Preparation, microstructure and oxidation resistance of SiCN ceramic matrix composites with glass-like carbon interface

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1. Introduction:
Pyrocarbon (PyC) is one of the mostly popular components as interface between matrix and fiber in the fiber-reinforced ceramic matrix composites (CMCs) due to its weak bonding which could maximize the strength and toughness of CMCs [1, 2]. However, the poor oxidation resistance of PyC above 400 ºC often makes it to be the origins of rupture if oxygen directly attacks interface, and could result in material failure quickly once onset of the oxidizing of PyC proceeds. In contrast, amorphous glass-like carbon (GC), which belongs to non-graphitizing carbon, displays an unusual combination of properties such as low thermal conductivity, high hardness, gas impermeability and relative high oxidation resistance [3]. The reportedly superior oxidation resistance of GC compare to PyC reminds us that introduction of GC interface into CMCs may be beneficial to oxidation resistance of composites containing carbon fiber (Cf) if appropriate fabricating methods are employed.

Though it is admitted by a few researchers [3, 4] that GC possesses superior oxidation resistance, the quantitative studies and its applications that embody such ability are still scarce up to now, plenty of researches are still centered on its preparation, structure and properties [5 - 9]. Based on these considerations, we perform our research on the introduction of GC interface into CMCs may be beneficial to oxidation resistance of composites containing carbon fiber (Cf) if appropriate fabricating methods are employed.

2. Experimental:
The reinforcement used here is 2.5 D fabric preforms (4.0 mm in thickness) of ex-PAN C fiber (T-300 1K, Nippon Toray Corporation). The precursors that utilize to prepare GC interface and SiCN ceramic matrix are commercially available thermosetting phenolic resin (carbon yield : ~ 48 %) and liquid hexamethyldisilazane (HMDS), respectively. HMDS is a SiCN ceramic precursor material [10] (HMDS : liquid, Molecular Formula = (CH₃)₃SiH(NH)Si(CH₃)₃; Purity ≥ 99.0; Density = 0.78 g/cm³; Boiling Point = 126 ºC). Scanning electron microscope (SEM, HITACHI S-4700) equipped with energy dispersive spectrometer (EDS) was employed to observe microstructure characteristics of the as-received C/GC/SiCN composite. The oxidation behavior of Cf containing GC coating and C/GC/SiCN was examined by means of weight change and residual strength ratio before and after oxidizing.

3. Results and Discussion:
3.1 Nature of the resin-derived GC:
In order to characterize the nature of the resin-derived GC, some phenolic resin liquid was placed in a crucible and heated to 1000 ºC under N₂ flow. The obtained GC was black, hard and porous substance, which also has glassy luster. XRD pattern of the as-received GC was shown in Figure (1). It does not reveal clear reflection peak and demonstrate amorphous nature.
3.2 Composite Preparation:
The preparation of C/GC/SiCN composite includes fabrication of GC coating on C fiber, as well as deposition of SiCN matrix on the fiber preform. C_{f} preform containing GC coating was produced via high pressure precursor impregnation and pyrolysis (PIP) by using phenolic resin as precursor. Prior to preparation, the resin need to be dissolved in glycol solvent to produce proper concentration solution (note: resin concentration is critical to obtain appropriate thickness GC film. Here, resin/glycol = 1:3, wt %). The C_{f} preform was placed in an impregnating vessel and pumped to create partial vacuum. Resins solution was then impregnated until preform was thoroughly immersed in liquid. The N_{2} was subsequently pumped in vessel until the gas pressure reached 1.0 MPa. After about 30 min, the preform was taken out and hung in air flow to make excessive liquid drop. At last the preform was heated to 1000 °C under N_{2} flow to make resin pyrolyze. C/GC/SiCN composite was prepared by electro-thermal pyrolysis technique using HMDS as precursor, the detailed processing has been described in lately patent [11]. As a result, C/GC/SiCN with approximately 40 % fiber volume fraction was finally produced. The density and porosity was 1.75 g/cm^{3} and approximately 15 % (measured by Archimedes principle), respectively.

