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Research on change of micro-structure and mechanical performance Si/C matrix composites for thermal process

Silicon carbide fiber reinforced silicon carbide composite material (Si/C) is a highly promising high-temperature structural material. The Si/C composites are prepared by means of the precursor impregnation (PIP) process. Under inert atmosphere, 1399-1801°C temperature range of Si/C composites for thermal process, as temperature measurement with infrared thermal imaging device tool monitoring temperature of the material, thermal process temperature on the Si/C composites are studied the effect of the micro-structure and mechanical performance. The results show that the 1399°C composites matrix crystallization degree increased after thermal process, the overall mechanical performance increase. While the temperature is rising further, the fiber of composite material is damaged, and the mechanical property also is decreased rapidly.

Keywords: *Si/C matrix composite, thermal process, micro-structure, mechanical performance, infrared thermometer.*

1. Introduction

Continuous Si/C fiber reinforced Si/C matrix composites (Si/C), which are characterized by high strength, high specific modulus, thermal shock resistance, high temperature resistance and low density, have vast potential for future development in high-temperature components of aero-engine. Meanwhile Si/C composites also have pseudo-plastic behaviour, low tritium permeability and good radiation stability, and are considered to be a lot of potential materials for fusion reactor. The preparation of Si/C composites processes include chemical vapour infiltration (CVI), precursor infiltration pyrolysis process (PIP) and nano-infiltrated transient eutectic process (NITE), etc., among which PIP process received much more attention for its suitability for preparing large special-shaped components and low production cost [1-3].

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Due to the applications in different high-temperature environments, the stability of Si/C composites in these environments is a hot spot of research. S. Ochiai et al [4] find the mechanical performance of Si/C compound will enlarge its decreasing amplitude with the increase of thermal process temperature at the range of 600~1399°C. The researches of H. Araki and some scholars [5] show that CVI-Si/C mechanical performance decreased during the thermal process at 1000-2000°C; A. Udayakumar and some others [6] find the mechanical performance of CVI-Si/C composites improved after the thermal process at 1200°C; W. Yang and some others [7] report that CVI-Si/C composites show good thermal stability at the temperature of 1599°C and 2000°C. Taken all mentioned above into consideration, the reinforced fiber and matrix properties of Si/C composites significantly influenced its stability in high temperature environments.

In this paper, domestic Si/C fiber is used to prepare 3-D braided Si/C composites by PIP technology. And the Si/C composites are heat-treated within the temperature range of 1399~1801°C in inert atmosphere. Meanwhile, thermal infrared thermometer is regarded as a tool for monitoring the temperature of the material temperature. The authors studied the changes in properties and structure of Si/C fiber and matrix before and after thermal process, and the overall influence of mechanical performance of Si/C composites for thermal process.

2. Experiment

2.1 Preparation of object

Reinforced fiber is KD-I-type homemade Si/C fiber, one can consult literature material for its performance [8]. KD-I-type Si/C fiber and precursor polycarbosilane (PCS) used in PIP process are synthesized by the National University of Defense Technology (NUDT).

The process of the preparation of PIP-Si/C composite material:

(1) Si/C fiber 3-dimensional prefabricated members are braided by Changzhou Bolong Three Dimensional Composites Limited Company through a four-step method, in which fiber volume fraction account for about 40%.

(2) To make deposition pyrolytic carbon (PyC) coating on the surface of Si/C fiber by chemical vapour deposition method (CVD). Coating has a thickness of about 0.5μm.

(3) To dissolve precursor PCS in xylene, and then bring PCS solution in fiber braided member through vacuum impregnation method.

(4) To make infused braided member sufficiently dry, and then pyrolyze it at 1100°C in N2 atmosphere, holding time of 1 hour. Repeat the process of vacuum impregnation - pyrolyzing, until the weight gain rate of the composite material is lower than 1%.

