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A new design for preparation of high performance recrystallized silicon carbide

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Abstract

Applications urgently demand higher flexural strength and oxidation resistance of recrystallized silicon carbide (RSiC), which is weakened by its relatively low density and porous structure. In this paper, a new approach of a cyclic process of polymer impregnation and pyrolysis (PIP), and recrystallization, has been used to decrease porosity and increase the density of commercial RSiC. As a result, a high performance RSiC with a density of 2.99 g/cm^3 and flexural strength of 162.3 MPa was obtained via three PIP-recrystallization cycles, in addition to an improved oxidation resistance. The pre-treatment of PCS has also been discussed to improve the purity of its pyrolysis product.

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Keywords: Polymer impregnation; Pyrolysis; Recrystallization; Silicon carbide; Polycarbosilane

1. Introduction

RSiC is a high purity material sintered without any sintering additives [1,2], and has many excellent properties, such as creep resistance and flexural strength maintained at elevated temperatures, high thermal conductivity, good oxidation resistance, chemical stability and so on [3,4]. It is widely used in high-quality furnaces, liquid or hot gas filtration, thermal exchanger, etc. [5–8]. Most importantly, it is the most promising load-bearing material serving at temperatures over 1500 °C in air for long time [9,10].

Due to its high purity, high flexural strength and dimensional stability at heat treatment temperatures, an important application of RSiC is as the essential parts (e.g. wafer boat) in the various processing furnaces for silicon wafers (diffusion, oxidation, low-pressure CVD, solar cell doping, etc.). The increasing size of silicon wafers is one of the most obvious trends in silicon material technology. Presently, 300 mm diameter wafers are expected to ultimately replace most 150 mm and 200 mm wafer applications and it is predicted that 450 mm wafer will be introduced in the near future [11,12]. The larger wafers must be thicker to increase their resistance to warping and other structural deformities. The use of larger diameter and heavier wafers presents challenges to processing furnaces, especially for load-bearing RSiC parts. The processing furnaces demand the RSiC parts with higher flexural strength and excellent oxidation resistance.

There is a higher requirement of excellent oxidation resistance for RSiC in the applications of igniter and structural parts in kilns at temperatures above 1350 °C [13,14]. The oxidation of RSiC deteriorates the strength of kiln parts and the electric conductivity of igniter, resulting in its aging, or even its destruction [13,14]. As a result, improving the flexural strength and oxidation of RSiC is important in meeting the development of silicon material technology and other applications.

Compared to dense SiC materials, the relative low strength and poor oxidation resistance of RSiC originates from its low density and porous structure in which the pores are interconnected and open. The non-shrinkage consolidation process, i.e. the evaporation–condensation process, which has been accepted as the recrystallization mechanism for preparing RSiC, resulted in the low density and porous structure of RSiC.

As a result, increasing the density of RSiC is critical to improving the flexural strength and oxidation resistance so as to meet the currently developing applications and extend its potential applications in the field of high temperature. However, simply modifying the producing process of RSiC based on the current mature and advanced technology and the consolidation

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mechanism of RSiC seems to be inefficient to achieve the object [1]. Attempts such as molten intermetallics infiltration have been conducted to obtain dense composites. Despite the fact that the oxidation resistance has been improved, the increase of flexural strength is inconspicuous [15]. However, in some particular cases the decrease in flexural strength was also observed [16]. This might be caused by the cracks in intermetallics resulting from the mismatch of thermal expansion coefficients (CTE) between SiC and intermetallics (e.g. $CoSi_2$). It may be feasible to improve this disadvantage if SiC was the infiltrator. The problem is that SiC has no liquid state, therefore it is difficult to fill the pores of RSiC by a melt infiltration process directly. Use of slurries containing fine SiC particles for infiltrating has also been proved improper because it is hard to fully infiltrate the particles into the porosity of RSiC by the methods of coating, brushing, vacuum infiltration and sonication infiltration [14] since the particles prefer to aggregate near the surface [17]. The alternative is to use a precursor in liquid state or in the form of a solution which can generate SiC after a particular treatment such as the polymer impregnation and pyrolysis (PIP) process, thereby densify RSiC. PIP has been developed as a new technology for preparing ceramic matrix composites (CMCs). Polycarbosilane (PCS) is one of the most popular polymer precursors for preparing high performance SiC fiber [18,19] and CMCs [20,21] and it is the general term for organosilicon polymers containing a –Si–C– backbone [22]. Near stoichiometric SiC products can be obtained by controlling the composition and pyrolysis process [23,24].

