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Influence of an initial hot-press processing step on the mechanical properties of 3D-C/SiC composites fabricated via PIP

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Abstract

Hot press is firstly used before infiltration and pyrolysis cycles to enhance the densities and the mechanical properties of three-dimensional-braided carbon fibers reinforced SiC composites (3D-braided C/SiC) fabricated via preceramic infiltration–pyrolysis (PIP) process. The influences of temperature, pressure, temperature at which the pressure should be applied, holding time and introduction of inert fillers during the hot-pressing process are especially studied. The results show that the hot-press step used before the PIP cycles is positive to the mechanical properties of the materials. The 1873 K, 1 MPa, 5-min hot-pressing parameters give good properties to the materials. It is beneficial to the properties that hot press is applied after PCS is pyrolyzed to β-SiC completely. Conversely, the introduction of inert filler SiC powders to enhance the properties of the materials is not effective under the above conditions.

Keywords: A. Precursors: organic; A. Hot pressing; B. Composites; C. Mechanical properties

1. Introduction

Fiber-reinforced ceramic matrix composites (FRCMC) via preceramic infiltration–pyrolysis (PIP) process have many advantages such as low cost and simple processing procedure similar to those for fiber-reinforced polymer matrix composites (FRPMC) and carbon/carbon (C/C) composites [1–3], etc. The PIP process relies on the conversion of a preceramic polymer precursor to inorganic matter and the use of highly cross-linked polymers emitting molecular fragments. During pyrolysis, there are many pores left inside the matrix and consequently the density is low (the density of preceramic polycarbosilane (PCS) is 1.0–1.2 g cm^{-3}, while that of the resulting SiC ceramic is 2.55 g cm^{-3}) resulting in volume shrinkage [4]. Nakano and co-workers [5,6] used hot-press process after seven infiltration–pyrolysis cycles under atmospheric pressure on three-dimensional carbon fiber braids. Although the overall porosity was reduced to 3%, the materials still had low failure strength (about 185 MPa) and toughness because of the occurrence of strong interface bonding and needle-like pores that are harmful to the properties. To resolve this contradiction, hot pressing was used in the first cycle in the present contribution. Hot-pressing process is a usual method in powder metallurgy and one of the methods applied in CMC preparation. The process densifies materials and shortens fabrication time. The three-point flexural failure strength of the materials is improved from 338 MPa to 503 MPa after using hot-pressing process. This result indicates that the process enhances the properties of materials evidently. Temperature, pressure, temperature at which the pressure should be applied, holding time and introducing inert fillers in hot-press process have much influence on materials properties. So the influence of these factors on the properties of 3D-braided C/SiC composites via PIP with hot-press process before the first infiltration–pyrolysis cycle is discussed in this paper.

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2. Experimental technique

2.1. Main raw materials

The fiber volume fraction of the selected 3D-B carbon fibers as the reinforcement part of the material is $V_f = 50\%$, which is two-step braided, 8:1:1 as the fiber volume fraction of *X*, *Y*, *Z* directions. The fibers in the main *X* direction are M40JB (Toray International, Inc., Japan). Those in the other *Y*, *Z* directions are Jitan fibers (Jilin Carbon Corp., China). PCS used as the precursor displays an average molecular weight of approximately 1300, and its softening point is 439–449 K. The average diameter of the inert filler β-SiC is 0.4 μm.

2.2. Experimental technique

The experimental procedure is outlined in Fig. 1. The infiltration slurry is composed of PCS as preceramic and xylene as solvent (volume ratio 1:1). Some of the slurries contain β-SiC powders (10 wt.%). Carbon fiber braids are infiltrated by the slurry in vacuum and ultrasonic shaking, hot pressed at certain temperatures and pressures. Then the hot-pressed specimens are infiltrated with the slurry mentioned above and pyrolyzed in N_2 at 1373 K. The specimens are densified gradually after seven infiltration–pyrolysis cycles.

2.3. Microstructure analysis and mechanical characterization

The phase morphology and the element distribution of the specimens after pyrolysis were characterized by SEM and EPMA linescan equipment (LEO435, LEO Elektronenmikroskopie GmbH, and Stereoscan 250 MK3, Cambridge Instruments). The microstructure was characterized by X-ray diffraction (XRD) using a Philips 1730/1820 instrument (Cu Kα, 40 kV, 40 mA). The three-point flexural strength of the specimens was measured by compression testing, with a cross-head speed of 0.2 mm min^{-1}, on samples 6 mm × 6 mm × 12 mm at room temperature (RT), using an Instron 1121 UTM. The fracture toughness was determined by the single edge notched beam (SENB) method with a cross-head speed of 0.05 mm min^{-1} and the span/height ratio of 4. The ratio of notch depth to specimen height was 0.48. Each data point reported represents the average value of five individual tests.