High-temperature thermal process took place in hi-multi 5000 multi-functional air pressure hot pressing furnace. Thermal process holding temperatures are 1399°C, 1599°C and 1799°C respectively, holding time of 1 hour. The temperature of target object is measured by dual-band thermal infrared thermometer, which was developed by Hunan Agricultural University. Extreme temperature difference infrared thermal image processing algorithm is internally installed, and the attenuation slices are installed in front of the lens, engineering temperature measurement precision is 0.1°C; compared to traditional thermocouple, its measuring range of temperature reaches over 2000°C. Meanwhile it can be directly targeted to material and realize real-time thermal imaging on detail parts, it is more convenient for its non-destructive, non-contact and other advantages.

2.2 Test representation

The lump density and porosity factor of the object are measured through Archimedes method, sample quality is measured by analytical balance.

Based on relevant national standards, the fracture toughness is detected through single edge pre-cracked beam method (SEPB), material bending strength is measured through three-point-bending method. The microscopic modulus and micro-hardness are analyzed by MTS nano-indenter XP nano-indenter.

The morphology of the sample surface and cross section are observed through scanning electron microscope Hitachi S-4800, the phase composition of the samples are analyzed by X-ray diffractometer X'pert MPD made by Philips. Raman spectrum of the testing sample is determined by laser Raman spectrometer LabRAM Aramis.

3. Results and discussion

3.1 Influence of thermal process on the structure of Si/C composite

Table 1 shows the weight loss as well as the density and porosity of Si/C composites after thermal process at different temperatures.

The density of Si/C composites prepared at the pyrolysis temperature of 1100°C is 2.17g/cm^3, lower than the theoretical density of Si/C crystals (3.21g/cm^3), in addition to high porosity, the properties of precursor converted Si/C ceramic are also concerned: Si/C matrix obtained from the pyrolysis at 1100°C of PCS comprise amorphous state Si-OC, a small amount of β-Si/C crystallite and free carbon; KD-I-type Si/C fiber is prepared by the conversion of PCS at 1200°C, and its structure is similar to Si/C matrix, but the oxygen content of 18.89wt% is significantly higher than the former (about 2.09wt%). The increase of oxygen content and amorphous degree led to a decline in the density of Si/C ceramics [9].

Table 1: Weightlessness, porosity and density of the Si/C before and after thermal process

Thermal process temperature (°C)	Density (g/cm^3)	Weightlessness (%)	Porosity (%)
As-fabricated	2.17	-	7.3
1399	2.15	0.79	8.3
1599	1.85	13.9	29.4
1799	1.53	35.2	46.7

After the thermal process at 1399°C, the weight of Si/C composites decreased a little, density and hole area changed a little as well. However, after the thermal process at 1599°C, the weight loss ratio of composite material, significantly increased to 13.9%. After the thermal process at 1799 °C, the ratio is 35.2%. It is reported that [10] carbon thermal reduction reactions start within the temperature range of 1399~1599°C. Through thermodynamic calculation, the theoretical temperature that the reaction starts is 1499°C at atmospheric pressure, it goes through a series of chemical reactions, the fiber and matrix Si/C composites decomposition and weightlessness, porosity increased while density is significantly decreased.

The changes of crystallization degree of Si/C composite material with the thermal process temperature according to the analysis by XRD is shown in Fig.1. At 1100°C, the pyrolyzed original sample share substantially amorphous, based on 2θ of 35.7°, 60.0° and the 71.8° three low strength and wide range of Si/C diffraction peak, the Si/C can be determined exist in β-Si/C state. With the increase of thermal process temperature, the degree of crystallize of Si/C composites increase gradually. After heat process at 1399°C, three distinct diffraction peaks sharpened. After thermal process at 1599°C, the diffraction peaks of 2θ as 41.5° and 75.5° appeared. Furthermore, the diffraction peak appeared as 2θ is 33.5° does not exist in the standard pattern of β-Si/C, but the position of the diffraction peaks of 2H-Si/C (100) crystal plane is identical. Given that at atmospheric pressure, the conversion from β-Si/C to α-Si/C requires a temperature above 2000°C, so the diffraction peaks are not derived from α-Si/C phase. According to the literature [11] reports, at the time of stacking faults exist in β-Si/C crystalline grains, weak diffraction peaks will appear at 2θ of 33.5°. The stacking fault energy of Si/C ceramic is low, resulting in a large probability of the appearance of stacking fault in the process of growth of crystalline grains. Therefore, the diffraction peak is related to the emergence of stacking