This work aims to employ PCS as polymer precursor via PIP process to fill the pores and increase the density of RSiC. Treatment by recrystallization of PCS-derived SiC via evaporation–condensation is also adopted to densify the RSiC further. Consequently, a new process for the densification of RSiC combining PIP and recrystallization will be discussed particularly in this work.

2. Experimental

2.1. Materials

Commercial RSiC (Tangshan FCT, Tangshan, China) with 10 mm × 100 mm × 100 mm was employed. Its typical properties are listed in Table 1. PCS (softening temperature: ~210 °C, from National University of Defense Technology, Changsha, China) as the precursor of SiC was dissolved in xylene (Huachang, Shenzhen, China, 99.9%) with a concentration of 40 wt%, which was used as the impregnant.

2.2. Densification process of RSiC

Generally, the pyrolyzed products of pure PCS at low temperature are rich in carbon. In order to obtain a relatively pure SiC product, partially oxidative cross-linking treatment to as-received PCS was conducted at 170 °C for 1 h in air [25]. Pure PCS and partially oxidative cross-linked PCS were carried out for pyrolysis at 1400 °C for 1 h and then heat treatment at 2200 °C for 1 h to compare the effect of cross-linking treatment. The temperature was set at 2200 °C under the consideration that the crystal transformation and growth of SiC can be complete and the recrystallization can be avoided.

Table 1
Properties of the as-received RSiC.

Material	Density (g/cm^3)	Open porosity (%)	Flexural strength (MPa)
RSiC	2.745	14.1	93.0 ± 3.1

The cyclic PIP process: To enhance the infiltration efficiency, a vessel containing RSiC samples was placed in a chamber that could be evacuated and pressurized. The chamber was first evacuated to 20 mTorr, then the impregnant (PCS solution) was introduced into the vessel by the pressure difference and next pressurized for 1 h at a pressure of 1.0 MPa with Ar. Under this pressure, the PCS solution can be sufficiently impregnated into the pores of RSiC. Subsequently, the impregnated RSiC samples were dried at 80 °C for 24 h, then cross-linked at 170 °C for 1 h in air and pyrolyzed at 1400 °C for 1 h in Ar atmosphere with a heating rate of 5 °C/min. The above PIP process was repeated several times to enhance density till the infiltration efficiency became very low.

Recrystallization: When the PIP efficiency became very low, the samples were heated to 2400 °C. The dwell time was 20 min to conduct the recrystallization of PCS-derived SiC.

The cyclic PIP-recrystallization process: After the recrystallization, the PIP cycles continued to repeat in order to enhance the density of RSiC. Then the recrystallization treatment was repeated. The whole process including three PIP-recrystallization cycles is shown in Fig. 1.

2.3. Characterization

Density and open porosity of samples were measured using the water displacement technique. Flexural strength was determined by three point bending method in a span of 80 mm at a crosshead speed of 0.5 mm/min at room temperature

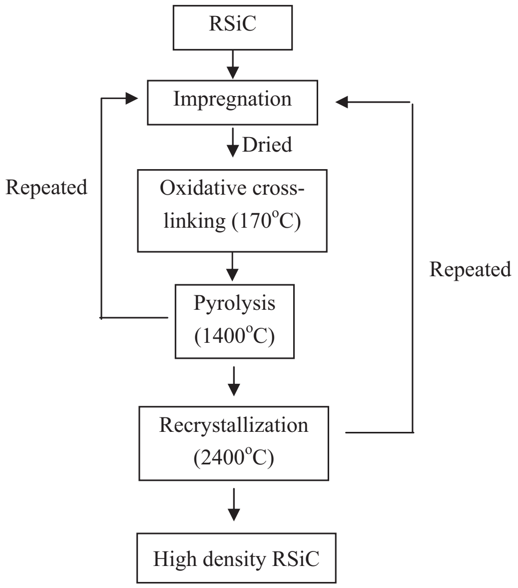


Fig. 1. Schematic diagram for the preparation of high density RSiC.

