

Effect of SiO₂ content on the microstructure and consolidation mechanism of recrystallized silicon carbide

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In this paper, the influence of SiO₂ on the microstructure and consolidation mechanism of recrystallized silicon carbide (RSiC) was studied by comparing the relationship of the weight losses and microstructural evolution with the SiO₂ contents at different firing temperatures. The results showed that the presence of SiO₂ resulted in a basic weight loss proportional to the SiO₂ content and an additional weight loss independent of the SiO₂ content. The consolidation mechanism of SiC was not altered by the introduction of SiO₂, involving surface diffusion at low temperatures and an evaporation-condensation process at the high temperature, while the residual ambient atmosphere primarily including SiO(g), Si₂C(g) and Si(g) inhibited the recrystallization of SiC by altering the mass transport from SiC₂(g), Si₂C(g) and Si(g) for pure SiC to that combined with the gaseous transport of SiO(g), Si₂C(g), Si(g) and SiC(g), and the surface diffusion of C(s) at the high temperature.

Key words: Recrystallized Silicon Carbide, SiO₂, Microstructure, Evaporation-Condensation.

Introduction

Recrystallized silicon carbide (RSiC) has been receiving more and more attentions as a high performance material because of its unique combination of properties, such as excellent mechanical properties maintained at elevated temperature [1], good oxidation resistance, high thermal conductivity, low electrical resistivity and good chemical stability. RSiC is widely used as structural parts in kilns, electrical heating elements, thermal exchanger and so on [2-3].

The covalent nature of SiC tends to retard the solid-state sintering of pure SiC compacts because of its slow bulk diffusion especially without an applied pressure. Surface diffusion or vapor-phase transport has been considered to be responsible for the consolidation of covalently bonded ceramic materials without sintering agents. The preparation of RSiC does not introduce any agents to enhance sintering and undergoes a non-shrinking course [4]. SiC has a relatively high vapor pressure at high temperatures, and the evaporation-condensation process (vapor-phase transport) has been accepted as the consolidation mechanism for RSiC through the difference of vapor pressures originating from different curvature between the surface of fine particles and necks between particles in the powder compact [5].

The density of RSiC is determined by the green density due to the non-shrinking consolidation process. Graded aggregate mixtures of SiC powders with different size are employed to obtain a high density RSiC product. Unfor-

tunately, oxygen will be introduced to the surface of SiC particles in the form of SiO₂ when prepared for the needed size distribution. And the oxygen content increases when the SiC particle size is finer. The existence of SiO₂ will have an influence on the partial pressure of SiC vapor species, which aggravates the vapor complexity. The essence of evolution of RSiC with a little oxygen is still unknown, and several explanations have been employed to describe the evaporation-condensation process [5-6]. Unfortunately, there is little research to discuss details of the influence of SiO₂ on the microstructural evolution and consolidation mechanism for RSiC. In the present study, SiC powders with different SiO₂ contents are used for the preparation of RSiC, and weight losses during firing and the microstructures of the RSiC samples prepared will be characterized in detail.

Experimental

Two commercial raw materials consisting of coarse SiC and fine SiC powders were used to reach a high packing density (Changle Xinyuan Carborundum Micropowder Co. Ltd., Changle, China). The particle sizes of the fine SiC powder ranged from 0.2 to 1.1 μm (SiC contents > 98.5%, $D_{50} = 0.65 \mu\text{m}$, $D_{90} = 0.85 \mu\text{m}$), while that for the coarse powder ranged from 48 to 120 μm (SiC contents > 99%, $D_{50} = 95 \pm 5 \mu\text{m}$, Tap density 1.86 g/cm³).

Considering vapor-phase transport is the main consolidation mechanism of RSiC, the fine SiC powders become the main evaporation unit under a high temperature, and the fine powders can easily import oxygen as the preparation of fine powders because of their high specific surface area, so oxygen was introduced in the form of SiO₂ by oxidizing the fine powders in this study. In order to obtain the SiC powders with different SiO₂ contents, the fine

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powders were first treated with a 10% HF solution and washed 10 times by deionized water. Then these fine powders were oxidized in air at 1000 °C. The oxidized fine powders gave SiO₂ contents of 1.1 wt%, 4.4 wt% and 6 wt% by controlling the oxidation time.

