DENSITY, MICROSTRUCTURE AND PROPERTY OF LARGE-SCALE CARBON/CARBON COMPOSITES PREPARED BY FAST THERMAL GRADIENT CVI

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Introduction

Carbon/carbon (C/C) composites are considered as new high-temperature thermal structural materials. It processes low density, high specific strength, and good friction properties etc, especially excellent strength retention at super-high temperature [1].They are mainly used in aviation and spaceflight fields, such as heat shields, nose tips and leading edges of re-entry vehicles, aircraft brakes [2]. The preparation technology of C/C composites is always a hotspot theme. At present, chemical vapor infiltration (CVI) is the most important technology for them. However, densification of C/C composites by traditional isothermal CVI needs hundreds of hours, which causes high cost and limits their applications. The other new rapid densification technologies (FCVI, TG-CVI, CLVI, etc.) remain many disadvantages in application [3]. Densification rate is affected severely by the size and shape of performs. A suitable method is active demand for C/C composites in industrial field. In the work, $\Phi 80mm \times 400mm$ solid cylindrical large scale 2D-C/C composites were fast prepared within 100 hours by thermal gradient CVI. The distribution of density, microstructure and the flexural property are studied. Thermal gradient CVI is confirmed as a potential technology for C/C composites.

Experimental

Industrial natural gas(CH_4 96.1%, C_2H_6 0.45%, C_3 0.07%, C_4 0.03%, CO_2 3.2%) was used as carbon source gas. 2D carbon fiber felt was used as the preform, the size was $\Phi 80mm \times 400mm$ and initial density of it was 0.43g/cm^3. 2D-C/C composites were prepared by thermal gradient CVI technology[4]. A temperature gradient was established in the preform, of which temperature was higher in the center than surface. Natural gas flowed from the surface to the center of the preform. At the beginning, a moveable thermocouple was placed in the center of preform to measure the temperature of deposition zones. Thermocouple was moved outwards with a fitting speed and the main deposition zones moved in a same speed during deposition. The power of furnace increased gradually with thermocouple moving to keep the set value of temperature. The direction of temperature gradient was reversed to gas concentration. According with Arrhenius equation, carbon source gas cracked only in the appropriate temperature. Deposited temperature ranges from 900～1200℃ in this experiment. Deposition time was 100 hours. The density of as-obtained C/C composites is 1.73g/cm^3.

Based on solid cylindrical structure of C/C composites and symmetric deposition, three specimens were cut averagely from top to bottom in turn along axial direction. Then, every specimen was divided into four small samples. The scheme of sample taking was showed in Fig.1. The whole density was measured before sampling and the density of every small specimen was measured by drainage method. The microstructure of as-obtained C/C composites at different locations was observed respectively under Germany Leica DMLP polarized optical microscope (PLM). The mechanical property was tested at room temperature in SANS CMT5304 (UNIVERSAL), which was produced in Shenzhen in china. The size of testing specimens was 55mm×10mm×4mm.
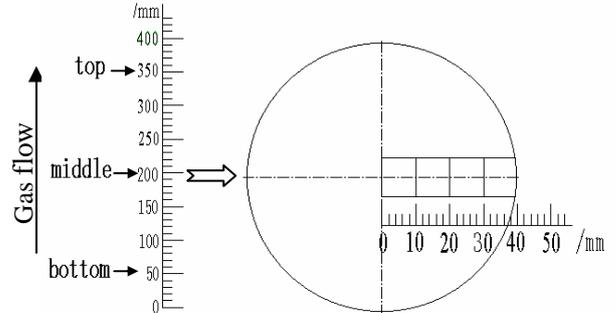

Fig.1 Scheme showing the sampling of C/C composites

Results and Discussion

Fig.2 demonstrates the density distribution at different locations of as-obtained C/C composites. The composite density was in the range of 1.69-1.74g/cm^3 at different locations. Deposition rate is about 0.013g/cm^3 or 2.6g/h. The density shows a decreasing trend form top to bottom in axial direction, and increases gradually from center to outside. The highest density is found in the bottom, due primarily to nature gas entering from the bottom of furnace. The concentration of gas is reduced gradually in the flowing towards the top, which affects cracking rate greatly at a fitting temperature. In the radial direction from the center to outside of C/C composites, the density increasing rate reduces gradually from bottom to top, and the density difference is narrowing. This is correlation to gas concentration difference reducing. However, the maximum density difference does not exceed 0.04g/cm^3 in radial direction. In a whole, the density distribution is uniform.
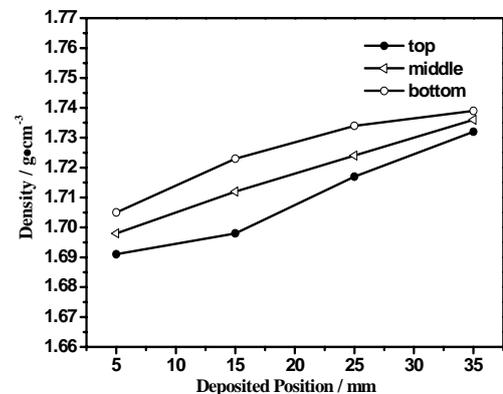

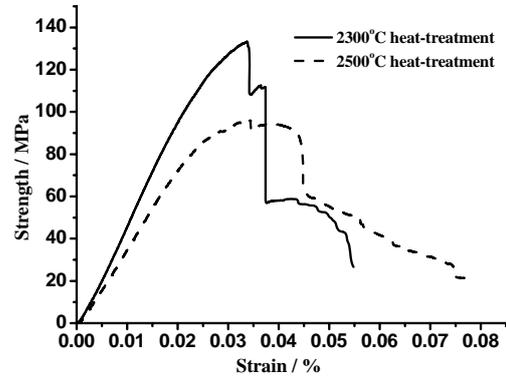**Fig.2** Density distribution of C/C composites at different locations