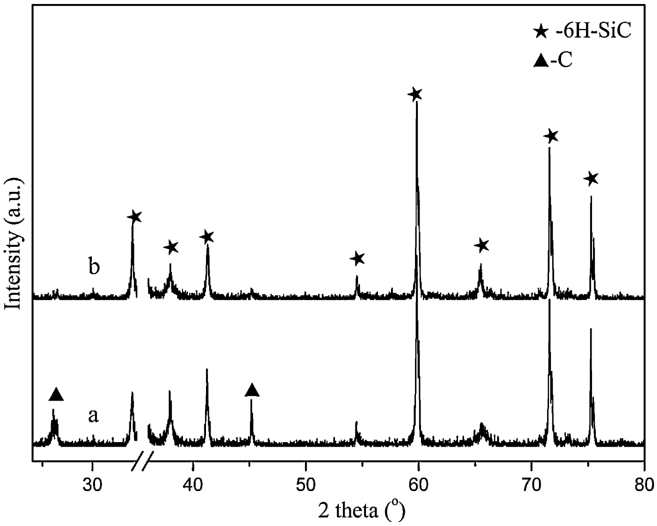


Fig. 2. XRD patterns of the products pyrolyzed at 1400 °C and then heat-treated at 2200 °C of the as-received PCS (a) and the oxidative cross-linked PCS (b).

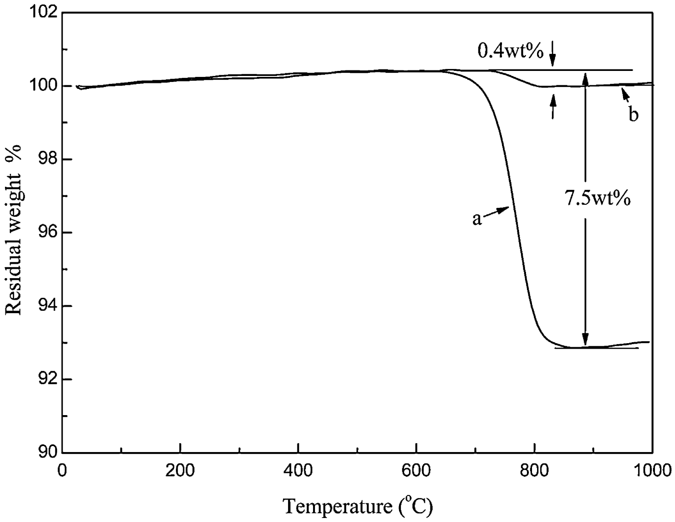
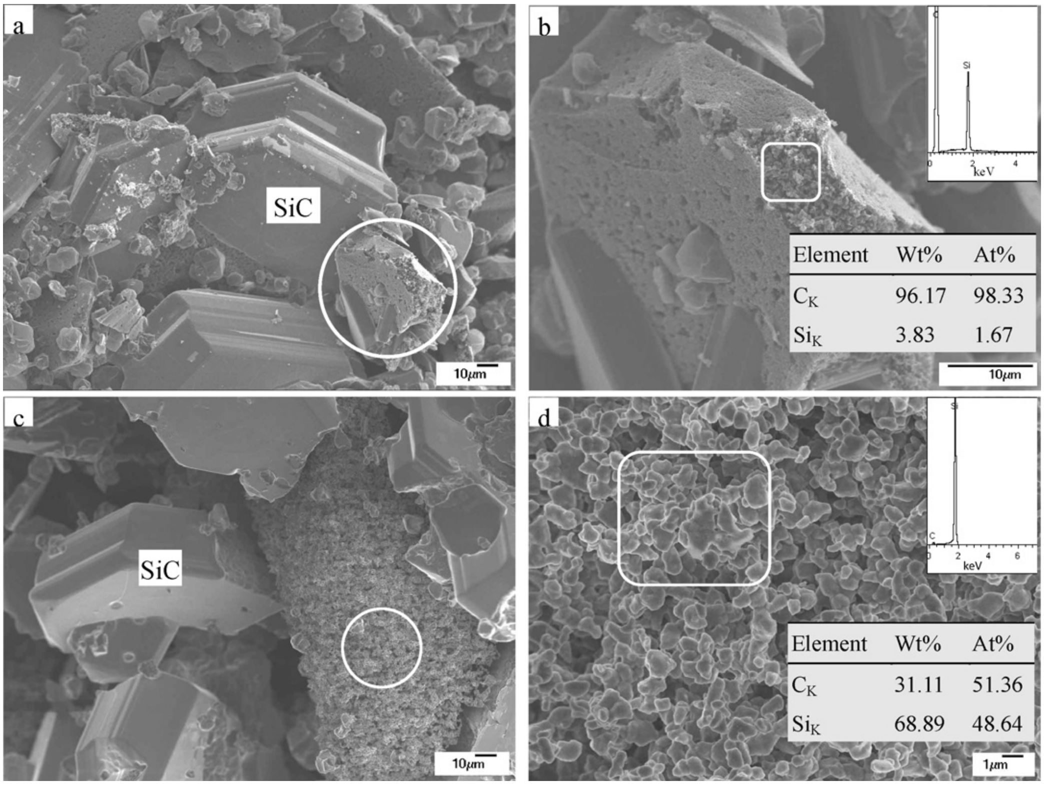


