

CVI CARBON-CARBON COMPOSITES: FIBER-MATRIX INTERACTION EFFECTS ON OXIDATION RESISTANCE

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INTRODUCTION

In previous studies we have examined the oxidation resistance of composites produced by chemical vapor infiltration (CVI) [1] and liquid phase impregnation (LPI) [2] of substrates of varying reactivity. One of the phenomena discovered in this effort was that upon high temperature treatment, composites produced by LPI of porous fibers were found to be more oxidation-resistant than those produced by LPI of non-porous, less reactive fibers. This effect was not observed in composites produced from CVI of similar substrates, a result that was attributed to the failure of the pyrolytic carbon to deposit in the fiber pores [3].

The present study was undertaken to see if the effect found in the LPI composites is exhibited also by CVI composites when they are produced under conditions favoring surface nucleation of pyrolytic carbon and pore filling rather than pore covering.

EXPERIMENTAL

The substrates used in this study were two rayon-based carbon cloths (VCL and WCA, Amoco Performance Products) as received and heat treated (ht) to 2850 °C in Ar. The initial BET surface areas of the samples were less than 1 m²/g. These were activated to 40-60% burn-off in CO₂ in order to develop their pore structure. Propylene was used as the pyrolytic carbon matrix precursor, deposited at 750 °C at a total pressure of 10 torr for 10 hours. Matrix yields varied from ~15-30% depending upon the surface area of the substrate. After deposition, the composites were heat-treated to 2850 °C in Ar.

The pore structure of the substrates was analyzed using N₂ and CO₂ adsorption. The oxidation behavior of the composites was studied using non-isothermal thermogravimetric analysis (1 atm O₂, 100 scc/min) at a heating rate of 5 °C/min.

RESULTS AND DISCUSSION

Figure 1 summarizes the oxidation resistance of the substrates prior to CVI. Upon heat treatment the reactivity of the VCL fabric increases dramatically, while that of the WCA fabric does not change, as it had already undergone high-temperature treatment in the manufacturing process.

Upon activation, the oxidation resistance of the fabrics decreases as surface area increases. Activation of the VCL fabric to 40% burn-off increased the BET surface area to ~900 m²/g. Activation of the WCA cloth to 60% only increased the surface area to ~125 m²/g. Even less porosity was developed in the heat-treated VCL cloth, ~70 m²/g, which is reflected in its oxidation profile, as compared to the activated WCA cloth.

Figure 2 presents the oxidation profiles of the composites before heat treatment. After CVI, the oxidation resistance of the VCL-based composite increases over that of the original substrate as porosity is filled (vcl-40/10 torr vs. vcl-40% b.o.). That of the WCA-based composite increases as well (ht wca-60/10 torr vs. ht wca 60% b.o.), although it is clear from the two steps in the burn-off profile that the pyrolytic carbon matrix is more reactive than the fibers. The oxidation resistance of the heat-treated VCL/CVI composite decreased with respect to the substrate alone, indicating that the pyrolytic carbon matrix is less oxidation-resistant than the fiber. Because of the low matrix yield (~15%) it is difficult to observe any two-step behavior.

Figure 3 shows the oxidation profiles of the heat-treated composites. The oxidation resistance of all the composites increases, but the composite made from the non-heat-treated, high-surface-area VCL fabric proves to be the most oxidation resistant upon heat treatment (Figure 3a). The pyrolytic carbon matrix in the VCL-based composite is less reactive than even the WCA cloth. Once the matrix is burned away (at ~70%) the reactivity of the composite becomes lower than that of the WCA (Figure 3a).

A similar result was found in the case of LPI composites made from fibers which had not been exposed to high temperatures [3]. This was attributed to good penetration of the liquid pitch into the pores and a good coupling between the fibers and matrix. Upon heat treatment, tensile stresses at the matrix-fiber interface from matrix and fiber shrinkage and realignment [4,5] are thought to induce enhanced graphitization of the matrix and a corresponding decrease in reactivity. A low-temperature substrate such as VCL will undergo shrinkage and realignment to a higher degree than WCA or heat-treated VCL.