3.3 Microstructure analysis:
The surface morphology of GC deposits on the Carbon fiber was observed on a high resolution SEM. As observed in Figure (2a), the fiber bundles still retain orderly sequence and clean appearance after PIP. Local image [inset in Figure (2a)] reveals the obtained GC coating is thin, homogeneous and adherent. It indicates that resin-derived GC film can be successfully generated by high pressure PIP. Figure (2b) shows the polished section of C/GC/SiCN composite. SiCN matrix fills the interspaces between warp and weft yarn, it displays dense structure and compact bonding state between matrix and fiber bundles. Figure (2c) exhibit morphology among fiber filaments, there also exist a high degree of coalescence between matrix and fiber filaments. The compositions of the SiCN matrix examined by EDS are shown in insert drawing in Figure (2c). It is mainly alloys of silicon, carbon, nitrogen, and a little of oxygen. The bonding morphology between Carbon fiber, GC interface and SiCN matrix is shown in Figure (2d). GC interface can be distinctly seen and it forms densely circular coating around Carbon fiber, the thickness is presumably 0.3 μm. Some extent of separation between GC interface and fiber can also be seen. Small opening can also be seen no matter between fiber bundles or among fiber filaments.
Figure (2) : SEM images showing the morphology of (a) Cf bundles containing GC coating produced by PIP (b) Polished section of C/GC/SiCN; (c) Coalescence among fiber filaments (d) Interface between matrix and fiber.

3.4 Oxidation Resistance Analysis :

In order to comparatively study the oxidation resistance of GC and PyC coating, C fiber containing PyC coating and C/PyC/SiCN composite were also prepared by chemical vapor infiltration (CVI), and the thickness of PyC coating was controlled to be 0.3 μm. The detailed process can be found elsewhere [12].

Three specimens, GC, C_f containing GC coating and C_f containing PyC coating were oxidized at 600 °C in air. Specimens were weighed via high precision electrical scale every interval of 20 min. The weight loss caused by oxidizing was calculated and the relations of weight loss rate to oxidizing time were then found (Figure 3). It can be seen that the weight loss rate of C_f containing PyC coating is bigger than that of C_f containing GC coating. It indicates C_f containing PyC coating has the poorest oxidation resistance, whereas C_f containing GC coating has superior oxidation resistance. So GC coating can provide superior protection against oxidizing than PyC coating. Microstructure observation has already indicated that GC can be homogeneously deposited on fiber surface and form dense inhibitory coating. So superior anti-oxidizing GC coating can delay oxygen directly attack C_f and effectively improve oxidation resistance.

Figure (4) : TEM image showing the interface morphology of C/GC/SiCN after oxidizing at 600 °C for 1h.

Figure (3) : Weight changes of GC, C_f containing PyC coating and C_f containing GC coating after oxidizing at 600 °C.

For further comparative study, the flexural strengths of C/GC/SiCN and C/PyC/SiCN before and after oxidizing were measured, and the residual stress ratios of two materials were calculated. Specimens with rectangular dimension of 5 × 10 × 70 mm were cut from green composite laminates and exposed to air at 600 °C (This oxidizing temperature can conveniently remove influence of resistance, whereas C_f containing GC coating has superior oxidation resistance. So GC coating can provide superior protection against oxidizing than PyC coating. Microstructure observation has already indicated that GC can be homogeneously deposited on fiber surface and form dense inhibitory coating. So superior anti-oxidizing GC coating can delay oxygen directly attack C_f and effectively improve oxidation resistance.

Figure (5) : Residual stress ratio of C/PyC/SiCN and C/GC/SiCN after oxidizing at 600 °C for 1 h.
SiCN oxidation (whose oxidation behavior is analogous to that of SiC [13]) and reflect effect of GC interface) for 1 h, then used for TEM observation and three-point flexural test. Figure (4) shows TEM image about the interface morphology of C/GC/SiCN after oxidizing. It can be seen that though there exist breakage at GC interface due to oxidizing (arrow side), the integrated GC interface still can be seen. The residual stress ratio of two materials was shown in Figure (5). It can be seen that the residual stress ratio of C/GC/SiCN is evidently higher than that of C/PyC/SiCN. The reason can be explained as that C/GC/SiCN has undergone smaller oxidation damage than C/PyC/SiCN. It further proves that GC interface can provide superior protection against oxidizing than PyC interface.

4. Conclusions :

SiCN ceramic matrix composite with GC interface was fabricated. Homogeneous, adherent GC film on Carbon fiber was successfully prepared by high pressure PIP using phenolic resin as precursor. Dense microstructure of C/GC/SiCN composite was also observed. GC film has superior oxidation resistance than PyC film, and SiCN matrix composite with GC interface has displayed high anti-oxidation than composite with PyC interface.

Acknowledgements :

This research has been supported by the National Natural Science Foundation of China (Program No. : 50772089), Program of Introducing Talents of Discipline in the Project of Advanced Materials and their Forming Technology.

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