3. Results and discussion

3.1. Influence of hot-press temperature

The materials listed in Table 1 were prepared at 1673 K, 1873 K and 2123 K hot-press temperatures under 1 MPa for 5 min.

The RT mechanical properties for the material hot pressed at 1873 K are the best, namely $\sigma_R = 503$ MPa, $K_{IC} = 17$ MPa $m^{1/2}$ due to apparatus and processing factors. Pyrolysis reaction cannot be complete at the high heat-up speed used in the hot-press furnace (that is 20–30 times higher than that in other temperature-controlled furnaces). At 1673 K, PCS in braids does not transform to SiC completely for the high heat-up speed in the first cycle. In latter infiltration–pyrolysis cycles, the polymer PCS touching carbon fibers left in the first cycle pyrolyzes and produces holes near fibers, which are enwrapped by ceramic formed by slurry infiltrated in latter cycles and will not be infiltrated again.

Preceramic PCS pyrolyzes relatively completely at 1873 K and bonds carbon fibers in a relatively efficient manner. So the density, flexural strength and toughness of the materials prepared under this condition improve remarkably.

Conversely, the RT properties for the materials hot pressed at 2123 K decrease markedly. The pulled-out fibers enwrapping thick matrix in Fig. 2(a) show that they are bonded to the matrix very tightly under this condition. The bonding force between fibers and matrix is stronger than the force between Si and C atoms inside the matrix. The characteristic of the interface between fiber and matrix in Fig. 2(b) suggests that the diffusion profiles through the interface or eventually an image of polished cross-section at an appropriate scale and after suitable etching would be better experimental evidence of diffusion. Strong interface bonding is one of the most important reasons for material properties decline.

The electron probe micro analysis (EPMA) linescan data in Fig. 3 show that the Si-content at the interface is higher than those in fibers and matrix. This result demonstrates that

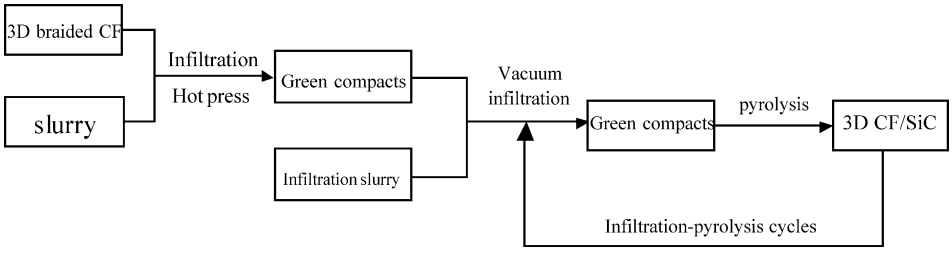


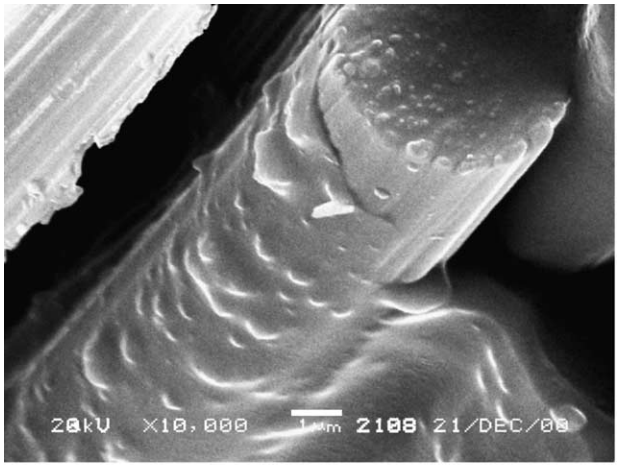
Fig. 1. Experimental flow diagram for 3D-braided C/SiC CMC prepared via hot-press infiltration–pyrolysis.

