STRESS GRAPHITIZATION OF PHENOLIC RESIN BASED CARBON-CARBON COMPOSITES

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ABSTRACT

Stress graphitization of the hard-carbon matrix in the thermosetting resin based carbon/carbon (C/C) composites has been reported. The stress induced at the fiber-matrix interface due to the restriction of the shrinkage of thermosetting resin by the fiber reinforcement during carbonization has been suggested to be responsible for the graphitization of the hard-carbon matrix. In this investigation, micro-Raman analysis was shown to be capable of characterizing the stress graphitization phenomenon of C/C composites. The distribution of stress graphitization and the effect of interfacial bonding between fiber and matrix on the stress graphitization in the phenolic resin based C/C composites will be investigated.

1. INTRODUCTION

Stress graphitization of the hard-carbon matrix in the thermosetting resin based carbon/carbon (C/C) composites has been reported [1,2]. The stress induced at the fiber-matrix interface due to the restriction of the shrinkage of thermosetting resin by the fiber reinforcement during carbonization has been suggested to be responsible for the graphitization of the hard-carbon matrix. Recently, stress graphitization in chemical vapor deposited pyrolytic carbon matrix composites has also been reported [3]. However, the stress induced at the interface by the difference of thermal expansion between carbon fiber and pyrolytic carbon during graphitization at high temperature is suggested to be responsible for the abnormal graphitization near the interface. Therefore, it is anticipated for the thermosetting resin based C/C composites that the interfacial bonding strength will influence the magnitude of stress generation at the interface and consequently, the degree of stress graphitization. Zaldivar *et al.*[4, 5] measured the fiber strength utilization (FSU) in unidirectional C/C composites as a function of heat treatment temperature for a series of DuPont pitch-based carbon fibers [4] and also other pitch- and PAN-based carbon fibers [5]. It was found that different types of fibers resulted in various degrees of fiber/matrix bonding, which consequently affects the fracture behavior and FSU. A fiber pre-heat treatment at 1400℃ was also reported to reduce the fiber/matrix bonding [6] and change the fracture behavior of C/C composites significantly. Therefore, C/C composites prepared using carbon fibers with and without a pre-heat treatment at 1400℃ will be used to investigate the effect of interfacial bonding on the stress graphitization in the phenolic resin based C/C composites.

2. EXPERIMENTAL

The reinforcements used for C/C composites were two-dimensional plain woven carbon fiber fabrics, which were woven using 3k PAN-based carbon fiber tows. For the matrix materials, the resol-type phenol-formaldehyde resin (Chang Chun Co., Taiwan) was used. The carbon fibers reinforced phenolic resin composites were fabricated using the vacuum bag hot pressing technique. The as-cured composites were then carbonized at a heating rate of 2℃/min to 1000℃ in a nitrogen atmosphere to convert into C/C composites. The hold time at the temperature was 2 hours. The carbonized composites were then heat treated at 2400℃ in an Astro 1000-3060-FP20 graphite furnace under a helium atmosphere. The heating rate was 5℃/min and the hold time was 30 minutes. For the investigation of the effect of interfacial bonding on the stress graphitization, the carbon fabric reinforcement was heat treated at 1400℃ prior to the composite fabrication in order to reduce the interfacial bonding strength. Micro-Raman spectroscopy (Renishaw system 2000) with a spatial resolution of ~ 1 μm was used to characterize the stress graphitization phenomenon of C/C composites.

3. RESULTS AND DISCUSSION

3.1 Distribution of Stress Graphitization in C/C Composites

Fig. 1(a) shows the optical micrograph, obtained using the optical microscope equipped with the Raman spectrometer, of the cross section of C/C composites heat treated at 2400℃. The positions of micro-Raman analysis in the C/C composites are also presented. Ten positions were analyzed along a line covering two fibers and the matrix between the fibers. Fig. 1 (b) shows the Raman spectra at positions 5, 6, 7 and 8. The