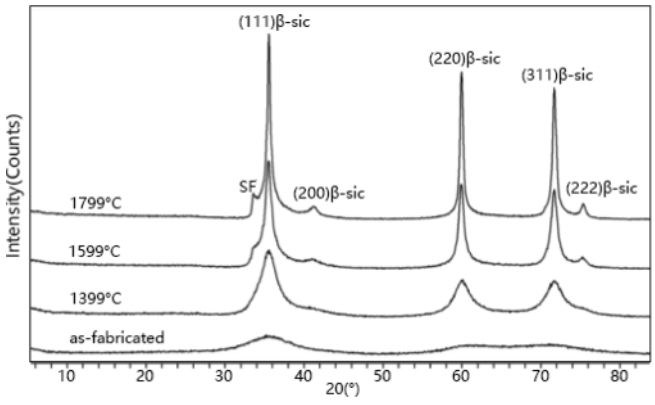

Fig.1 XRD patterns of the Si/C before and after thermal process

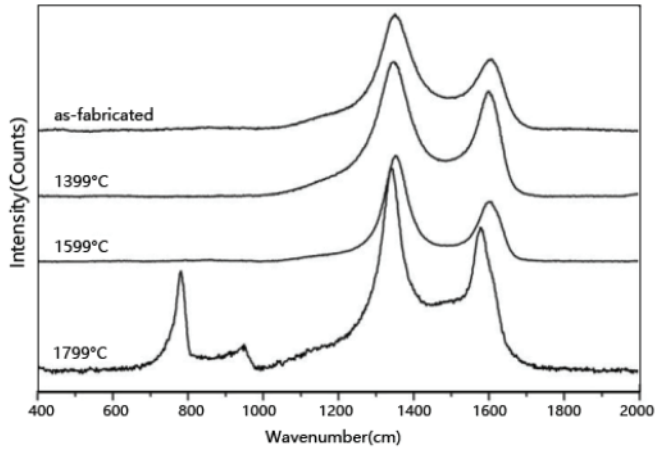

Fig.2 Raman spectra of the Si/C composites before and after thermal process

fault. Finally, when the thermal process temperature reached 1799°C, the respective diffraction peaks sharpened. In addition, the free state of C phase transmitted from amorphous to turbostraticgraphitic structure after the thermal process at 1599°C. Due to low order degree, it is difficult to observe the crystalline peaks of graphite in the XRD patterns.

The distribution and structural evolution of the C-phase in Si/C composites are studied through laser Raman spectroscopy (Fig.2). Since the Raman scattering rate of C-phase is at least ten times of Si/C phase, and therefore in carbon-rich Si/C ceramics, Raman feature peaks of C phase always exist that is peak D at 1250-1450cm^{-1} region, and peak G at 1550-1650cm^{-1}. Si/C phase characteristic peak is observed after thermal process at 1599°C, they are two optical phonon modes of β-Si/C in point in Brilouin region respectively, which is TO mold near point 796 cm^{-1}and LO mold near point 972cm^{-1}.

According to Rayleigh criterion, Raman feature peaks of C phase in Si/C composite material are peak-split processed, where peak D is the Lorentz mode, peak G is the Gaussian model, the data after analysis is shown in Table 2.

TABLE 2: RAMAN CHARACTERISTICS OF THE SI/C BEFORE AND AFTER THERMAL PROCESS

Thermal process temperature (°C)	Graphite band		ID/IG
	Wave number (cm^{-1})	FWHM (cm^{-1})	
As-fabricated	1606.4	63.4	1.60
1399	1599.1	60.7	1.28
1599	1598.8	52.2	1.74
1799	1587.1	41.9	1.42

The data in the table shows that, with the increase of thermal process temperature, peak position of peak G gradually moves left and its half-peak width gradually reduces, indicating that PCS converted free carbon phase in Si/C is gradually ordered. The tendency that ID/IG value is increased first then decreased, reached its maximum at 1599°C. The reason is that for amorphous carbon, ID/IG value is in direct proportion to the square of the size of graphene plane [12]; for crystalline carbon, ID/IG value is inversely proportional to the size of the graphene plane [13]. The date illustrates that the extent of graphitization of dissociate carbon phase in Si/C ceramics gradually increase with the thermal process temperature.