Table 1
Mechanical properties of materials fabricated under different HP temperatures (1 MPa, 5 min, Ar)

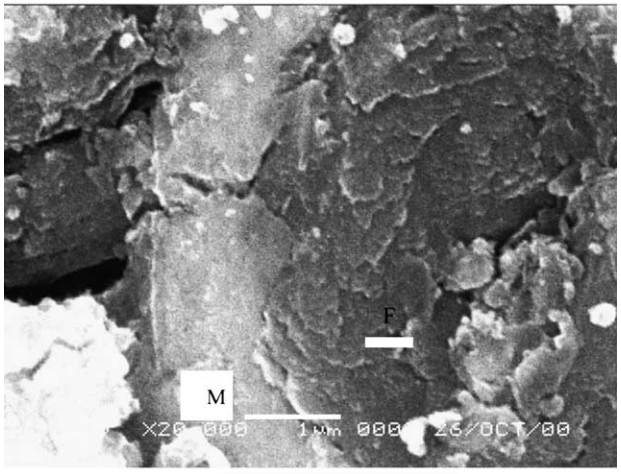
Hot-press temperature (K)	Density (g cm^{-3})	Three-point flexural strength (MPa)
1673	1.856	374
1873	1.883	490
2123	1.884	212

elements diffusion exists in the material. Si from matrix has a tendency to diffuse into carbon fibers during pyrolysis. The C-content in fibers is much higher than that in matrix and Si will attain the 1:1 SiC atom ratio at the interface while it reacts with carbon fibers. So the Si-content at the interface is higher than those in fibers and matrix. Fibers property decline caused by element diffusion influences the properties of the whole material. The O-content in fibers and matrix seems to remain qualitatively low from the O Kα line scan as shown in Fig. 3(c).

On the other hand, from the point of view of matrix, crystallization occurs in the matrix when the hot-press

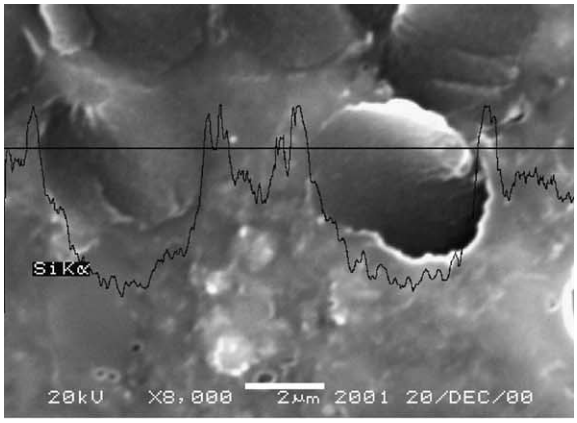


(a) ×10000

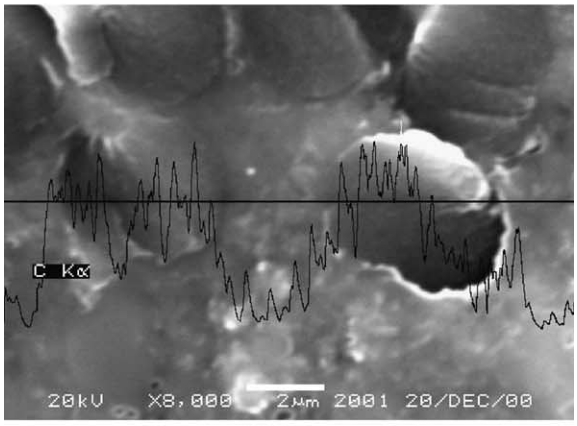


(b) ×20000

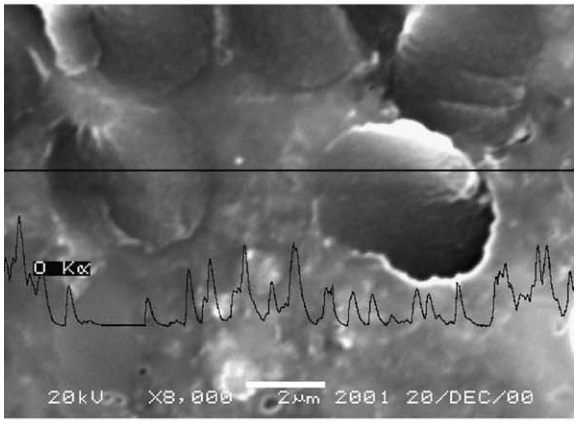
Fig. 2. SEM photographs of materials hot pressed at 2123 K.