The fine powder series without or with different SiO₂ contents and the coarse powders were mixed in a weight ratio of 35 : 65. Hence the SiO₂ contents in the mixtures are 0 wt%, 0.39 wt%, 1.54 wt% and 2.1 wt%, and the particle sizes of the mixtures with the fine series powder and coarse powder were in a bimodal distribution. The mixtures were molded under a pressure of 100 MPa to form the samples with a size of 12 mm × 12 mm × 130 mm. The specimens were heated to firing temperatures of 1800, 2000, 2200, 2400 °C with the heating rates of 35 K·minute⁻¹ and with a dwell time of 1 h in an Ar atmosphere. Recrystallization was conducted in the firing process by the evaporation of the fine SiC particles and deposition onto the necks of the coarse SiC particles.

The weight losses of samples were measured with the recorded weights before and after firing. The morphology and microstructures were investigated by field-emission scanning electron microscopy (FE-SEM; JEOL JSM-6700F).

Results

Weight loss

The variation of weight loss with firing temperature for 1 h is illustrated in Fig. 1 for SiC compacts with different SiO₂ contents. The weight loss of samples with the same SiO₂ content is basically consistent in the temperature range of 1800–2200 °C, then has a significant increase up to 2400 °C. And all the weight losses of samples are higher than the initial contents of SiO₂. The different weight loss trends below and up to 2400 °C indicate there are different mechanisms resulting for the two temperature ranges.

As displayed in Fig. 1, the sample weight loss increases

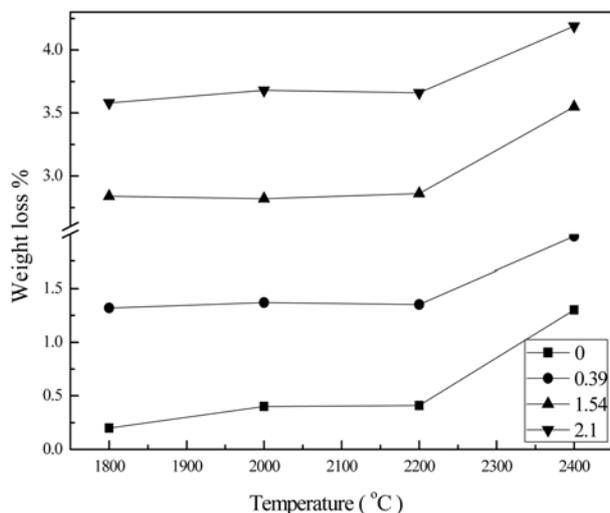


Fig. 1. Weight losses of the SiC samples with different SiO₂ contents heat treated at different firing temperatures for 1 h.

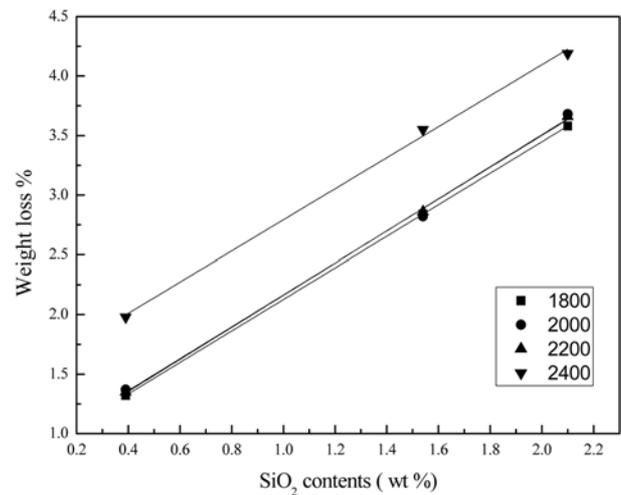


Fig. 2. The linear relationship of weight losses to the SiO₂ content at the same temperature.