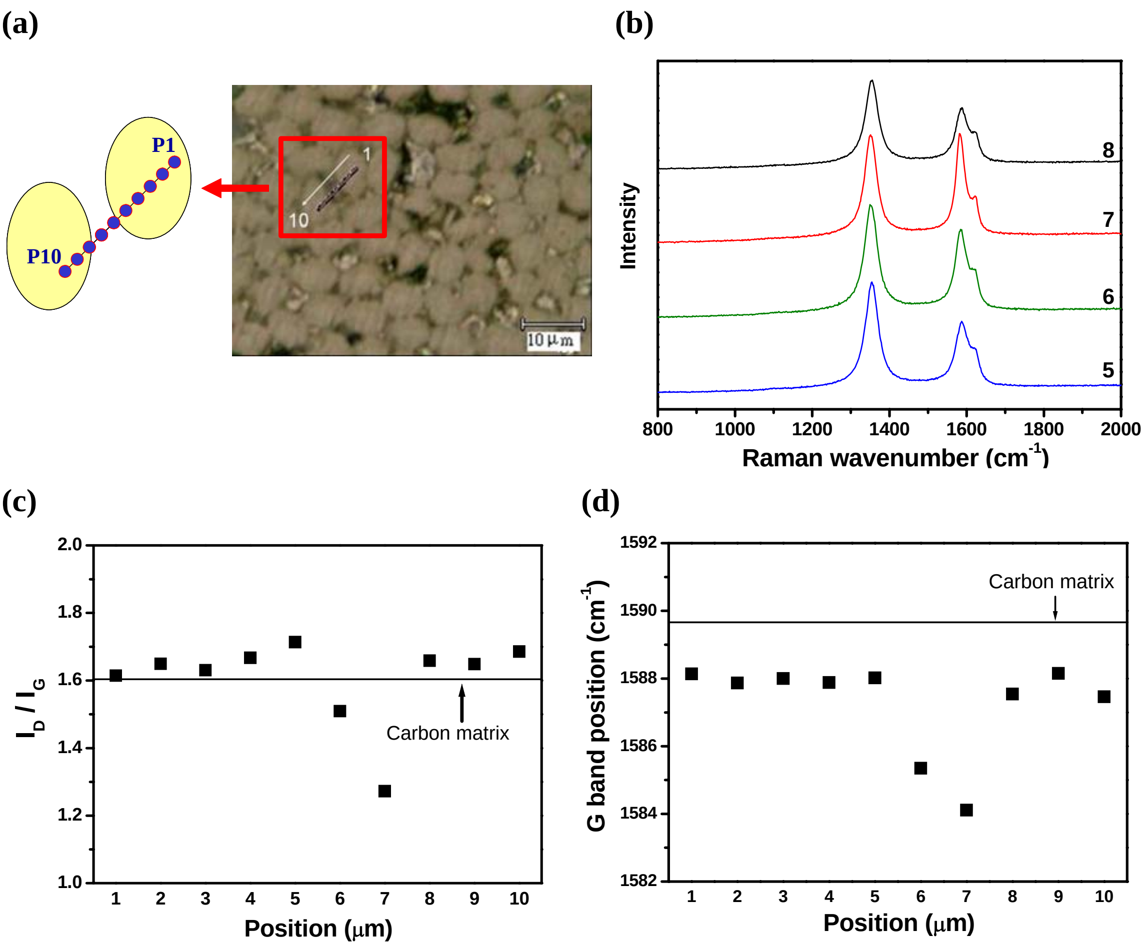

Figure 1: (a) positions of micro-Raman analysis in C/C composites; (b) Raman spectra at different positions; (c) I_D/I_G ratio at different positions; (d) G band wavenumber at different positions.

Raman spectrum at position 7, located in the matrix, shows lower I_D/I_G ratio (ratio of D band area and G band area) and G band position as also presented in Fig. 1(c) for the I_D/I_G ratio and in Fig. 1(d) for the G band wavenumber at different positions. The lower I_D/I_G ratio and G band position at position 7 indicate that the matrix has a degree of graphitization better than that of the fibers. The I_D/I_G ratio and G band position were also measured for the carbon matrix alone without fiber reinforcement and the results are also included in Fig. 1(c) and 1(d). It is found that the carbon matrix in the C/C composites possesses better degree of graphitization than that of the carbon matrix alone without fiber reinforcement, indicating that the carbon matrix is stress-graphitized as suggested by several researchers [1,2]. It must be mentioned that for the carbon without fiber reinforcement, the Raman analysis must be carried out inside the carbon, instead of on the surface, due to the surface graphitization [7].

3.2 Effect of Interfacial bonding

Figure 2 shows the I_D/I_G ratio of C/C composites heat treated at 1400℃ using as-received carbon fabrics (CC-A) and 1400℃ pre-heat treated carbon fabrics (CC-B). The micro-Raman analysis results of pure carbon fibers and pure carbon matrix, both also heat treated at 1400℃, are also presented in Figure 2 for comparison. As shown, the I_D/I_G ratio of pure carbon matrix is lower than that of pure carbon fibers. Also, the I_D/I_G ratios of carbon matrices in both CC-A and CC-B composites are lower than those of carbon fibers in composites. The I_D/I_G ratios of carbon matrices and carbon fibers in both CC-A and CC-B composites are similar to each other within the experimental errors. Above results indicate that both composites have similar degree of graphitization and that no stress graphitization phenomenon could be observed presumably due to the low heat treatment temperature.