Fig. 3. TGA curves of the products pyrolyzed at 1400 °C and then heat-treated at 2200 °C of the as-received PCS (a) and the oxidative cross-linked PCS (b).

for samples with size of 10 mm × 10 mm × 100 mm. The 8 h cyclic oxidation tests for samples with 10 mm × 10 mm × 15 mm and surface polished were carried out at 1500 °C in static air. Weight changes were recorded before and after each oxidation cycle. The reported values are the averages of at least 5 independent measurements.

TGA was carried out on a simultaneous thermal analyzer (Netzsch, STA449C) in air atmosphere (flow rate of 50 ml/min) with a heating rate of 10 °C/min from RT to 1000 °C to detect the content of residual carbon in PCS-derived products. Phase identification was performed by XRD (Rigaku D/max2200 VPC). The morphology, microstructure and chemical composition of the samples were examined by SEM (JEOL, JSM-6700F) equipped with EDS (Oxford).



Element	Wt%	At%
C_K	96.17	98.33
Si_K	3.83	1.67

Element	Wt%	At%
C_K	31.11	51.36
Si_K	68.89	48.64

Fig. 4. SEM photographs of the products pyrolyzed at 1400 °C and then heat-treated at 2200 °C of the as-received PCS (a, b magnified image of a (circular area)) and the same product after oxidation at 800 °C (c, d magnified image of c (circular area)), and corresponding EDS results (rectangular area in b and d).

3. Results and discussion

3.1. Products characterization of PCS

The XRD pattern of product pyrolyzed at 1400 °C and subsequent heat-treated at 2200 °C of the as-received PCS is shown in Fig. 2a, indicating that the product phases of the as-received PCS are 6H-SiC and C (graphite). The weight loss based on TGA in Fig. 3 shows that the product contains about 7.5 wt% residual C, indicating the PCS is carbon-surplus for SiC. The morphology of the products heat-treated at 2200 °C in Fig. 4a and b shows large hexagonal SiC grains, and clusters which mainly consist of carbon with a little SiC confirmed by the corresponding EDS (in Fig. 4b) and XRD results. SiC grains with sizes about 1 μm were observed in the product after oxidized (Fig. 4c and d) at 800 °C, demonstrating the small SiC

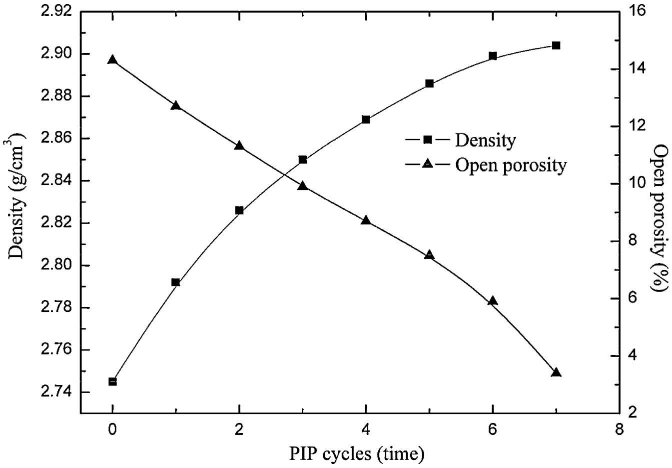


Fig. 5. The variation of density and porosity of RSiC with PIP cycles.