Table 1. The parameters for the fitted linear relationships of weight losses with SiO₂ contents at different temperatures

T (°C)	slope	Intercept	R-square
1800	1.32	0.80	1.0000
2000	1.34	0.83	0.9500
2200	1.35	0.82	0.9991
2400	1.30	1.49	0.9965

with an increase of the SiO₂ content at the same temperatures. And Fig. 2 indicates that there may be a linear relationship between the weight loss and SiO₂ content at the same temperature except for the pure SiC compact. The slopes for the linear relationship seem to be approximately equal as shown in Table 1, which indicate approximately parallel lines despite different temperatures. Hence it may be concluded that the linear phenomenon reveals a basic weight loss which is proportional with the SiO₂ content at the same temperature, and the approximately parallel relationship indicates an additional weight loss with little difference for different SiO₂ contents. The weight losses of the pure SiC compacts below 2200 °C are low, while significantly higher weight loss is found at 2400 °C. Moreover, compared to the weight loss differences between 2400 °C and 2200 °C for the samples with SiO₂ introduced, that for pure SiC is more distinct, which illustrates that the introduction of SiO₂ has an influence on the ambience of SiC.

Microstructure

Fig. 3 shows the fracture morphology of the SiC compacts at the experiment temperatures for 1 h. From Fig. 3, we can see that when the temperature was lower than 2400 °C, the coarse particles showed no change of configuration, and were surrounded by fine particles. At 1800 °C, the fine particles have an apparent change of shape and particles less than 1 μm in diameter have almost disappeared, resulting in grown necks or merged by larger ones directly. With an

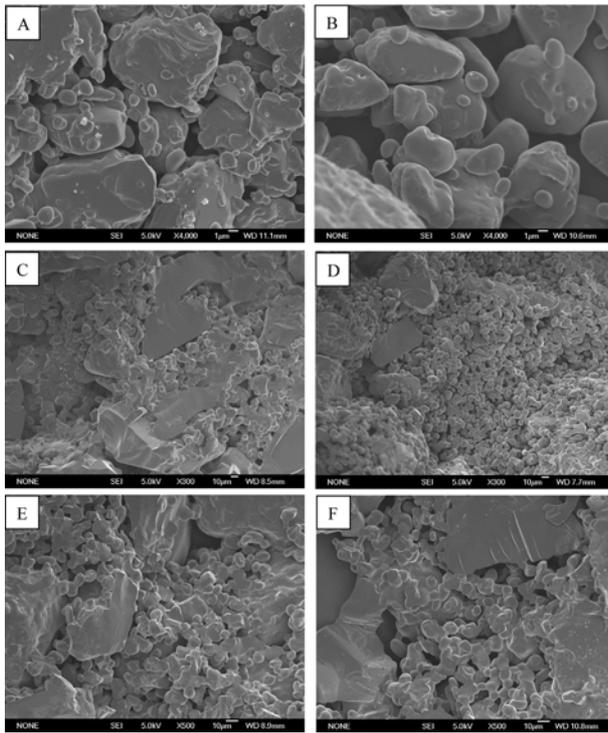


Fig. 3. Microstructures of fracture surfaces of fired pressed samples without (A, C, E) and with 2.1 wt% SiO₂ (B, D, F) at firing temperatures: (A, B) 1800 °C, (C, D) 2000 °C, (E, F) 2200 °C.

increase of the firing temperature, larger fine particles disappeared and the finest particles displayed in the figures after firing increase in diameter which became equal in diameter by spherical particle combination. When up to 2200 °C, a structure with only coarse particles and particles about 10 μm in diameter has formed, and the necks between coarse particles with diameter ~100 μm are still small. The partial large pores among the large particles are filled by the small particles, leading to the coexistence of large pores and local small pores.