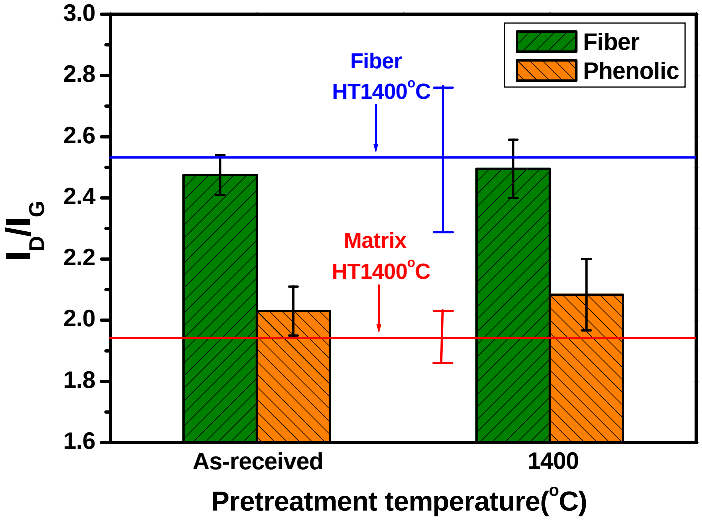

Figure 2: Micro-Raman analysis of C/C composites heat treated at 1400℃.

The I_D/I_G ratios of both CC-A and CC-B composites heat treated at 2400℃ are presented in Figure 3, in which the results of pure carbon fibers and pure carbon matrix, both also heat treated at 2400℃, are also included. The I_D/I_G ratios of carbon matrices in both CC-A and CC-B composites are found to be lower than that of pure matrix, indicating stress graphitization occurs in both composites. Furthermore, the I_D/I_G ratio of carbon matrix in CC-A composites is lower than that in CC-B composites, suggesting the higher degree of stress graphitization in CC-A composites which is attributed to the stronger interfacial bonding. On the other hand, the I_D/I_G ratios of carbon fibers in both CC-A and CC-B composites are considered to be similar within the experimental error, which is consistent with the literature results.

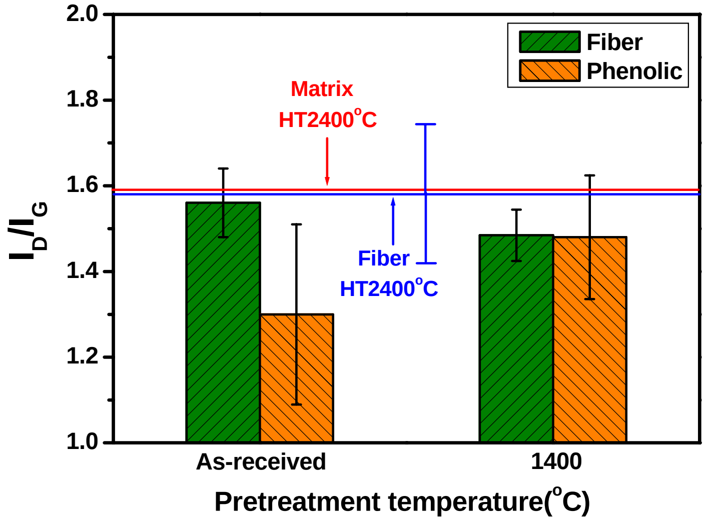

Figure 3: Micro-Raman analysis of C/C composites heat treated at 2400℃.

4. CONCLUSIONS

Stress graphitization of the phenolic resin-based C/C composites was investigated using micro-Raman spectroscopy. By performing the micro-Raman analyses on carbon fibers, carbon matrix and the fiber-matrix interface, the stress graphitization phenomenon of C/C composites can be characterized in more details. Micro-Raman analyses on C/C composites heat treated at 2400℃ using as-received carbon fabrics and 1400℃ pre-heat treated carbon fabrics show that stress graphitization in the carbon matrices occurs for both composites. However, the C/C composites using as-received carbon fabrics show higher degree of stress graphitization than that using 1400℃ pre-heat treated carbon fabrics due to stronger interfacial bonding.

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