

MICROSTRUCTURAL OBSERVATIONS OF PURE PYROLYTIC CARBONS FOR HEART VALVES

J.L. Kaae, J.L. Ely,* A.D. Haubold,* and A.S. Schwartz†

General Atomics, P.O. Box 85608, San Diego, CA

*Medical Carbon Research Institute, 8200 Cameron Road, Austin, TX

†Medtronic Carbon Implants, 8605 Cross Park Drive, Austin, TX

INTRODUCTION

Near-isotropic pyrolytic carbon containing a small amount of co-deposited silicon carbide has been used for years as the materials from which prosthetic heart valves are fabricated [1]. Silicon carbide was introduced into this material to increase the hardness and thereby the wear resistance of the material. Silicon carbide, however, has poor thrombo-resistance relative to pyrolytic carbon, so its removal might improve the thromboresistance of the material.

Recently, a study of the possibility of using pure pyrolytic carbons for heart valves was initiated. In the first step of this study a series of pure near-isotropic pyrolytic carbons was deposited in a fluidized particle bed coater with improved process control characteristics that reduce variability in the coatings deposited. Subsequently, the mechanical properties of these carbons were measured [2]. It was expected that the pure pyrolytic carbons would not be as strong or as tough as the silicon-alloyed pyrocarbons, but surprisingly, under the best deposition conditions the flexural strength and the fracture toughness of the pure pyrolytic carbon were higher than those of silicon-alloyed pyrocarbon. Furthermore, the hardness of the pure pyrolytic carbon was only slightly below that of the silicon-alloyed pyrolytic carbon.

The strength of the pure pyrolytic carbons peaked at deposition temperature intermediate between the extremes utilized and therefore it peaked at an intermediate density (Fig. 1). This behavior contrasts with that observed in prior studies of near-isotropic pure pyrolytic carbons where the strength was highest for carbons deposited at temperatures near 1300°C and thus for the carbons with the highest densities [3,4]. This paper describes a study of the structure of the recent pyrocarbons to determine the reason for the unusual variation of strength with deposition temperature. The structural properties that were measured were the apparent crystallite size, the layer plane spacing and the crystallite preferred orientation.

EXPERIMENTAL

Free-standing strips of each carbon were stacked to make up a specimen for X-ray diffraction analysis. Diffraction angles were scanned from 18 to 38 degrees using a Norelco goniometer and copper $K\alpha$ irradiation. Carbon (002) planar

spacings were calculated from the positions of the (002) diffraction peaks using the Bragg equation, and apparent crystallite sizes were calculated from the broadenings of the (002) diffraction peak using the Scherrer equation.

Preferred orientations of the crystallites in the pyrolytic carbons were determined by measuring the intensity of polarized light reflected from each carbon both with the plane of polarization parallel and perpendicular to the deposition plane. The intensity ratios was converted to the Bacon Anisotropy Factor through an empirical relation [5].

RESULTS

The layer plane spacings of the carbons are essentially all the same having a value of $\sim 3.47\text{\AA}$. This value is consistent with layer plane spacings measured previously for near-isotropic pyrolytic carbons deposited below 1500°C [6].

The preferred orientations of the carbons increase with decreasing deposition temperature. Stevens has shown that the preferred orientation of near-isotropic carbons deposited below 1500°C is affected by both the density and the deposition rate; it increases with increasing density and decreasing deposition rate [7]. Since the density increased and the deposition rate decreased as the deposition temperature decreased for the carbons of this study, the variation of preferred orientation with deposition temperature is that which is expected. Furthermore, an increase of preferred orientation with increasing density cannot explain the observed variation strength with deposition temperature.

The crystallite sizes of the carbons also increase with decreasing deposition temperature (Fig. 2). Slight increases of crystallite size with decreasing deposition temperature have been reported previously, both for cases where the size of the fluidized particle bed was not regulated [8] and where the size of the fluidized particle bed was held in a steady state [9]. To facilitate comparisons among the crystallite sizes of these various carbons, it is probably best to do so on the basis of a structural parameter such as the density rather than on the basis of the deposition temperature since the difference between the temperature of the fluidized particle bed which is the fundamental temperature that controls the

process and the recorded deposition temperature at some position on the coater can vary with coater design. The crystallite sizes of carbons deposited in the three different series of deposition runs are shown in this way in Fig. 3. The crystallite sizes of the carbons of this study are consistently larger than those of the prior studies, especially at the higher densities.