When the temperature is lower than 2400 °C, the SEM observations of the development of pore-grain structure in the fired compacts of SiC without and with different SiO₂ contents reveals strikingly similar microstructural development. It is difficult to discover a microstructural difference of SiC samples with different SiO₂ contents. Yet the difference is clear at 2400 °C in this study as shown in Fig. 4. For the pure SiC sample, a structure with coarsened particles and grown necks between coarse particles combined each other can be observed directly by the disappearance of smaller particles, and the segmented small pores by smaller particles at lower temperatures also have grown and formed connected large pores. However, for the samples with SiO₂ added, similar to the pure SiC sample the combined structure with coarse particles and large pores can also be observed, but there are still some fine spherical particles with a diameter about 10 μm in the form of a united conformation filled into the large pores. And the united fine particles increase with an increase of the

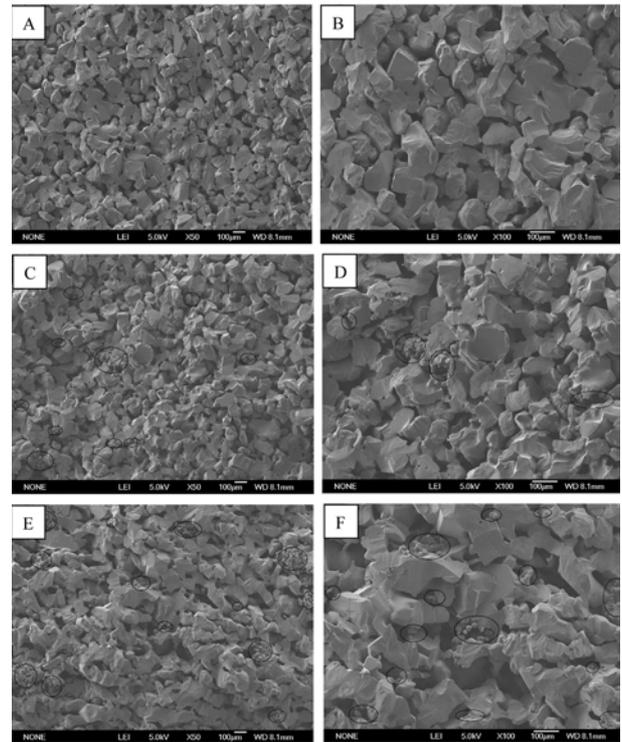
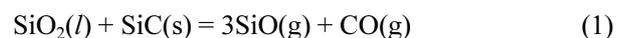


Fig. 4. Microstructures of fracture surfaces of fired pressed samples with different SiO₂ contents at 2400 °C: (A, B) pure SiC, (C, D) SiC sample with 1.54wt%, (E, F) SiC sample with 2.1wt%.

initial SiO₂ content. The appearance of the fine particles illustrates that SiO₂ will affect the recrystallization of rSiC.

Discussion

With microstructural evolution mentioned above, the existence of SiO₂ can affect the recrystallization of SiC. For covalently bonded SiC materials, the consolidation of SiC free of sintering agents achieves mass transport via surface diffusion or an evaporation-condensation process which is determined by the firing temperature [7]. However, SiO₂ can react with SiC under an inert atmosphere at high temperatures, generating gaseous products which lead to weight loss by these products escaping to the outside of samples. And the higher weight loss than the initial SiO₂ content illustrated in Fig. 1 confirms the truth of this reaction. The previously obtained linear relationship between weight loss and the SiO₂ content, and the almost equal slopes are in agreement with the reported reaction mechanism by other researchers [8-9], through the reaction:



The proportion of the weight loss to SiO₂ caused by reaction (1) is $(m_{\text{SiO}} + m_{\text{CO}})/m_{\text{SiO}_2} = 1.33$, which exactly coincides with the experiments (Table 1, slopes of the linear relationship). The agreement reveals the existence of the reaction (1) leading to a basic weight loss for SiC samples with SiO₂. And we define the theoretical weight

Table 2 The theoretical weight losses (w_t) resulting by reaction (1), additional weight losses (w_a) and recrystallized weight losses (w_r) vs SiO₂ contents

SiO ₂ (wt%)	w_t (wt%)	w_a (wt%) at different temperatures (°C)				w_r (wt%)
		1800	2000	2200	2400	2400
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0.39	0.52	0.80	0.85	0.83	1.46	0.63
1.54	2.05	0.79	0.77	0.81	1.40	0.59
2.10	2.80	0.78	0.88	0.86	1.39	0.53

loss resulted by reaction (1) as the basic weight loss.

