POROSITY FORMATION IN PYROLYTIC CARBON COATINGS

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Introduction

Pyrolytic carbon (PyC) heart valve components are fabricated by depositing carbon onto graphite mandrels using a fluidized CVD reactor containing ZrO_2 particles. In order to investigate the importance of collisions between ZrO_2 particles and the growing coating, PyC was deposited onto stationary and free floating substrates, which had been prepared with notches cut into their surfaces. The notches were cut so as to reduce or eliminate collisions between the ZrO_2 particles and the growing coating. Additionally, to explore how different rates of ZrO_2 collisions may affect the coating porosity, coatings were deposited onto unnotched stationary graphite rods using the CVD reactor with no ZrO_2 particle charge. At the tip of the rod, these coatings were impacted with various rates of ZrO_2 particle bombardment. All of these coatings were examined using metallographic and SEM analysis. Employing the droplet picture of the deposition process, a simple simulation has been developed that can illustrate some of the mechanisms that influence macro porosity formation in PyC coatings formed using a fluidized CVD reactor [1,2].

Experimental

The CVD reactor and the process employed has been described previously [3]. Three types of substrates were employed in the investigations described here: notched graphite rods, notched rectangular graphite slabs, and unnotched graphite rods. In separate runs, the notched and unnotched graphite rods were suspended parallel to the CVD coater's central axis at the coater center. The rods were suspended so that the tip of the rod was about 8-10 cm from the point at which gas first entered the reactor. The notched rods were prepared so that the notch was about 2-3 cm from the rod tip. All of the graphite rods were about 0.5 cm in diameter and had a rounded tip. The notched rectangular slabs of graphite, which were allowed to float freely during the coating process, were approximately 2.8 cm x 0.6 cm, with a thickness of about 0.04 cm. These slabs were prepared with four notches; one cut into each side of the rectangular face. The notches cut into the rods and slabs were V-shaped with the widest portion of the notch equal to about 300-400 microns. When coating the notched rods or rectangular slabs, the CVD reactor was arranged with an initial charge of about 200 grams of ZrO_2 particles, which were coated with PyC. The particles had diameters ranging from about 500 to 700 microns. The substrates were coated using 6 l/m (STP) of propane and 12 l/m (STP) of nitrogen at about 1350 °C. In some cases, 6 grams/m of MTS were added to the coating gas/diluent mixture. During the coating process, ZrO_2 particles with diameters of about 300 to 425 microns were inserted into the reactor through the gas inlet. Run times were typically between 120 – 200 minutes. The unnotched rods were coated using the conditions listed above except that no initial charge of ZrO_2 particles was employed. During the run the rate at which ZrO_2 particles were introduced into the reactor was varied. These particles were through the gas inlet and given the position of the substrate, collisions between the coating depositing on the rod tip and ZrO_2 particles were very likely. The rates employed were 0, 2, 4, 10, 20, and 30 grams/m. The notched substrate coatings were examined using metallography and SEM. Focus was given to the regions within and near the notch sites. In some cases, the samples were fractured across the notch sites and examined. The coatings deposited on the unnotched rod tips were examined metallographically by mounting the tip of the rod and polishing the rod until a portion of the graphite tip was exposed.

Results

The metallographic analysis of the notched rod and slab samples indicated that the coating within the notches was much more porous than the coating formed outside of the notches. See Figure 1. In many cases voids were observed within the notch sites. Under polarized light, most of the coating inside the notch was seen to be optically isotropic. Evidence of anisotropic coatings was found at the notch bottom and at the edges of the pores and voids. This was more pronounced for the coatings deposited on the rods. The coatings deposited outside of the notches were seen to be optically isotropic. SEM analysis showed the coating deposited within the notches to be very porous and to be comprised of stacks of coalesced spheroids. The coating deposited outside of the notch sites was seen to be much more dense and with fewer features.