Fig.3 shows pyrocarbon PLM microstructure distribution in radial direction, which are in the middle location. The a, b, c, d, e, f are pyrocarbon PLM microstructure at 5mm, 10mm, 15mm, 20mm, 30mm and 40mm locations distance to the center of composites respectively. It can be found that PLM microstructure changes from RL to RL+SL, then changes to pure SL. However, it does not contain ISO pyrocarbon closed to carbon fiber surface. The content of RL pyrocarbon decreases gradually from the center to the outside. According to Figs.3b and c, it seems that the SL pyrocarbon is formed at outside of carbon fiber/matrix cells firstly and occupies main components gradually while the RL pyrocarbon vanish. At 20mm location (d), the microstructure starts pure SL pyrocarbon until 40mm location (f). The variety of pyrocarbon microstructure is due to gas cracked atmosphere difference at micro-cells and some influences relate to temperature. Temperature gradient is also an important factor [5].
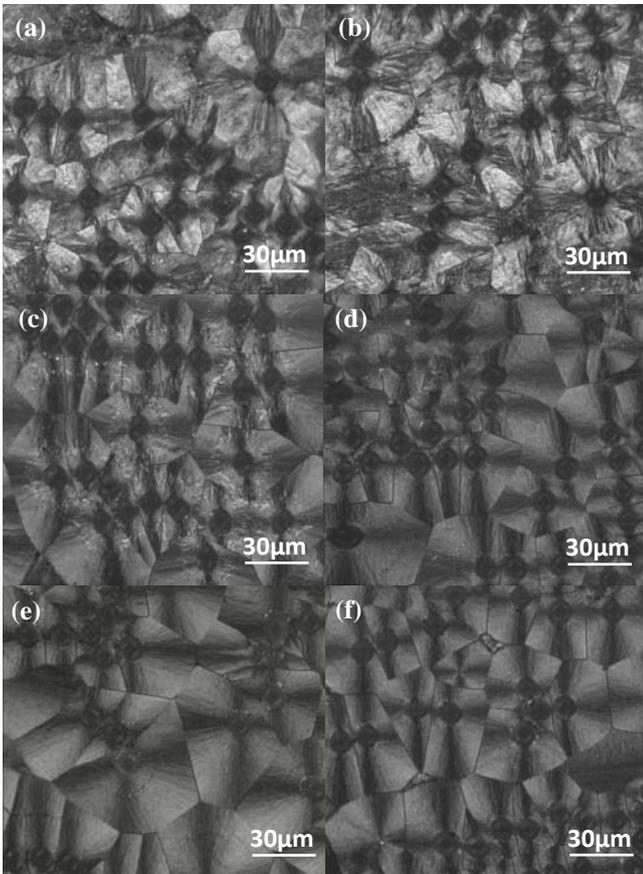
Fig.3 PLM microstructure of C/C composites at different locations
(a:5mm; b:10mm; c:15mm; d:20mm; e:30mm; f:40mm)

Fig.4 illustrates the flexural property of as-obtained C/C composites after 2300℃ and 2500℃ heat-treatment respectively. The strength is 131.88MPa after 2300℃ heat-treatment and that is 94.03MPa after 2500℃. The reduction is about 28.7%. The fracture mode also changes from brittleness to Pseudo-plastic with temperature increasing. It indicates that there are a lot of residual thermal stresses in pyrocarbon matrix of as-obtained C/C composites, which were produced in CVI process. With temperature increasing thermal stress was freed fast while the strength decreases greatly. However, the PLM microstructure is RL or RL+SL. The residual thermal stress in pyrocarbon matrix of C/C composites plays an important role for mechanical property.

Fig.4 strength-strain curves after 2300℃ and 2500℃ heat-treatement of C/C composites

Conclusions

Large scale 2D-C/C composites were prepared fast within 100 hours, the density reached 1.73g/m^3 in whole. The density distribution is uniform at different locations and the maximum difference can not exceed 0.04g/cm^3 in radial directions. However, pyrocarbon microstructure is difficult to control because of imprecise deposition atmosphere at every micro-cell. The mechanical property of 2D-C/C composites reduces greatly because of a lot of residual thermal stress in pyrocarbon matrix, with temperature increasing, residual thermal stress is freed and fracture mode changes from brittleness to Pseudo-plastic. By adjusting deposition parameters appropriately, a desired C/C composite can be prepared fast by thermal gradient chemical vapor infiltration. It is a flexible, potential method for C/C composites.

References
[1] Savage G. Carbon-carbon composites. London: Champman & Hall.1993, 351-359.
[2] Buckly J D, Edie DD. Carbon-carbon materials and composites. New Jersy: Noyes Publication, 1993:1-12.
[3] Golecki I. Rapid vapor-phase densification of refractory composites. Mater Sci Eng 1997; 20:37-124.
[4] Li KZ, Zhao JG, Li HJ, Zhang XL. Solid cylindrical C/C composites prepared by self-heating method. Chinese patent 1583673A. 2005.
[5] Zhao JG, Li KZ, Li HJ, Wang C. The influence of thermal gradient on pyrocarbon deposition in carbon/carbon composites during the CVI process. Carbon 2006; 44:786-791.