3.2 INFLUENCE OF MECHANICAL PERFORMANCE OF SI/C THERMAL PROCESSED

Table 3 listed the mechanical performance of Si/C after Γthermal process at different temperatures. The Si/C composites prepared at the temperature of 1100°C have good mechanical performance, fracture toughness and flexural strength are 520.0MPa and 23.0MPa·m$^{1/2}$ respectively. After thermal process at 1399°C in inert atmosphere, the entirety mechanical performance of Si/C have been promoted, fracture toughness reached 26.0MPa.m$^{1/2}$, the flexural strength reached 577.0MPa, and the modulus increased slightly. However a higher temperature thermal process then make the mechanical performance of Si/C declined sharply.

Fig.3 is a displacement/load curve of Si/C before and after thermal process at different temperatures. Seen from the figure, the preparation of Si/C by pyrolysis at 1100°C are in a typical pseudo-plastic fracture mode. In the initial stage of load, the composite material is elastic deformation, when applied stress exceeds the matrix cracking stress, composite matrix micro cracks. Due to the function of PyC interface layer

TABLE 3: INFLUENCE OF MECHANICAL PERFORMANCE OF THE SI/C THERMAL PROCESSED

Thermal process temperature (°C)	Flexural modulus (g.cm^{-3})	Flexural strength (%)	Fracture toughness (%)
As-fabricated	89.6	521.3	22.8
1399	98.4	576.8	25.6
1599	46.2	123.6	9.6
1799	33.8	43.2	1.7

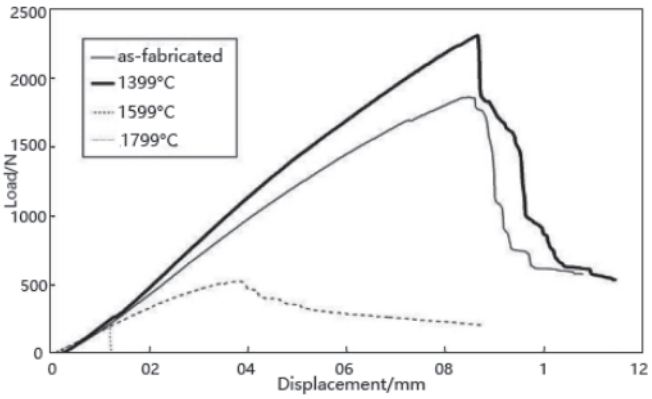

Fig.3 Displacement/load curves of the Si/C object before and after thermal process

[14-16], matrix cracks deflected, bifurcated or are blocked in the expansion process, and load continues to rise, while the modulus of the composite material gradually reduced, these changes reflected as the reduction of slope of curve. The fiber breaks when the curve rises to the highest point, then the fibers realized pseudo-plastic fracture of composite object through debonding and pull out, which is reflected in the step-wise downward phase of the curve. Si/C composite object is also showing a pseudo-plastic fracture characteristics after thermal process at 1399°C and 1599°C. While after the thermal process is at 1599°C, the object becomes brittle fracture, load sharply declines when reaches its highest point, and the cracks rapidly expand without deflection.

The fracture behaviour of Si/C composite object also (Fig.4) reflected in the fracture appearance that the Si/C prepared at the temperature of 1100°C and the composite object experienced a thermal process at 1399°C all have a great deal of fiber pull out. After the object fracture 1599°C there are some fiber pull out in fracture of the composite object that is heat-treated, and the pull out in part of the region are also short. When the composite object is heat-treated at 1599°C, there is no fiber pull in the section. Each appearance of fracture corresponds to its fracture mode.