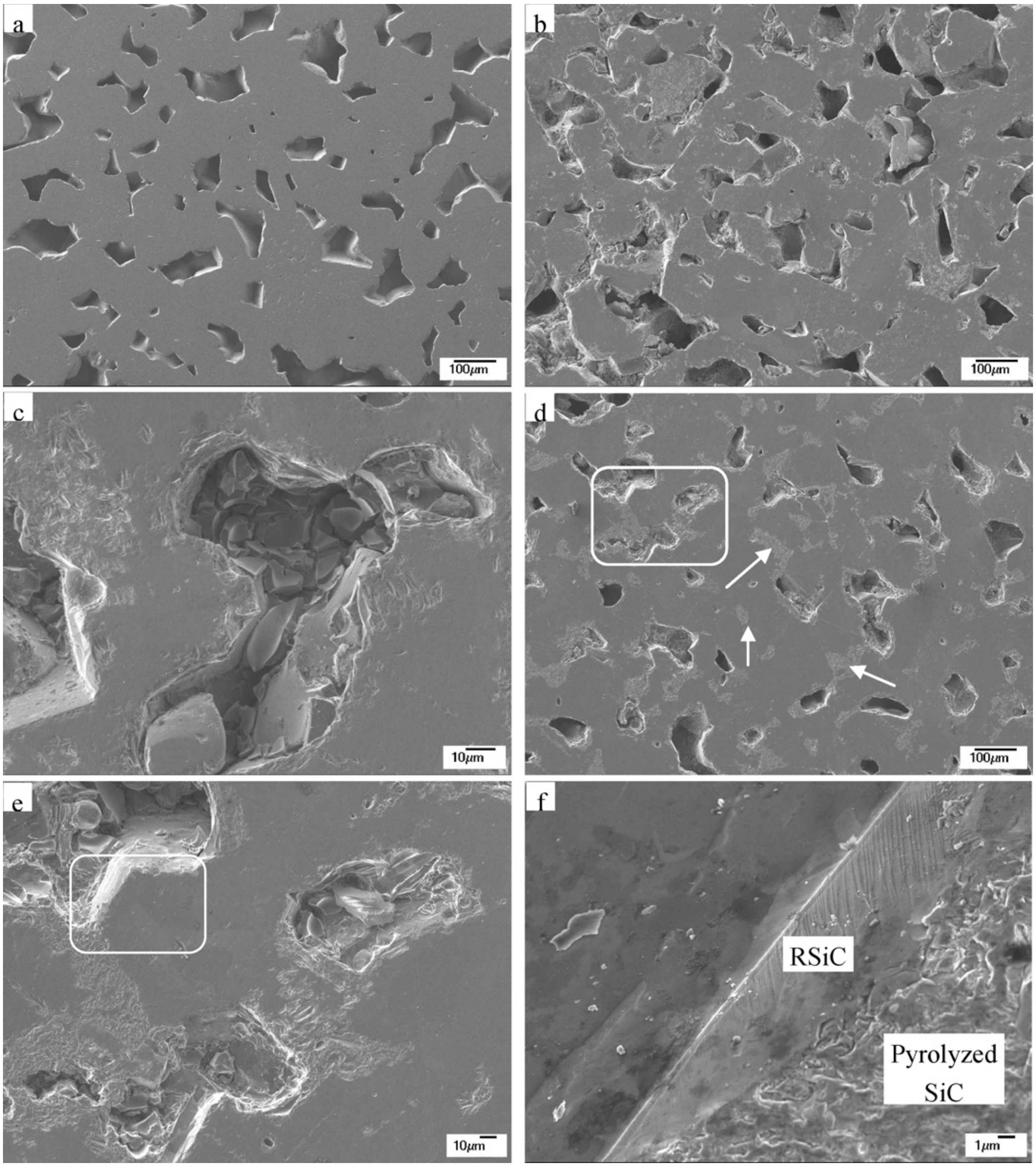


Fig. 6. SEM observation of the microstructural evolution of polished RSiC with PIP cycles: the as-received RSiC (a), that after two PIP cycles (b, c) and after seven PIP cycles (d, e); and the fracture surface of RSiC after seven PIP cycles (f).

grains existed in clusters C. Compared to the large SiC grains, the small ones indicate the grain growth was inhibited by the residual C, which may be detrimental to the recrystallization of SiC at 2400 °C. The residual C may also be harmful to the properties of RSiC.