Although present, this synergistic effect was not found to be as pronounced for the CVI composites. This may be because the pyrolytic carbon matrix is more graphitizable than the petroleum pitch used to form the matrix in the LPI composites.

CONCLUSIONS

As was found to be true for LPI composites, the most oxidation-resistant CVI-based composites are not necessarily made from the most oxidation resistant fibers. Optimizing the fiber porosity not only increases the matrix yield, but also may increase the oxidation resistance of the composite.

ACKNOWLEDGMENT

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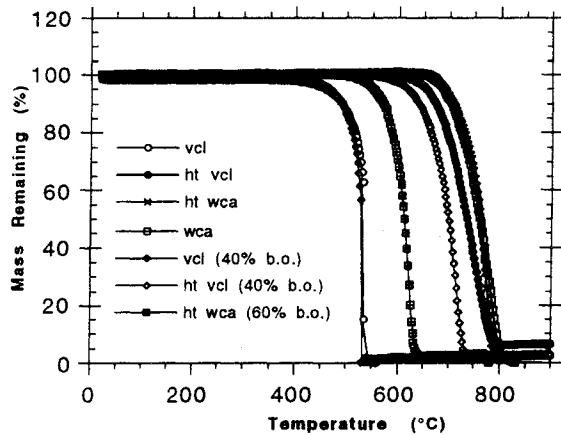


Figure 1. Oxidation profiles of different carbon cloths.

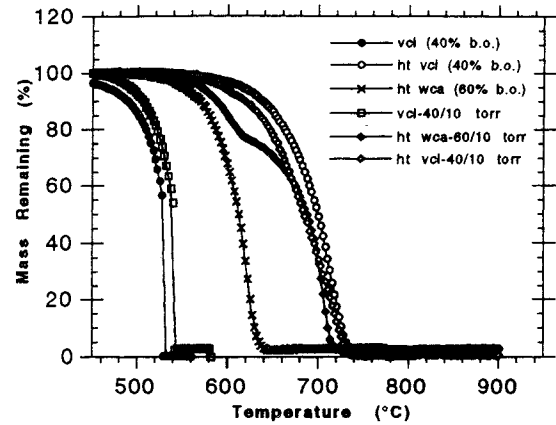


Figure 2. Oxidation profiles for low-temperature composites.

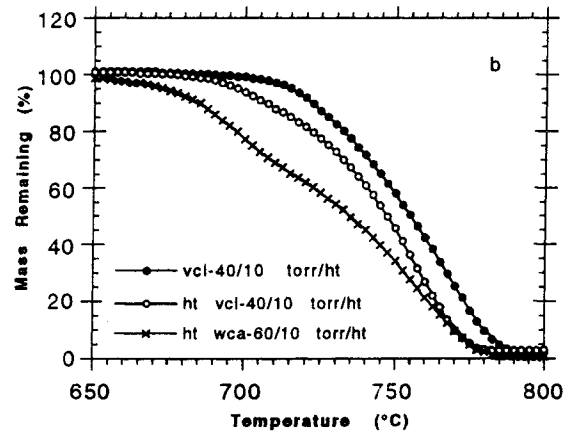
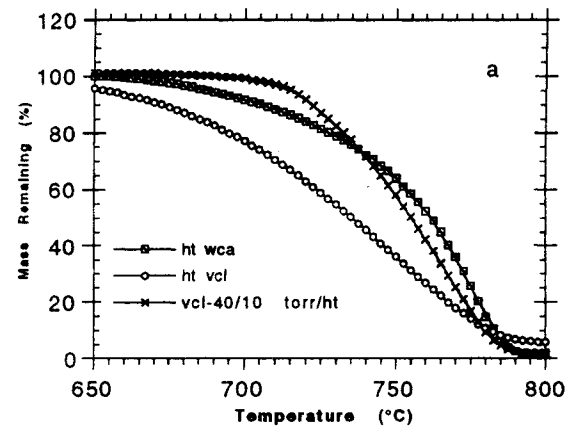


Figure 3. Oxidation profiles for high-temperature composites.