Original Article

Porous process and its effects on the microstructure and properties of SiC ceramics sintered with Mg additive

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\textbf{A B S T R A C T}

Seeing that opinions vary, no unanimous conclusion has been drawn on mechanisms of SiC sintered with Mg additive. In this work, SiC porous ceramics were sintered at 1300°C/30 MPa for 2 h and 6 h. The X-ray diffractometer (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), were used to study the microstructure and mechanism, relative density and mechanical properties were tested. Results show that relative density and most of the mechanical properties decreased with prolongation of sintering time, while hardness increased. \(M_2C_3\) forms during sintering and has a pinning effect on the boundary between SiC and Mg. Both SiC and \(M_2C_3\) are strongly bonded with Mg with coherent boundary. The mechanism of microstructure evolution has been discussed.

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1. Introduction

As one of the primary ceramic materials, silicon carbide has been widely developed in various industrial fields, including aerospace engineering, manufacturing industry, semiconductor industry and nuclear power [1,2]. Owing to the covalent nature of Si–C bonding, SiC has higher specific strength, hardness, modulus and thermal stability [3,4]. However, the binding energy of Si–C is so strong that SiC can only be sintered at a temperature higher than 2000°C [5]. Adding additives is an effective way to reduce the sintering temperature, such as boron [6], carbon [3] and boron carbide [7].

Compared to traditional additives, novel liquid phase additives can realize sintering at a lower temperature. Al is an economical and effective element of the novel liquid phase additives. Previous researches have reported the good wettingability between the SiC surface oxide film and Al [8,9], and the Al/SiC composites have excellent mechanical and corrosion properties [10]. However, a great number of \(Al_2N_3\) phases formed during sintering. The other additives, such as Si and Mg, must be added to prevent the formation of complex \(Al_4N_3\) phase [11].

Mg is another element with low melting point. The effect of Mg on SiC is well identified. Firstly, Mg can enhance the covalent bonding strength of SiC [12,13]. Secondly, reaction which products between SiC and Mg/Al has a crystal structure closer to Mg than to that of Al [14]. Finally, Mg has an improving effect on a oxidized SiC surface [9].

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Seeing that opinions vary, no unanimous conclusion has been drawn on mechanisms of the reaction between SiC and Mg during sintering. Thus, the microstructure of SiC ceramic sintered with Mg additive is still unclear. Therefore, the current study aims at improving relative density and mechanical properties of SiC ceramic, a novel Mg sintering additive was proposed. Ordinary industrial silicon carbide and magnesium powders were used as main raw materials, where Mg was served as the additive and pore former. The SiC ceramic were hot press sintered at 1300 °C/30 MPa for 2 h and 6 h. The phase compositions, pore characteristics, microstructures and properties were investigated from the sintering time. Reaction between SiC and Mg and the sintering mechanism were discussed.

2. Experimental methods

2.1. Samples preparation

Industrial SiC powder (purity is higher than 99%, average size is 3.31 μm, which is measured by a laser particles analysis) was used as the raw material. Besides, the magnesium alloy powder (average size is 86.4 μm) was used as sintering additive. The mass fraction of magnesium additive is 8%. In order to synthesize the final samples, silicon carbide and magnesium alloy powder were weighted by electronic balance and mixed by a three-dimensional mixing machine for 2 h. After mixing, the powders were cold compacted into a cylindrical graphite mold with 90 mm in diameter and 30 mm in thickness. Sintering stage was carried out in hot pressure sintering furnace. Schematic diagram of experimental procedures is shown in Fig. 1a. The heating profile consisted of the heating rate 15 °C/min from room temperature to 1000 °C followed by the heating rate 10 °C/min from 1000 °C to the maximum temperature, as shown in Fig. 1b. Sintering was performed at 1300 °C for 2 and 4 h with pressure of 50 MPa under pure flowing argon atmosphere and freely cooled down to ambient temperature.