(a) Si



(b) C



(c) O

Fig. 3. EPMA linescan for Si, C, and O of the materials hot pressed at 2123 K (8000×).

temperature is increasing. Fig. 4 is the XRD pattern of the materials treated under 10 MPa, 1 h hot press at different temperatures and after six additional PIP-cycles. AlN–Y_2O_3 (7:6 wt.%) denoted as YAG is added to the materials hot pressed at 2123 K as sintering aid (10 wt.%). The diffraction peak of carbon gets sharper gradually with increasing hot-press temperature. This indicates that the degree of crystallization of carbon (in fiber and in matrix) gets higher. SiC has the trend of crystallization with high temperature

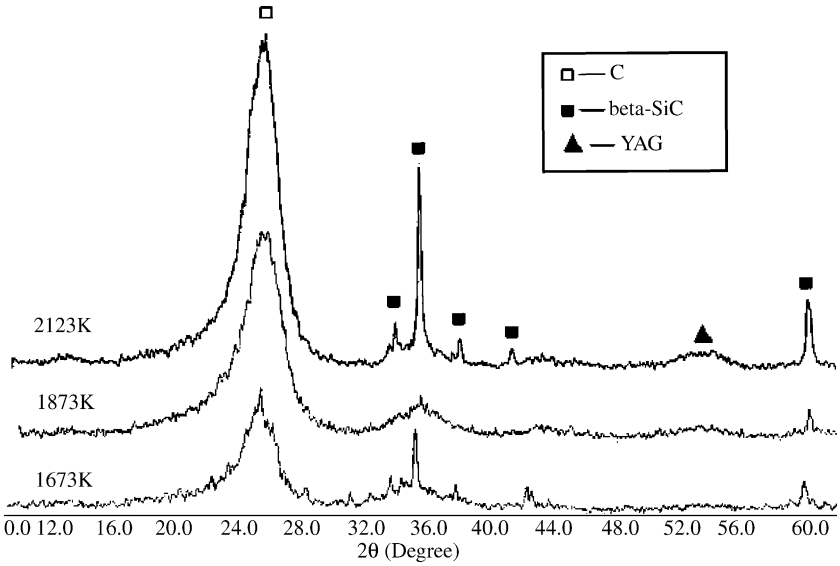


Fig. 4. XRD pattern of the materials treated with 10 MPa, 1 h hot press under different temperatures.

treatment. SiC crystal nuclei grow partially in the matrix treated at 1673 K and 1873 K. There are sharp diffraction peaks of SiC in XRD pattern (2123 K), which indicate SiC crystals grow relatively perfectly at this temperature. As we know, perfect crystals have a negative influence on matrix strength [7]. It is one of the reasons of the 2123 K-treated materials low RT-properties. The peaks of SiC (1873 K) are weaker than the peaks (1673 K) possibly because the influence of the amorphous SiC formed in the later six fabrication cycles. But it is obvious that SiC crystals grow more perfectly under higher treatment temperature. All these factors give the main reason of the low RT-properties of the materials hot pressed at 2123 K.

3.2. Influence of hot-press T_a

Hot-press T_a means the temperature at which the pressure should be applied during furnace temperature increase. It influences the properties of the materials greatly as seen from the results reported by Nakano and co-workers [5,6].

As seen from Table 2, it is beneficial for the enhancement of the density and the failure strength to apply the pressure when the furnace temperature is about 1000 K, which is the main period of the PCS-pyrolysis. A significant amount of pores are left in the matrix when the pressure is applied before the PCS-pyrolysis. Further, hot press applied above 1000 K, i.e. when the pyrolysis is almost finished, would close the pores. The results show that the failure strength of the materials hot-pressed during heating up is lower than that of the materials hot-pressed when it reaches the final temperature. It seems not beneficial to the properties when the materials are hot-pressed before PCS is pyrolyzed to β-SiC completely. It would counteract the free molecular recomposition when hot press is applied during the transformation of PCS. Furthermore, β-SiC grains would still grow more matured under this condition. While the grains would be fine when hot press is applied at the final temperature and the properties of the material would be enhanced.

Table 2
Influence of hot-press T_a[a] on the bending strength of the materials (1873 K, 10 MPa, 1 h, Ar)

Hot-press T_a (K)	Density (g cm^{-3})	Three-point flexural strength (MPa)
673	1.752	275.2
1073	1.776	306.3
1473	1.762	227.4
1873	1.762	322.8

[a] T_a: temperature at which pressure is applied in the hot-press step.