The theoretical weight losses (w_t) to the SiO₂ content by reaction (1) have been listed in Table 2, which are much lower than the experimental values. This indicates other weight losses existed. The differences are also listed in Table 2, and we named them as additional weight losses (w_a). The additional weight losses are approximately equal when the temperature is lower than 2400 °C, indicating the same weight loss mechanism for w_a is independent of the SiO₂ content. In addition, there may be another weight loss mechanism at 2400 °C besides the two mentioned mechanism previously compared to the lower temperatures.

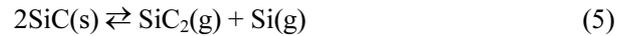
The almost equal weight loss for the samples with the same content of SiO₂ at different temperatures lower than 2400 °C indicates a mechanism went through surface diffusion to achieve consolidation. Otherwise, if it went through an evaporation-condensation process, the weight loss would be great with the increase of the firing temperature because of the enhanced vapor pressure of SiC, which is not consistent with the experimental results. The increased weight loss at 2400 °C reveals the enhanced SiC vapor pressure which resulted in the consolidation of SiC via evaporation-condensation process.

There may be some other reaction creating the additional weight loss. Rijswijk and Shanefield considered that the SiO(g) generated might continue to react with SiC(s) as described in the following [10]:

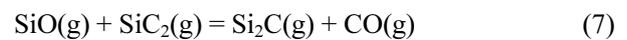


However, even if all the SiO(g) had been consumed by SiC(s), and all of the products escaped to the outside of samples, the calculated weight loss by reaction (2) would be 0.39 wt% for the sample with a SiO₂ content of 0.39 wt%, which is still less than the actual additional weight loss of about 0.80 wt% (Table 2). Hence this is not suitable to explain this phenomena.

The basic components of the evaporation of SiC are Si, SiC₂(g), Si₂C(g) and SiC(g) detected by mass spectrometry [11], besides the neglectable components such as Si₂, C, C₂ and C₃ because of their insignificant contents. The dissociative evaporation of SiC(s) can be represented by the following reactions:



For the pure SiC samples, the partial pressures of Si(g), Si₂C(g), and SiC₂(g) are in roughly an order of magnitude at the same temperature as calculated by Lilov [12], yet about 2-3 orders of magnitude higher than that of SiC(g). However, as to the samples with SiO₂, the SiO(g) generated can affect the dissociative evaporating process of SiC(s), as a result of an altered constituent of the vapor pressure. SiO(g) may react with SiC₂(g) described as follows:



This reaction, with $\Delta G < 0$ at the firing temperatures in this study is shown in Fig. 5, should be very efficient. And the $P_{\text{SiO}}/P_{\text{CO}} = 3$ generated by reaction (1) which determined the ambient pressure makes the SiC₂(g) move to Si₂C(g) with a high conversion rate. The consumption of SiC₂(g) will make the reaction (5) move to the right, and the escaped gas products result in a large weight loss, therefore it is possibly responsible for the weight losses in this study due to incomplete consumption of SiO(g).

In this study, the authors believe that the promoted dissociative evaporation reaction (5) of SiC(s) happened at the same time as SiO₂(l) being consumed by SiC(s) (Reaction (1)), not after the SiO₂(l) layer disappeared. Because if it happened after the SiO₂(l) layer was consumed, large amounts of SiO(g) would have escaped rapidly out of the SiC samples through the pores before it reacted with SiC₂(g). And with an increase of the temperature, the weight loss caused by SiO(g) will increase because of the elevated pressure of SiC vapor species. This is not consistent with the facts.

