

Tough Nanocomposite Coatings Using New Self-Organized Carbon Forms

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Several exciting themes associated with nanoscale carbon materials have emerged in recent years. One is the ability to create new structural forms of carbon, both as components in emerging nanotechnologies and as subjects of scientific inquiry. The classical picture of sp^2 hybridized carbon as flat sheets has given way to a host of structural possibilities based on closed spheres, onions generated in electron beams and in immersed arcs, multi- and single-walled nanotubes, nanotubes that are Y-shaped, bent, or helical, and graphite fibrils with scroll-like structures. A second theme is the use of carbon nanotubes (CNTs) as reinforcements in polymer and metal matrices so as to take advantage of the high stiffness and purported exceptional strength of this special form of carbon. A third theme is the use of templating methods to accurately control the structure of nanomaterials. This research program brings these three themes together by using templating methods to create novel carbon fibrous reinforcements in ceramic and metal matrices, with the resulting composite coating systems engineered to enhance wear and contact damage resistance in applications relevant to the automotive industry. The novel carbon materials have a host of other potential applications as well. Relative to the seven NSF-identified areas of interest for NIRT proposals, our work contains elements related to three of these areas: nanomaterials and control of nanostructures; nanoscale and multiscale modeling; nanofabrication methods.

Research in the first 14 months of this program has focused on a number of inter-related projects, primarily associated with synthesis of carbon nanomaterials, ceramic and metal matrix processing, and mechanical testing. Hurt, Sheldon, and Crawford have collaborated to demonstrate for the first time that the graphene layer structure in nanofibers can be controlled by changing the preferred surface anchoring state. We used a novel hybrid scheme that combines chemical vapor deposition (CVD) and liquid crystal templating. In this process, CVD is first used to form a thin layer of pyrolytic carbon on the pore walls of the alumina templates. When the liquid templating method is applied to these materials, the graphitic layers template onto the CVD material. This produces structures with graphene layer orientations that are roughly parallel to the pore walls (e.g., analogous to rings in the trunk of a tree). The initial CVD carbon layer in this material was less than 2 nm thick, such that most of the dense nanofiber was formed from the liquid precursor. Mechanical properties of composites formed with these nanofibers have not yet been measured, however, we anticipate that the Hurt-Sheldon-Crawford hybrid nanofibers will exhibit superior axial strength and stiffness than materials fabricated with only one of these techniques (i.e., CNT's formed by CVD, or carbon nanofibers formed by liquid crystal templating). Continuing research on hybrid schemes is expected to produce a wide range of different nanofiber materials. The team has recently submitted a publication on this new technique.

Also this year, we applied the new liquid crystal engineering techniques to the fabrication of carbon thin films. Conventional sp^2 -hybridized carbon films are either amorphous or have strong preferential orientation of the graphene layers parallel to the substrate. We have used two liquid crystal precursors to produce a suite of films in which the graphene layers lie uniformly edge-on at the upper surface with the in-plane orientation being either multi-domain (by spin coating) or uniform (by bar coating). Both of these anisotropic, all-edge carbon films are wholly new materials. We have also demonstrated the ability to make patterned carbon films with spatially periodic patches

of basal and edge sites using polyimide/photoresist composite templates fabricated by lithographic methods. The basis of the crystal orientation control is the different anchoring states on polyimide (homeotropic, or 'face-on') and photoresist (planar or 'edge-on'). We anticipate a variety of applications for these films as interfacial bonding layers in composites, or as active surface carbon materials for catalysis or electrochemistry.

Crawford and Hurt have explored the fabrication of carbon nanotubes using liquid crystal solutions. A benefit of this approach is that an automated fluid dispensing system can be used to apply the nanotube precursor to the alumina template. A syringe with a narrow tip diameter is filled with a solution of indanthrone disulfonate and water. The syringe is part of an automated fluid dispensing system, which is computer controlled. Using a software interface, the writing conditions used for the application of the carbon precursor can be precisely controlled. A wide array of shapes from simple dots to complex linear and arc patterns can be dispensed using this method. Currently, the smallest tip size available for the fluid dispensing system is 150 microns. Using this tip, we estimate a line width of 160 microns; however, by optimizing the writing procedure, we hope to improve on this. We also hope to further develop this patterning technique in order to take advantage of existing inkjet printing technology.

Indentation and wear properties of a variety of CNT/alumina samples have been measured at General Motors Research, in collaboration with Dr. Y.T. Cheng. It should be noted that one postdoctoral associate supported by the NIRT, Dr. W. Ni, is primarily located at GM. Mechanical testing has focused on materials produced by three different research groups at Brown (Profs. Hurt, Sheldon, and Xu). Hardness and Young's modulus were obtained from indentation measurements. Friction coefficient and wear rate were measured by reciprocal pin-on-disk wear test. It was found that incorporation of CNT's can effectively increase the hardness and modulus and decrease the friction coefficient of the porous alumina. However, the hardness of the CNT/ alumina composites tested to date is much lower and its friction coefficient is much higher than most tribological coatings. This is primarily due to the poor properties of the amorphous, alumina templates. To remedy this difficulty, we are currently exploring several approaches to obtain ceramic matrices with better mechanical properties. This includes fabrication of improved anodic materials at GM, and the crystallization of anodic alumina templates at Brown.

An electroless plating method is being employed by Dr. Ni at GM to produce metal matrix composite coatings. Current work is focused on Ni-P-Carbon nanofiber (Ni-P-CNF) and Ni-P-Carbon Nanotube (Ni-P-CNT) coatings on aluminum substrates. The as-deposited Ni-P coating is amorphous and its hardness and modulus are 8.2GPa and 127GPa respectively. The influence of heat treatments on the mechanical properties of Ni-P coatings have also been studied, to obtain matrices with high hardness. We then studied the effects of carbon nanofibers and nanotubes on the mechanical properties. The wettability of the CNF and CNT reinforcements created some initial difficulties with fabrication, however, this has been solved by the use of acid treatment and surfactants. The initial nanoindentation and wear tests of these composite materials do not show improved performance, compared with the unreinforced Ni-P matrix. One issue is that the bonding at the matrix-carbon interface appears to be very weak. Methods for altering the interfacial bonding between the matrix and the CNT/CNF reinforcements are currently being investigated.

For further information about this project, email:

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