The XRD result of the products pyrolyzed at 1400 °C and then heat-treated at 2200 °C with prior oxidative cross-linking in Fig. 2b, shows only the 6H-SiC phase. TGA curve (Fig. 3b) presented the weight loss only about 0.4 wt%, indicates a small amount of residual carbon. It can be concluded that prior oxidative cross-linking is feasible to eliminate the excess C for PCS, and the near stoichiometric SiC can be obtained. In addition, the oxidative treatment to PCS can even help to facilitate the pyrolysis because free of fused PCS spreads out of the RSiC during pyrolysis after the treatment.

3.2. *Density and microstructural evolution of RSiC by PIP*

The variation of density and porosity of RSiC with PIP cycles is shown in Fig. 5. The density of RSiC increases with the increase of PIP cycles, corresponding to the decrease of open porosity. After the 6th PIP cycle, the open porosity of RSiC is less than 6%, and it is hard to infiltrate the PCS solution into RSiC. Thus there was almost no improvement to the density of RSiC for the 7th PIP cycle. Moreover, the treatment in the 7th PIP cycle resulted in a notable decrease of open porosity of RSiC, which indicates that further impregnation is impossible.

The microstructure evolution of RSiC with PIP cycles is presented in Fig. 6. The as-received RSiC shows an interconnected porous structure with pore-diameter above 100 μm (Fig. 6a), which provides the access for the impregnation of PCS solution. As visible in Fig. 6b and c, the pyrolysis particles with the diameter about 10 μm, which distributed in units, filled in the pore of RSiC. With the increase of PIP cycles, interspace among the pyrolysis particles and the pores were filled gradually. The decrease of pore size increased the difficulty of impregnating, however, the applied gas pressure helped force the PCS solution to get through the narrowing paths. After several cycles, the pores were blocked and became isolated (Fig. 6d and e). The SiC products generated from different PIP cycles seem to be compact (arrow marked in Fig. 6d), resulting in the interconnected pores becoming closed and the decrease of open porosity. The blocked pores and the relatively low residual open porosity makes further impregnation more difficult. The density at the 7th PIP cycle exhibited almost no further increase, and the final porosity of PIP-derived RSiC is only 3.4%. Meanwhile, based on the SEM observation of the fracture surface for the RSiC treated after seven PIP cycles in Fig. 6f, the combination between the RSiC and pyrolyzed products is relatively dense and strong.

The PIP treatment can increase the density of RSiC to a certain extent. However, to increase the density of RSiC to a high level cannot be complete by simple PIP cycles due to the volatility of the xylene, significant shrinkage of the PCS during pyrolysis and the blocking effect of the pyrolyzed SiC to the pores.