The equilibrium partial pressures of SiO(g) and CO(g) according to reaction (1) are given in Fig. 6, assuming that

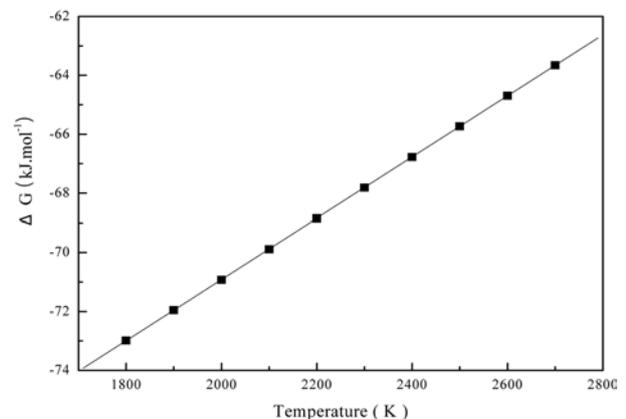


Fig. 5. Relationship between ΔG and T for the reaction (7). Thermodynamic data that was used to calculate ΔG are taken from NIST-JANAF [13].

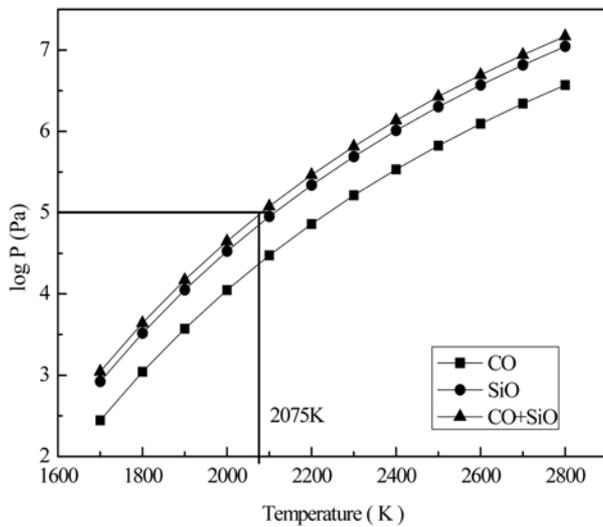


Fig. 6. Equilibrium partial pressures of SiO(g), CO(g), and their sum, as a function of the temperature according to reaction (1). Thermodynamic data that was used to calculate the vapor pressures are taken from NIST-JANAF [13].

the surface layer of SiO₂ on SiC was a viscous liquid. The sum of the partial pressures of SiO(g) and CO(g) will exceed the ambient pressure of 0.1 MPa in this study, thus the gaseous products generated will break apart the surface layer and escape out quickly.

In the process of the SiO₂(l) layer being consumed, the SiO(g) generated behaves with a high vapor pressure at the interface of SiC(s) and SiO₂(l). The narrow interfacial space for SiO(g) gave it a large collision probability with SiC₂(g). As a result, it consumed the SiC₂(g) as soon as the SiO(g) generated, which promoted the dissociative evaporation reaction (5) of SiC(s). The products of reaction (5) and (7) escaped out of the SiO₂(l) layer along with the SiO(g) and CO(g) whose pressure exceeds the environmental pressure, then to the outside of samples through the connecting pores. The consumption of SiO₂(l) finished may be in a short time, so in spite of the different thicknesses of the SiO₂(l) layer with the different SiO₂(l) contents, there was little difference of the additional weight loss because of the short reacting time.

After the consumption of SiO₂(l), large amounts of SiO(g) and CO(g) escaped out of the samples due to the generated vapor pressure being greater than the ambient pressure of 0.1 MPa. The residual SiO(g) in the pores had little influence on the weight loss of the samples because of the large space for the molecular motion and low partial pressure of SiC(s) vapor species despite the long firing time after the SiO₂(l) was consumed.