2.2. Characterization

2.2.1. Phase compositions, microstructures and pore characteristics

The phase compositions were characterized using a Ultima IV XRD analysis with Cu target between 30° and 80° at a 0.02°/s step at 35 kV/40 mA. And the fraction of phases were calculated according to the Internal Standard method [15]. Microstructure of ceramics, distribution of pores and chemical compositions were characterized by using the LEO1450 SEM with energy dispersive spectrometer (EDS) attachment. Selected area electron diffraction (SAED) was conducted under FEI Tecnai F30 G2 transmission electronic microscopy (TEM). High resolution transmission electron microscopy (HRTEM)
Table 1 – Mechanical properties of the sintered samples.

<table>
<thead>
<tr>
<th>Sintering time</th>
<th>Hardness/GPa</th>
<th>Elastic modulus/GPa</th>
<th>Bending strength/MPa</th>
<th>Fracture toughness/MPa m(^{1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2h</td>
<td>6.7 ± 1.3</td>
<td>236.3 ± 24.5</td>
<td>172.3 ± 32.0</td>
<td>4.6 ± 0.3</td>
</tr>
<tr>
<td>6h</td>
<td>8.3 ± 0.6</td>
<td>108.9 ± 8.2</td>
<td>67.0 ± 4.5</td>
<td>1.2 ± 0.1</td>
</tr>
</tbody>
</table>

Fig. 2 – Relative density, pore characterization and microstructure of ceramics: (a) relative density; (b) (c) pore characterization of 2 h and 6 h sintered ceramic respectively; (d) (e) microstructure of 2 h and 6 h sintered ceramic respectively.

and bright field images were used to observe the boundaries between SiC and Mg.

2.2.2. Relative density
Bulk density of ceramics were measured by the Archimedes’ principle and calculated based on Eq. (1).

\[ D_b = \frac{m_3}{m_3 - m_2} \]

where \( D_b \) is bulk density (g/cm\(^3\)) of the tested sample, \( m_1 \) is the mass of the dried sample in air (g), \( d \) is the density of water (1.00 g/cm\(^3\)), \( m_2 \) is the mass of the sample in water (g), \( m_3 \) is the mass of the sample with free bubbles on the surface (g) [1]. The relative density of each specimen was calculated as the quotient of bulk density to theoretical density (TD = 3.08 g/cm\(^3\)).

2.2.3. Mechanical properties
Hardness and elasticity modulus were tested by using nano indenter (NanoIndenter XP). Flexural strength was measured on rectangular bars (3 mm × 4 mm × 30 mm) by using a three-
point bend fixture with a span of 20 mm at room temperature. The crosshead speed was 0.5 mm/min. Fracture toughness was measured on single-edge notched beam (SENB) specimens (3 mm × 4 mm × 20 mm) using a three-point bend fixture with a span of 16 mm at room temperature. The notch was made with 1.5 mm in depth and 0.2 mm in width. The crosshead speed was 0.05 mm/min. Five measurement runs were carried out to determine the average value of every property.

3. Results

3.1. Relative density, pore characteristics and microstructures

Fig. 2 presents the relative density, pore distribution and microstructure of the samples. As can be seen from Fig. 2a, relative density of the samples decreases from 92.76% to 75.02%. The change of relative density can also be verified by the micrographs. The sample sintered 2 h appears only a small number of equiaxed pores on the surface and the pores distribute uniformly (Fig. 2b). On the contrary, the sample sintered 6 h has significantly more pores than that of sintered 2 h and a large number of open pores can be observed. Fig. 2d and e represent microstructure of sintered samples respectively. The pore sizes of sintered 2 h sample are ranging from a few tenths to two micron, which are much smaller than the particle sizes (Fig. 2d). The pore sizes of sintered 6 h sample are around 3 μm, almost equal to the particle sizes (Fig. 2e).

3.2. Mechanical properties

Mechanical properties of the sintered samples are presented in Table 1. It is observed that the elastic modulus, bending strength and fracture toughness decrease when sintering time increases from 2 h to 6 h. The changes can be attribute to the difference of relative density. High-porosity results a decrease in strength of the sample sintered 6 h, indicated by Eq. (2) [16],

\[ \sigma = \sigma_0 \exp(-bP) \]  

where \( \sigma \) is the actual strength of the tested material with a P porosity; \( \sigma_0 \) is the strength of the ideal material without porous, \( b \) is an empirical constant which is directly related to the pore characteristics, \( P \) is the porosity. However, hardness increased when sintering time increased from 2 h to 6 h, which is contrary to our understanding. In some literatures, abnormal increase of hardness can be defined as the formation of hard compounds [15,17]. In this way, it is reasonable to hypothesize that some intermetallic compounds has formed during sintering process. However, further characterization is necessary.