Table 3
Properties of materials fabricated under different pressure (1673 K, 5 min, Ar)

Pressure (MPa)	Density (g cm^{-3})	Three-point flexural strength (MPa)
1	1.873	363
5	1.884	413
10	1.902	433
15	1.904	409

Table 4
Properties of the materials for different hot-press time (10 MPa, Ar)

Hot-press temperature (T) (K)	Hot-press time (t) (min)	Three-point flexural strength (MPa)
1673	5	433
1673	60	448
1873	5	490
1873	60	307

Table 5
Influence of the inert filler SiC powders on the properties of the materials

Conditions	Adding fillers	Three-point flexural strength (MPa)	Densities (g cm^{-3})
1673 K, 1 MPa, 5 min	No	374	1.856
1673 K, 1 MPa, 5 min	Yes	363	1.867
1873 K, 10 MPa, 1 h	No	307	1.833
1873 K, 10 MPa, 1 h	Yes	298	1.854
2123 K, 10 MPa, 1 h	No	312	1.887
2123 K, 10 MPa, 1 h	Yes	260	1.890
1673 K, 10 MPa, 5 min	Yes	433	1.883
1673 K, 15 MPa, 5 min	Yes	409	1.897

3.3. Influence of pressure during hot pressing

The pressure applied during the hot-press step has much influence on the materials properties (Table 3).

Table 3 shows the different trends in the density and the failure strength evaluation with the pressure increase. The green compacts become more compact and the density is improved. The density improvement becomes significant (about 1.90 g cm^{-3}) when the pressure comes to 10–15 MPa. However, the flexural strength has a different improvement trend. The failure strength evaluation is similar to that of density as long as the pressure is lower than 10 MPa. The average strength reaches its maximum (433 MPa) when the pressure is 10 MPa. Conversely, it decreases to about 410 MPa, as the hot pressure is 15 MPa. As a matter of fact, the densification extent and properties increase with a pressure increase. Excessive high pressure could damage the carbon fibers and degrade the materials properties.

3.4. Influence of hot-press time

The hot-press time is a relatively important processing factor (Table 4).

The RT properties are improved when the materials are hot-pressed from 5 min to 1 h at 1673 K. But the RT properties decrease by about 40% for the material hot pressed at 1873 K. That is mainly because PCS can not be pyrolyzed to SiC completely at 1673 K for 5 min due to the high heating-up velocity in the hot-press furnace, as previously mentioned. This is the reason for the material low properties. Prolonging the time of hot-press results in a complete pyrolysis, which is a good basis for the latter cycles to prepare high property materials. The parameters of T = 1873 K and t = 5 min are well-suited to the process. Prolonging hot-press time not only damage the fibers but also β-SiC crystals grow too much in the matrix with defects. These are harmful to the properties of the materials.

3.5. Influence of inert filler β-SiC

Commonly, active and inert fillers are used in composite processing. Active fillers can react chemically with be-filled while inert fillers do not but increase the density and have physical effects. Table 5 shows the influence of the inert filler β-SiC powders on the properties of the materials.

From Table 5, it could be considered that the β-SiC filler enhances the density of the materials. The powders are injected into the matrix and improve densification. But the fillers have also a negative effect on the failure strength. The RT properties for the materials hot pressed at 1673 K, 1873 K are either maintained or even slightly lowered after adding the fillers. The RT properties decline evidently after hot pressing at 2123 K. The erosive β-SiC powders in the matrix and among the carbon fiber braids have an influence on the properties. The sharp edges of the β-SiC grains would damage the carbon fibers. The fibers when heated at very high temperature (2123 K) are more easily damaged by the powders. Further, the RT properties of the materials decline relatively evidently when the pressure is raised from 10 MPa to 15 MPa at the 1673 K, 5-min hot-press condition with the introduction of the β-SiC powder. This indicates that an excessive pressure leads to the distortion of the carbon fiber braids and the β-SiC powder seriously damaged the carbon fibers mechanically. So the introduction of β-SiC powders with a view to enhance the properties of the materials is not effective under the hot-press conditions used in the present work.

4. Conclusions

In this paper, the three-point flexural strength of the materials fabricated via PIP is improved from 338 MPa to 503 MPa by applying a hot-press step before the first infiltration–pyrolysis cycle. The process improves the properties of the materials obviously. The following parameters, namely, P = 1 MPa, t = 5 min and T = 1873 K have a positive influence on the properties of the materials. The average three-point flexural strength can reach 490 MPa (maximum of 503 MPa) under this condition. But the properties decrease severely at 2123 K hot-pressing temperature. The main reasons of the properties decrease are thought to be the growth of SiC crystals in the matrix, the heat damage to the carbon fibers and the excessive interface reaction. A pressure of 10 MPa can enhance the properties while an overhigh pressure may damage the fibers and decrease the properties of the materials. So the optimized

parameters of the hot-press process are 1873 K, 5 min. It seems not beneficial to the properties when hot press is applied before PCS is pyrolyzed to β-SiC completely. The introduction of SiC powders with a view to enhance the properties of the materials is not effective under such conditions. This paper gives a set of relatively optimized parameters for the hot-press process which will be helpful for future research in this area.

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