MORPHOLOGY CHANGES OF CARBON SPHEROID STRUCTURES WITH DEPOSITION FROM MOLECULAR SPECIES

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Introduction

Pyrolytic carbon is an important material for the production of prosthetic heart valve components. These components are typically fabricated by depositing carbon onto graphite mandrels using a fluidized CVD reactor containing ZrO_2 particles.

Studies have shown that the coating process involves deposition from planar molecular carbon species and gas phase nucleated spheroids of carbon, which are either very viscous or solid [1,2]. It has also been demonstrated that when depositing PyC coatings on substrates with features that restrict collisions between the coating and ZrO_2 particles, the morphology of the coating appears as coalesced stacks of spheroids [3]. These structures, which were seen to be quite porous, exhibited various sizes of carbon spheroids with some appearing to be more coalesced than others.

The work described in this document was executed in order to explore how these structures may be formed. In particular, the investigation focussed on how deposition from molecular species can affect the morphology of stacks of previously deposited carbon spheroids.

To accomplish this, coatings were first deposited on stationary rods using conditions favoring the formation of gas phase nucleated species (*spheroid conditions*) and then subsequently coated using conditions that encourage deposition from molecular species (*molecular conditions*). These samples were examined after each coating sequence using SEM. Additionally, the evolution of the morphology of coatings, formed from molecular species, was examined by coating graphite rods for several different time periods, and examining the samples using SEM.

Experimental

The CVD reactor employed has been described previously [4]. Coatings were deposited onto notched stationary graphite rods suspended along the coater's central axis. Coatings formed under *molecular conditions* employed 0.5 l/min (STP) of propane mixed with 19.5 l/min (STP) of nitrogen. Coatings deposited with *spheroid conditions* used 9.0 l/min (STP) of propane mixed with 3.0 l/min (STP) of nitrogen. In both cases, the coating temperature was 1350 °C and no charge of ZrO_2 particles was employed.

First coatings were formed, in separate runs, using *molecular conditions* and *spheroid conditions* and subsequently prepared metallographically. These samples were examined under bright field and polarized light.

After this, in three separate runs, graphite rods were coated using *spheroid conditions* for 10, 15, and 20 minutes. A scratch (datum) was made near the coated notch and the coating within and near the notch was examined using SEM. Care was taken to record the position, relative to the datum, where images were recorded. These samples were then coated for 10, 20, and 40 minutes, respectively, using *molecular conditions*, and examined at the locations where images were obtained previously. Metallographic samples were also prepared and investigated.

Lastly, in four other runs, graphite rods were coated using *molecular conditions* for 5, 10, 20, and 40 minutes respectively. In each case, the morphology of the coating was examined using SEM. Metallographic analysis was performed on the thicker coatings.

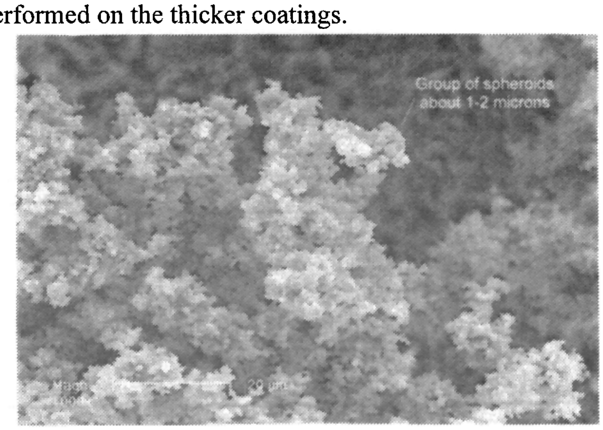

Figure 1: Shows coating deposited with notch. Coating formed using 10 minutes of *spheroid conditions*.

The SEM analysis was performed with a direction normal to the deposition surface; in some cases, the coated rods were fractured at the notch sites and examined in cross section. The metallographic samples were investigated in cross section.

Results and Discussion

The metallographic analysis of the rods coated prior to this experiment using *molecular conditions* were seen to be either columnar or granular and optically anisotropic. Coatings deposited under *spheroid conditions* were observed to have no visible grain structure and were seen to be optically isotropic. These results lend confidence that the deposition conditions for depositing predominantly molecular species or spheroids were chosen appropriately.

SEM analysis of the samples coated with *spheroid conditions* revealed stacks of spheroid features that showed some coalescence of the features. These features were typically about 1.0-2.0 microns in diameter; see Figure 1. This analysis reveals that it is probably difficult to deposit only spheroid features. Coating these samples with *molecular conditions* showed that the agglomerate structures first grew in size and, with further direct deposition, started to form highly coalesced structures. Following about 5 minutes of direct deposition, most of the features were seen to have diameters of about 2.0-3.0 microns; see Figure 2. Many features greater than 5 microns were seen following 10 minutes of direct deposition. Coating with molecular species for more than 20 minutes resulted in large spherical features. Metallographic analysis showed large conical anisotropic grains, which were deposited onto isotropic coatings.

This analysis shows that when coating stacks of spheroid features with direct molecular deposition, the spheroid features grow by the coalescence of adjacent spheroid stacks. As the extent of direct deposition increases, large conical grains can grow on these stacks.

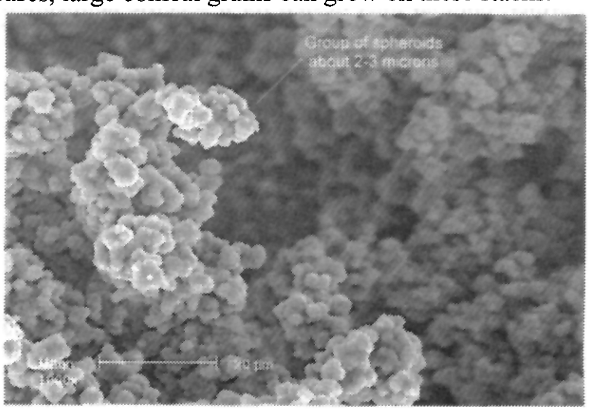

Figure 2: Shows same regions as seen in Figure 1 following 5 minutes of molecular deposition.

All of the rods coated using only *molecular conditions* were seen to have a silver-gray appearance. After about 5 minutes of direct deposition, the graphite rod surface morphology was seen to have changed slightly. Deposition was seen to have occurred near the edges of pores and a few small nodules are present. Following 10 minutes of direct deposition, the surface was seen to be more continuous with many more nodules. After 20 minutes of direct deposition, analysis revealed an undulating and continuous surface with many nearly hemispherical features about 2-5 microns in diameter. Metallographic analysis indicated the coating was comprised of granular features. Coatings formed after 40 minutes of direct deposition showed large polygonal features and some nearly hemispherical features. Metallographic analysis revealed the coating to be comprised of tightly packed conical grains.

The nodules observed after 5 and 10 minutes of direct deposition were probably formed at random nucleation sites and are the precursors of the large hemispherical features. The polygonal features are likely formed when the grains grow together. When viewed from a position normal to the deposition surface these features appear polygonal.

Conclusion

In separate studies, many features of different sizes and degrees of coalescence have been observed in PyC coatings formed on notched rods and slab samples [3]. These features can likely be explained by different degrees of direct molecular deposition onto previously deposited stacks of carbon spheroids.

Acknowledgments

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