3.3. Phase evolution and composition distribution

Relative density of the samples (Fig. 2a) is synthetically affected by both factors of apparent porosity and phase composition [5]. The XRD patterns reveal that the phase compositions are significantly changed with prolongation of sintering time (Fig. 3). The mixed powders are mainly comprised of SiC (both \( a \) and \( b \)) and Mg. However, new (112)Mg_{2}C_{3} and (121)Mg_{2}C_{2} peaks are found in the samples sintered 2 h and 6 h respectively. It reveals that a hard Mg_{2}C_{2} phase formed during sintering. The sample sintered 2 h contains only 6.8%
Mg$_2$C$_3$, while the sample sintered 6 h contains 14.6% Mg$_2$C$_3$. Moreover, both SiC and Mg composition in the sample sintered 6 h decreased compared to that of the 2 h sintered one. It reveals that phase transformation undergoes compared to the raw materials.

Backscatter images (BSE) and element surface distribution were conducted to investigate chemical composition distribution of samples sintered by different time. The sample sintered 2 h shows a quasi homogeneous in microstructure and Si, Mg element distribution, as is shown in Fig. 1a, c and e. It should however be noted that some segregation can be observed in the sample sintered 6 h. It indicates an inhomogeneous microstructure, as shown in Fig. 4b. Combined with Fig. 4d and f, Si distributes uniformly in the sample, however, Mg segregates obviously. Moreover, a pore can be observed in the sample sintered 6 h, which locates in the Mg-segregation region. It seems that the formation of pore is related to the segregation of Mg.

### 4. Discussion

#### 4.1. Mechanism of pores formation

In order to further study the effect of magnesium on the formation of pores, line distribution of Si and Mg elements were conducted for the samples sintered 2 h and 6 h. It is obvious that both Si and Mg distribute homogeneous in the sample sintered 2 h, however, Mg segregates in the pore-concentration region.

Fig. 6a shows the magnification map of pore-concentration region in Fig. 3b. A network structure consisting of sintered necks can be clearly observed. Fig. 6b–e show the results of EDS patterns (regions 1–4 in Fig. 6a) and the results are presented in Table 2. A higher Mg content can be clearly observed in sintering necks (points 3 and 4 in Fig. 6a). It reveals that Mg has significant effect on the formation of sintering necks as well as the pores.
Fig. 5 – BSE images of samples sintered 2 h (a), 6 h (b) and elements line distribution of samples sintered 2 h (c), 6 h (d).

Fig. 6 – SEM micrograph (a) and EDS analysis (b)–(e) of the pore-concentration region in Fig. 5b.

Fig. 7 – TEM image of sintering neck, micropores and dislocation lines.
Fig. 7 shows the TEM image of the sintering neck and surrounded pores. It should be noted that a long dislocation line goes across the neck. It proves a stress concentrate effect and has strengthening effect on the neck. Moreover, some dislocation lines also formed under presence of internal stress around the pores, which can refine microstructure and contribute to the improvement of the mechanical properties of the composites [17].

4.2. **Reaction between silicon carbide and magnesium**

Fig. 8a shows the boundary between SiC and Mg, where some micro particles can be observed. It should be noted that the boundary is not straight, indicating the pinning effect of micro particles [17]. Fig. 8b shows the HRTEM image of boundary without micro particles and Fig. 8c represents the pattern after FFT translation of Fig. 8b. As shown in Fig. 8c, both SiC and
Mg grains clearly display lattice fringes up to the boundary. Lattice fringes are interspersed with each other to form the relatively wide (about 1–2 nm) grain boundaries. The mismatch of (10–12) crystal plane of Mg and (10–19) crystal plane of α-SiC is only about 25°. The pattern in Fig. 8c also reveals the favorable crystallographic relationship of SiC and Mg. Such the coherent boundaries suggest that the strong bonding strength between SiC and Mg phase interface.