As is shown in Fig.5, PyC coating in section of the Si/C object prepared at the temperature of 1100°C and experienced a thermal process at 1399°C are significantly tore, peeled and other destructive phenomenon, indicating that cracks deflected in interface layer region and fiber played a good role of strengthening toughness. All the fiber sections show typical fracture characteristics of brittle fiber, the mirror area, fogging area and feather area is clearly visible. After the composite material is heat-treated at 1599°C, the debonding between the fiber in fracture region and PyC coating is more obvious, but the fiber cross-sections show granular-shape stack, which is due to Si-CO carbothermic reduction reaction occurs in amorphous phase, the reaction released CO small molecules, amorphous continuous phase becomes loose, while generating Si/C, prompting the original β-Si/C crystallites grow up. Simultaneously, fiber strength declined sharply, due to the fiber has not been completely failed at this time, the composite material still displaying a pseudo-plastic fracture mode. After the composite object is thermal process at 1799°C, the Si/C matrix continuous phase can still been seen in fracture, PyC coating remains intact, while the Si/C fiber has been very loose, completely lost carrying capacity, and therefore composite material exhibits brittle fracture behaviour of matrix ceramics.

Fiber in ceramic matrix composite material is difficult to directly obtain its performance characteristics of taking its place. In this paper, an experiment on in-situ of micro-hardness and micro-modulus of fiber and matrix in Si/C object by nano-indentation method was launched, and thus characterized variation tendency of properties of fiber and matrix.

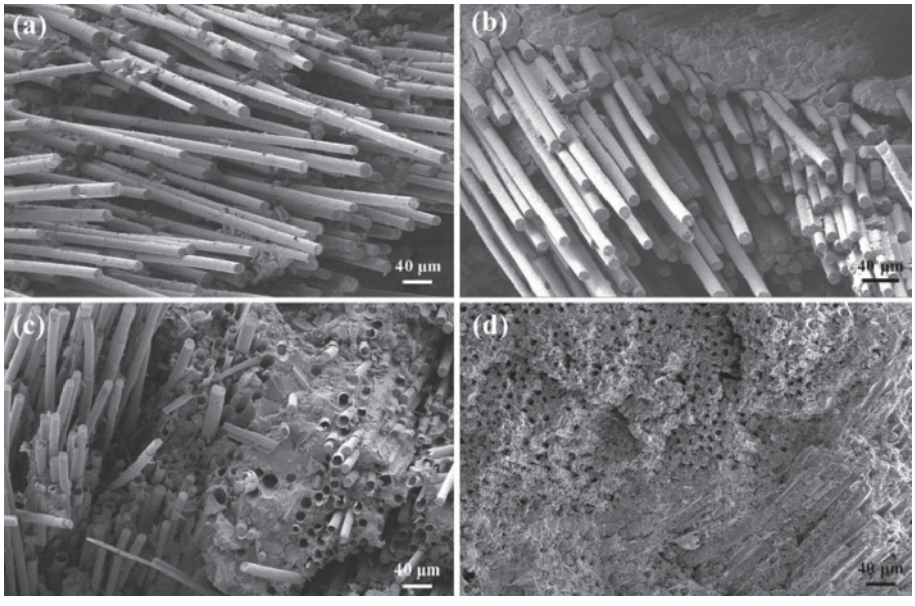

Fig.4 Fracture surfaces of Si/C object, (a) As-fabricated (b) 1399°C (c) 1599°C and (d) 1799°C

As is shown in Table 4, there is a significant differences in variation tendency of mechanical performance of Si/C fiber and matrix, which mainly reflected as fiber property declined slightly while the matrix performance improved significantly after the thermal process at 1399°C and at 1599°C, both showed a downward trend. And after at 1799°C, the properties of fiber degraded severely while matrix is relatively small. The main cause for the differences is that the oxygen content in fiber significantly higher than it in matrix, and oxygen's strong decarbonization