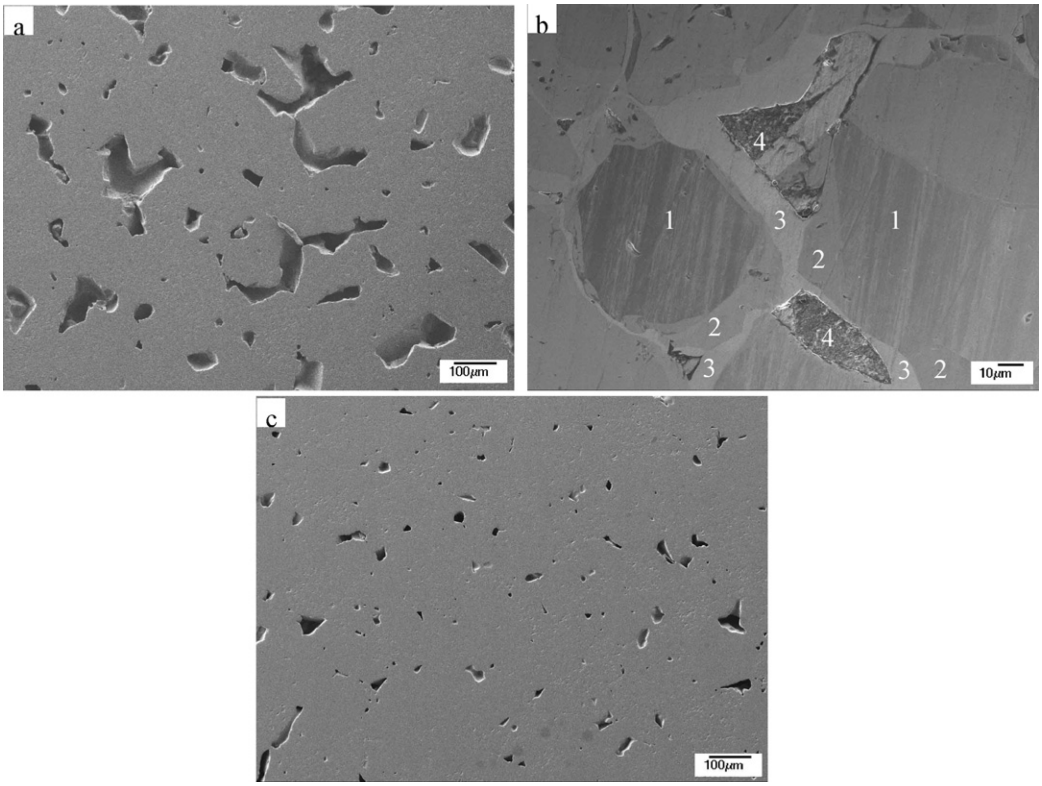


Fig. 7. SEM photographs of the microstructural evolution of polished RSiC with PIP-recrystallization cycles: after the first cycle (a), after two PIP-recrytallization cycles and the third PIP-cylces (b), and after the third cycle (c). The numbers “1–4” in (b) represent different SiC originated from different treatment periods.

3.3. Recrystallization

Recrystallization at 2400 °C is utilized to remove the SiC particles which have a high tendency to deposit on necks of original RSiC via the evaporation–condensation process to reopen the blocked pores. After this treatment, the density of RSiC sample obtained by PIP in Section 3.2 decreased from 2.91 g/cm^3 to 2.86 g/cm^3, correspondingly, the open porosity increased from 3.4% to 10.2%. The microstructure of recrystallized cyclic-PIP-treated RSiC is shown in Fig. 7a. The pyroled SiC particles disappeared (Fig. 7a) and the pore sizes of RSiC after the first PIP-recrystallization cycle are smaller than that of the as-received RSiC (Fig. 6a). There is no residual carbon detected in the pores or the interface, which confirms the oxidative cross-linking treatment of PCS to be satisfiable to eliminate the excess carbon for SiC. The slight decrease of density may result from the continued decomposition of composed SiC_xO_y phase at 1400 °C [26] and some SiC sublimation escaped via the interconnected open pores during the recrystallization.

The density variations of RSiC before and after recrystallization via PIP-recrystallization cycles are shown in Fig. 8. The density of RSiC increases with the successive PIP-recrystallization cycles. The downtrend of density before and after recrystallization decreases due to the enhanced densities and less porosity of RSiC. Before the 3rd recrystallization, that is, RSiC was treated after two PIP-recrytallization cycles and the 3rd PIP-cylces, the distinctive SiC phase from different treatment periods can be obviously observed, despite the unknown explanation of the contrast origin between the SiC phases in Fig. 7b. The pores among the original grains (shown as "1" in Fig. 7b) of RSiC are progressively filled by the deposited SiC via the first and second recrystallization treatment ("2" and "3"), and eventually filled up by the pyrolyzed products ("4"). The bonding between the different SiC phases seems to be close and dense. After three PIP-recrystallization cycles, a notably denser structure with only a few small pores formed (Fig. 7c), and its density achieved to 2.99 g/cm^3 and the open porosity is only about 3.9%.