Fig. 8d shows HRTEM image of boundary between Mg and the micro particle and Fig. 8e represents the pattern after FFT translation of Fig. 8d. As shown in Fig. 8c, plane defects like stacking fault can be observed in both HRTEM image and the pattern, which may work as the induced nuclei of deformation twin and benefit the formation of twin in deformation process [18]. It also reveals that the micro particles which pins on the boundary between SiC and Mg are Mg2C3. The mismatch of (10–12) crystal plane of Mg and (211) crystal plane of Mg2C3 is only about 20°. It also proved to be a coherent boundary with strong bonding strength between Mg and Mg2C3.

The presence of Mg2C3 in Fig. 3 suggests that some of the SiC particles break down with the prolongation of sintering process. The following reaction is likely to occur between SiC and Al [19]:

\[ 3\text{SiC}(s) + 2\text{Mg}(s, l) \rightarrow \text{Mg}_2\text{C}_3(s) + 3\text{Si}(s) \]  (3)

Fig. 8d and e provide the direct evidence of the formation of Mg2C3. Since the lattice mismatch between SiC and Mg as well as Mg2C3 and Mg is very similar, the bonding strength can be guaranteed in the porous ceramic sintered 6 h.

Fig. 9 shows the reaction mechanism during sintering process. When the powders are sintered for 2 h, a strong coherent bonding formed between SiC and Mg, which plays a significant role in improving the relative density. However, with the prolongation of sintering time, more and more Mg reacts with SiC on the boundary, resulting in a number of Mg2C3 and free Si. On one hand, the hard Mg2C3 pinning on the boundary that improves the strength of ceramic; on the other hand, it leads to a lack of Mg, which is necessary in the formation of sintering necks. It prevents the growth of sintering necks. Therefore a porous region formed in the Mg-concentrated regions.

### 4.3. Sintering mechanism

Liquid phase sintering mechanisms mainly contains diffusion and particles rearrangement. The diffusion mechanisms include volume diffusion, boundary diffusion and surface diffusion [20] and particles rearrangement realized by grain-boundary migration and grain rotation [21].

It is generally known that both grain-boundary migration and grain rotation are accompanied by grain growth [18]. However, grain growth effect is not obvious according to the SEM images of Fig. 2d and e. Thus the effects of grain-boundary migration and grain rotation are limited.

The diffusion mechanisms are belonging to a pore driving mass transport mechanism. However, surface diffusion may only work on continuous network pores [20]. So it cannot play a key role in the samples with closed pores (Fig. 2d, e and 7). Since all the pores are locate on grain or substructure boundaries, boundary diffusion may plays a key role in sintering. Shi et al. suggested that local boundary network would form in the initial and intermediate stage of sintering [21]. Thus, boundary diffusion will take place via the local boundary network and a boundary diffusion mechanism is beginning to take effect.

### 5. Conclusions

The SiC porous ceramics have been successfully prepared at 1300 °C/30 MPa for 2 h and 6 h. Based on the experimental results and theoretical analysis, the following conclusions can be drawn:

1. The relative density of SiC ceramics can be up to 92.76% after sintering and homogeneous microstructure with fine quasi-equiaxed pores; the relative density decreased to
75.02% after sintering 6 h and the microstructure becomes inhomogeneous with open pores concentrated.
(2) Mechanical properties including elastic modulus, bending strength and fracture toughness decreased when the sintering time increased from 2 h to 6 h while the hardness improved.
(3) The porous regions are Mg-concentrated, where network of sintering necks can be observed. Mg has a positive effect on the formation of sintering necks.
(4) Coherent boundaries formed between SiC and Mg, which indicates a strong bonding. Fine Mg2C3 micro particles have a pinning effect on the boundary. A coherent boundary also formed between SiC and the Mg2C3 particles.
(5) Mg reacts with SiC on the boundary, resulting in a number of Mg2C3 and some free Si. The hard Mg2C3 pinning on the boundary that improve the strength of ceramic, however, it leads to a lack of Mg which is necessary in the formation of sintering necks, prevents the growth of sintering necks, leading to a porous ceramic.

Conflicts of interest

The authors declare no conflicts of interest.

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