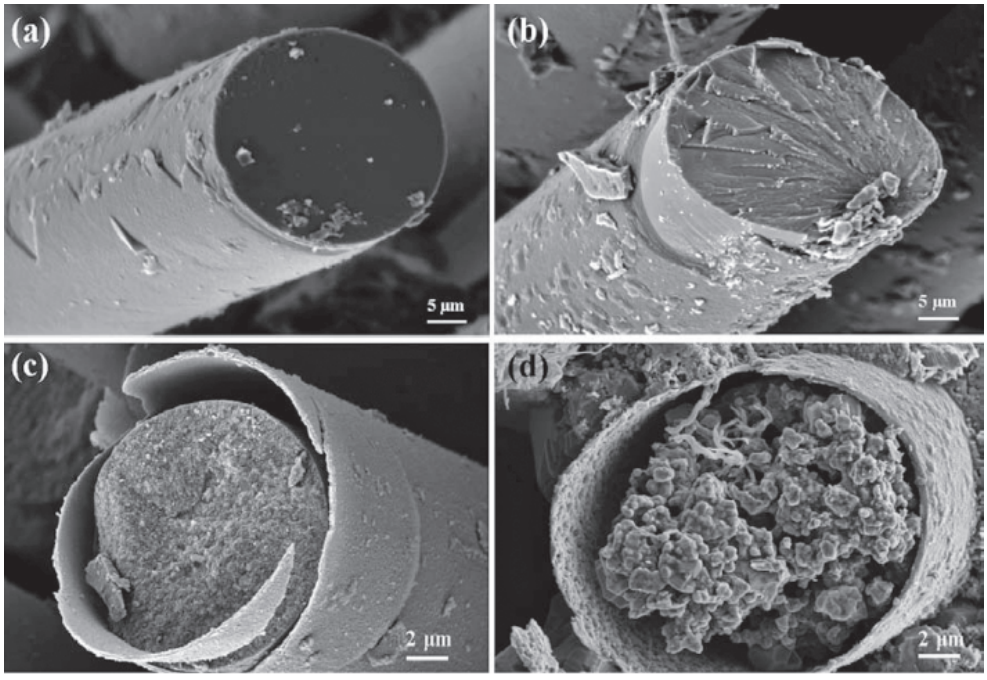

Fig.5 Interfaces of the Si/C object and morphology of the fibers before and after thermal process (a) As-fabricated (b) 1399°C (c) 1599°C and (d) 1799°C

TABLE 4: HARDNESS AND MODULUS OF FIBERS AND MATRICES OF THE SI/C OBJECT BEFORE AND AFTER THERMAL PROCESS

Thermal process temperature (°C)	Modulus (GPa)	Hardness (GPa)	Modulus (GPa)	Hardness (GPa)
	Matrix		Fiber	
As-fabricated	15.2	15.9	148.8	144.0
1399	14.1	20.0	131.0	187.7
1599	9.4	14.0	116.5	151.3
1799	1.3	7.6	45.2	104.6

reduced the high temperature stability of Si/C ceramics [17-20].

Generally, for ceramic matrix composite material, the value of elastic modulus of reinforced fiber and matrix is close, so the two bear a similar proportion of load. The role of fiber is not as main load-bearing units, but to increase the toughness of the composite material, namely, an increase of energy absorption of composite material before destroyed. After the Si/C object is thermal process at 1399°C, the crystallize degree of Si/C increased, which resulted in a substantial increase in micro modulus and micro-hardness, indicating deformation resistance of matrix are improved. And stress value that produce initial cracks in matrix is improved as well, resulting in an improvement of composite material strength. After the thermal process at 1599°C, the performance of fiber declined sharply due to the carbon thermal reduction and crystalline grains' grown up, and produced a significant reduction of the mechanical performance of composite object. After the thermal process at 1799°C, the fiber completely failed, the ceramic composite material exhibits brittle fracture mode.

4. Conclusions

The Si/C composite object prepared at pyrolytic temperature of 1100°C through PIP technology have good mechanical performance, their fracture toughness and flexural strength are 520.0MPa and 23.0MPa·$m^{1/2}$. After the thermal process at 1399°C, the degree of crystallization of Si/C composite object increased, a significant increase in micro modulus and micro hardness of matrix, their overall mechanical performance are improved, fracture toughness reached 26.0MPa·$m^{1/2}$ and bending strength reached 577.0MPa. After thermal processing at 1599°C and 1799°C, fibers of Si/C composite material are severely damaged, and the overall mechanical performance declines significantly.

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