Metallographic analysis of the unnotched rods indicated that the coatings deposited using the highest feed rate of ZrO_2 particles had the densest appearance. All of the coatings deposited on the unnotched rods were seen to be optically isotropic.

Discussion

The metallographic and SEM analysis of the coatings deposited within the notches suggests that collisions between the growing coating and the ZrO_2 particles may be important in order to form non porous PyC. Additionally, the metallographic analysis of the coating deposited on the unnotched rod tip suggests that the rate of ZrO_2 bombardment may be important in controlling the degree of porosity.

Assuming that the deposition process is influenced by deposition from planar molecular species and gas phase nucleated spheroids of carbon, as described by Bokros [1], and that for the operating conditions employed in these experiments, the spheroids are solid, as indicated by Kaae [2], a simple model of the deposition process can be proposed that may, in part, explain the above observations. It is conjectured that in the absence of particle collisions, the spheroids of carbon stack randomly forming a branched and porous structure. In the presence of particle collisions, the tallest branches are removed, through energetic particle collisions, leaving the surface open to deposition. In a sense, the particles act to polish the growing coating. As this is occurring, deposition from molecular species can act to glue the spheroids together, as described by Kaae [2]. It is further suggested that the relative rate between deposition from carbon spheroids and ZrO_2 collisions and the removal efficiency of each collision may be important in controlling porosity.

To illustrate this mechanism, a simple deposition simulation has been developed. In this simulation, the spheroids of carbon atoms are approximated as circles. Each circle is launched from a horizon and allowed to proceed under ballistic trajectory until it intersects with a circle deposited previously. After some number of spheroids have been deposited, a bed particle collision is deemed to have occurred; some percentage of the freshly deposited circles are removed; see Figure 2

Lastly, the anisotropic coatings observed at the notch bottoms and at pore and void edges are likely the result of deposition from molecular species. The coalesced nature of the spheroids stacks seen in the notches is likely the result of molecular species depositing onto the porous stacks of carbon spheroids.

Conclusion

Collisions between bed particles and the growing coating are important to forming non porous PyC in a fluidized bed CVD reactor. The relative rate between these collisions and the deposition of carbon spheroids may control the degree of porosity.

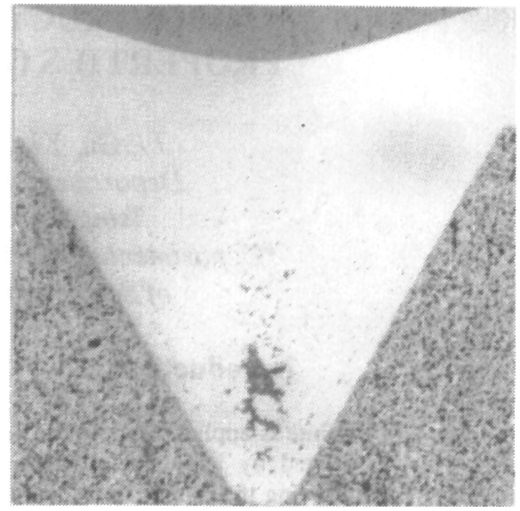

Figure 1: Coating deposited within notch of slab.

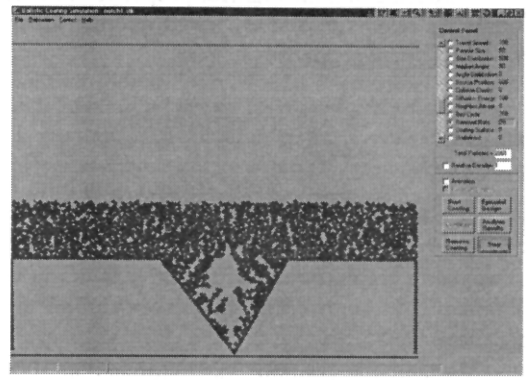

Figure 2: Coating deposited within notch not subjected to removal by particle collisions. Coating deposited outside of notch exposed to particle collisions.

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