Surface diffusion is responsible for the material transfer and consolidation of SiC at low temperatures. And the existence of vapor species of SiC caused by SiO₂ might not affect the consolidation of SiC compacts, as a result, little difference can be observed in the microstructure for the samples without or with different SiO₂ contents.

When fired at high temperature up to 2400 °C, the

recrystallization of pure SiC finished by the evaporation-condensation process, and gave a notable weight loss compared to the relatively lower temperatures in this study.

The basic weight loss caused by SiO₂ and the additional weight loss affected by SiO(g) at lower temperatures are hardly affected by the temperature. The enhanced weight loss at 2400 °C compared to lower temperatures may be induced by the elevated vapor pressure of SiC, which is named the recrystallized weight loss (w_r). The recrystallized weight losses of the SiC samples with SiO₂ (Table 2) are much lower than that of pure SiC (Fig. 3, 0.89 wt%), and the existence of SiO₂ causes the appearance of an unfinished microstructure with small particles in Fig. 5, indicating that SiO₂ restrained the recrystallization of SiC. And the reduced recrystallized weight losses have been affected by the residual SiO(g) in the pores by decreasing the partial pressure of the available recrystallization vapor.

The complex process can be described as follows: after the consumption of SiO₂(l), the residual ambience of SiO(g) and CO(g) accompanied by Si(g) and Si₂C(g) generated by reaction (5) and (7) filled in the pores of SiC compacts. It could not promote the dissociative evaporation reaction (5) of SiC(s) because of long collision distances and a decreased pressure of SiO(g). In addition the relatively high partial pressure of Si(g) and Si₂C(g) in the residual ambience would inhibit the dissociative evaporation reactions such as (3), (4) and (5) over a long time, not like the interface between SiO₂(l) and SiC(s). The normal recrystallization of SiC would not continue until the consumption and escape of SiO(g). Before that, the consolidation of SiC proceeded by the evaporation-condensation process of a relatively low SiC(g) pressure generated by reaction (6), and the condensed reaction of Si₂C(g) and Si(g) with the C(s) by the process of surface diffusion of C(s) enhanced by the occurrence of silicon vapor [14]. The increased initial SiO₂ contents of SiC can increase the proportion of P_{SiO}/P_{CO} near to 3, which extended the time for consuming SiO(g). So the increased SiO₂ contents resulted in shorter times for normal recrystallization which displayed as the microstructural evolution with an increase of the SiO₂ content.

Conclusions

In order to study the influence of SiO₂ on microstructural evolution and the consolidation mechanism of RSiC, specimens composed of fine SiC powders with different initial amounts of SiO₂ on the surface and coarse SiC powders in a bimodal distribution were fired at 1800–2400 °C in inert atmosphere.

The introduction of SiO₂ can react with SiC at the SiO₂/SiC interface of the fine SiC particles, resulting in gaseous products of SiO(g) and CO(g) with a total pressure higher than the ambient pressure. The SiO(g) generated would promote the dissociative evaporation reaction of SiC with enhanced contents of Si(g) and Si₂C(g) at the interface and at the same time at the consumption of SiO₂(l). In addition, the consuming and promoted reaction time

might be very short. Then the generated gaseous species escaped out of SiC samples resulting in a basic weight loss and additional weight loss.

The consolidation mechanism of SiC has not been altered by the introduction of SiO₂, keeping it as surface diffusion at low temperatures (1800-2200 °C) and as an evaporation-condensation process at high temperature (2400 °C), while the mass transport altered from SiC₂(g), Si₂C(g) and Si(g) to those including SiO(g). Just after the consumption of SiO₂, the high partial pressure of SiO(g) remaining in the pores of SiC samples might inhibit the effective recrystallizing atmosphere, resulting in the initial consolidation mechanism with the SiC(g) vapor and surface diffusion of C(s). With the decreasing and escaping of the partial pressure of SiO(g), the atmosphere in the pores becomes normal and completed the recrystallization.

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