DISCUSSION

The strength of the near-isotropic pyrolytic carbons is known to depend strongly on the crystallite size as well as on the density, decreasing as the crystallite size increases [10]. This undoubtedly explains the maximum of the strength at an intermediate density. (In the prior studies the crystallite size did not increase strongly as the density increased so that the strength increased continuously with the density while in the present study the crystallite size increased strongly with increasing density thus producing a decrease in strength at the highest densities.)

The most likely explanation of the difference between the crystallite size variations of this study and those of the prior studies is differences in the deposition times employed. The deposition times employed in the present study were significantly longer than those of the prior studies. This could produce larger crystallites in the carbons of the present study by affording time for crystallite growth during the deposition run. Crystallite growth is known to occur during annealing at temperatures higher than the deposition temperature [11], but this is the first indication that crystallite growth can occur during deposition. The suggestion that crystallite growth can occur during deposition is surprising because the largest crystallite growth occurs at the lowest deposition temperatures in relatively short times (~1 h). This must be explained by the ease of crystallite growth in the high-density carbons that are deposited at the low temperatures relative to the low-density carbons that are deposited at the high temperatures.

ACKNOWLEDGMENT

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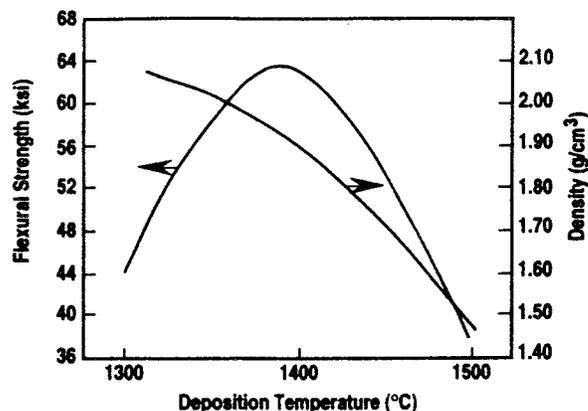


Fig. 1. Strength and density of the carbons of this study.

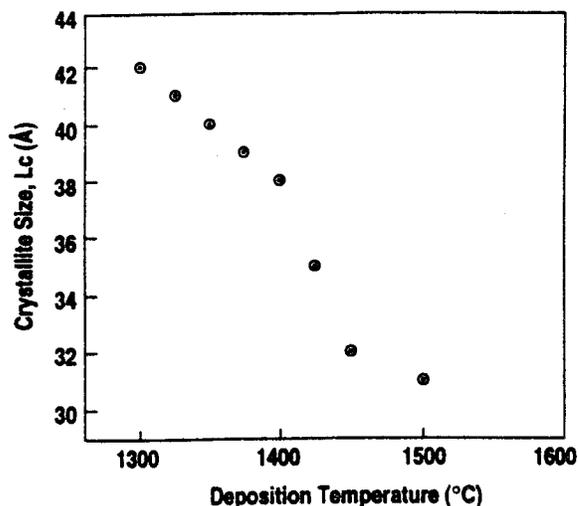


Fig. 2. Crystallite sizes of the carbons of this study.

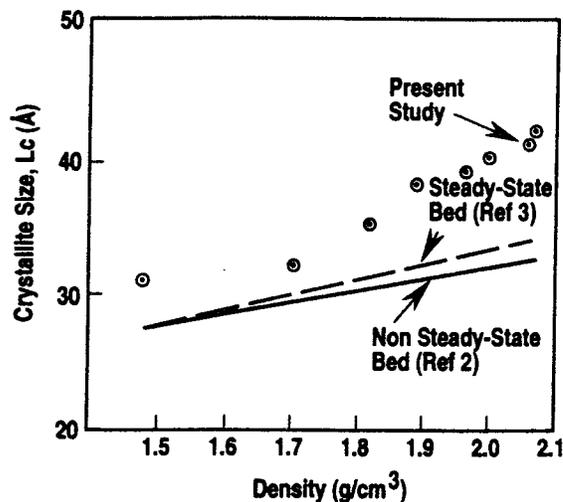


Fig. 3. Crystallite sizes of pure pyrolytic carbons.