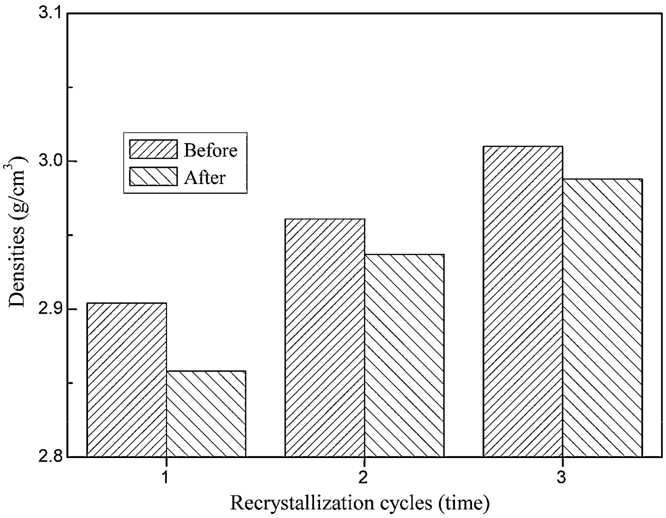


Fig. 8. Density variations of PIP treated RSiC before and after recrystallization.

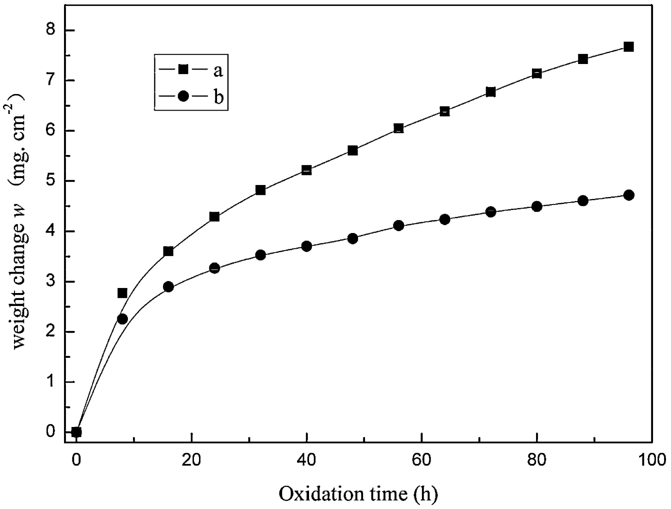


Fig. 9. Weight changes per unit area of as-received RSiC ((a), 2.745 cm^{-3}) and PIP-recrystallization treated RSiC ((b), 2.99 g/cm^3).

3.4. Mechanical strength and oxidation resistance

The as-received RSiC (2.745 g/cm^3) and PIP-recrystallization treated RSiC (2.99 g/cm^3) were oxidized at 1500 °C for different times, and the weight changes of them are shown in Fig. 9. The weight gain of cyclic PIP-recrystallization treated RSiC is about half of that of the as-received RSiC. The flexural strength of the cyclic PIP-recrystallization treated RSiC is 162.3 ± 2.6 MPa, which is 75% higher than that of as-received RSiC (93.0 ± 3.1 MPa). The improvement of flexural strength and oxidation resistance of the cyclic PIP-recrystallization treated RSiC are mainly due to the decrease of porosity caused by the new technological process.

4. Conclusions

The object of increasing the density of RSiC in this work has been achieved by a cyclic combination process of PIP and recrystallization. Relative pure SiC filled in the pores of RSiC obtained by PIP is beneficial to improve the properties of RSiC and recrystallization. Despite the pure PCS employed in this work is carbon-surplus for SiC, relative pure SiC product has been obtained successfully through a prior oxidative cross-linking treatment. The PIP treatment improved the density of RSiC to a certain degree, but it is not effective by a single way of PIP cycles owing to the volatility of xylene, significant shrinkage of PCS during pyrolysis and the blocked pores. The recrystallization treatment at 2400 °C reopened the plugged pores and made the pores intercommunicate by the evaporation–condensation of SiC particles, which resulted in a continued PIP density increasing process. It brought a slight decrease of density after recrystallization, however, after three PIP-recrystallization cycles, a high performance RSiC with a density of 2.99 g/cm^3 and flexural strength of 162.3 ± 2.6 MPa was obtained finally compared to the as-received RSiC.

Acknowledgments

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