase sintered, and YAG phase forming ahead of the sintering and uniform distribution of YAG in the SiC/YAG composite powder decreased the sintering temperature and improved the densification of SiC ceramic.

2. Silicon carbide ceramic exhibited over-sintering phenomenon above 1950 °C, and the sintering temperature of 1860 °C is recommended; specimen sintered at 1860 °C had higher sintering and mechanical properties, smaller crystal size and fewer microstructure defects than those sintered above 1950 °C; and the main crystalline phase was α-SiC(6H) with secondary phase of YAG.

3. Three characteristics of improved toughness of SiC ceramic with YAG added by sol-gel method were microstructural densification with fine grains, main-crack deflection by microcracks and intergranular fracture, and 'bridging' of YAG crystals.

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