Annual Progress Report

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Principal Investigator: Renato P. Camata

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Novel Carbon-Based Nanostructured Materials for Low-Weight, High-Strength, and High-Temperature Applications
Among the multiple technologies needed for the realization of low-cost, high-reliability space travel and exploration, protective coating materials have been identified by NASA as potentially playing an enabling role in future space transportation and aerospace systems. Hard and tough protective coatings with low wear and superior thermal stability characteristics are required for lightweight materials and systems that operate in hostile environments and conditions. These coatings are of particular interest for the development of advanced spacecraft propulsion systems that demand high specific strength materials operating safely and reliably at high temperatures, for long periods of time.

The B_xC_yN_z ternary system is one of the most promising materials systems for the engineering of superhard materials with enhanced thermal and chemical stability for aerospace applications. The recent high-pressure synthesis of cubic BC_2N with hardness higher than that of single crystal cubic BN, reaffirms the long-standing technological potential of these materials. In the first year of this project we have focused on the steps necessary for the creation of hard, yet tough B_xC_yN_z nanostructured materials with enhanced chemical stability at high temperatures. Using our expertise in nanocrystalline diamond coatings as a starting point, we have conducted studies to determine their thermal stability in an oxidizing environment. Although various groups have reported nanocrystalline diamond coatings with good mechanical properties, the thermal stability of these nanophase materials had not yet been investigated. As we target the engineering of new carbon-based nanostructured materials and composites by the addition of N and B species as well as B_xC_yN_z nanocrystals, it was crucial to establish a benchmark for the thermal performance of nanostructured films made solely of carbon, in our case, nanocrystalline diamond. Our research has determined that nanocrystalline diamond films grown on mirror-polished titanium alloy substrates by Microwave Plasma Chemical Vapor Deposition, with 80% the hardness single crystal diamond and excellent adhesion, are stable only up about 600°C in open air. These results establish for the first time the thermal stability of nanostructured diamond materials and will be used as a reference point for improvements of B-doped and composite carbon-based coatings.
During the period covered by this report significant effort was also allocated for the installation and commissioning of a new NSF-funded Pulsed Laser Deposition (PLD) facility at the University of Alabama at Birmingham headed by the PI, which is now ready to generate results in the creation of BxCyNz nanocrystal/amorphous C:N matrix composites. Because the mechanical properties of these BxCyNz nanostructured materials are inextricably tied to their nanoscale interfacial chemistry, our goal will be the engineering of chemical states at the nanocrystal/nanocrystal or nanocrystal/matrix interface that may lead to controllable interfacial binding, delivering mechanical properties that could be “tuned” on demand by the processing conditions. We will achieve this by independently tailoring nanocrystal and matrix characteristics to obtain viable interface chemistries for effective mechanical exchange at the nanoscale. These materials with ordered structures and interfaces at the nanometer scale may provide the properties required of protective coatings for propulsion applications. Interactions at this scale produce behavior that cannot be extrapolated from properties at higher length scales, and therefore, extensive experimentation guided by state-of-the-art modeling produced by other groups will be used to achieve our goals.

We expect that the results obtained in this project for coatings and thin films could point the way to specific lightweight/high-strength nanostructured composites that could then be produced in bulk quantities by other techniques for structural components.

This NASA/EPSCoR Seed Grant has provided support for one graduate student in the UAB Physics Ph.D. Program. This student has been working full time in this project producing the thermal stability results reported here and being a major player in the installation of our new PLD facility. In less than six months we have submitted two abstracts for presentations at the Fall 2002 Meeting of the Materials Research Society (Boston, MA, December 2002) and the 5th Conference on Aerospace Materials, Processes, and Environmental Technology (AMPET, Huntsville, AL, September 2002). A manuscript is currently in preparation for publication of these results. With our PLD facility in operation, this graduate student is now focusing his efforts on the initial experiments in deposition of tetrahedral amorphous carbon. His tentative thesis title is “B-C-N nanostructured materials.”
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Overview of program

This document reports the technical progress achieved in the project entitled “Novel Carbon-Based Nanostructured Materials for Low-Weight, High-Strength, and High-Temperature Applications.” In order to maximize our potential for successful carbon-based nanostructured coating materials, we have focused on two independent fabrication strategies: (1) Microwave Plasma Chemical Vapor Deposition (MPCVD), and (2) Pulsed Laser Deposition (PLD). Given the complementary nature of these two processes we expect to generate nanostructured materials with a wide range of properties. This dual synthesis focus will also enable us to identify the strengths and weaknesses of each approach for a particular materials system. Within each synthesis effort we have devised a sequence of specific tasks to be performed to achieve our objectives:

(1) Carbon-based nanostructured materials by Microwave Plasma Chemical Vapor Deposition (MPCVD).
   a. Establish a benchmark for the thermal stability of nanocrystalline diamond coatings deposited by MPCVD. *(completed)*
   b. Effect of boron doping on mechanical properties and thermal stability of nanocrystalline diamond deposited by MPCVD. *(in progress)*
   c. Deposition of B-doped nanocrystalline coatings on selected high-specific strength candidate materials for structural and propulsion applications.

(2) Carbon-based nanostructured materials by Pulsed Laser Deposition (PLD).
   a. Installation and commissioning of PLD Facility. *(completed)*
   b. Deposition of Tetrahedral Amorphous Carbon (TAC) by PLD. *(in progress)*
   c. Mechanical Properties and Thermal Stability of Tetrahedral Amorphous Carbon (TAC) coatings. *(planned)*
   d. Generation of boron carbide nanocrystals using Nanoparticle Beam PLD. *(planned)*
   e. Incorporation of boron carbide nanocrystals into the TAC matrix. *(planned)*
   f. Mechanical Properties and Thermal Stability of composites comprised of B_xC_yN_z in a TAC matrix. *(planned)*
   g. Effect of boron and nitrogen doping on Mechanical Properties and Thermal Stability of TAC and B_xC_yN_z/TAC composite coatings. *(planned)*
Carbon-based nanostructured coating materials

Chemical Vapor Deposition
  (achieved previously)

Thermal Stability of Nanocrystalline Diamond
  (completed)

Effect of Boron Doping on the Mechanical Properties and Thermal Stability of Nanocrystalline Diamond
  (in progress)

Deposition of B-doped nanocrystalline coatings on selected high-specific strength candidate materials for structural and propulsion applications.
  (planned)

Pulsed Laser Deposition
  (completed)

Deposition of Tetrahedral Amorphous Carbon
  (in progress)

Mechanical Properties and Thermal Stability of Tetrahedral Amorphous Carbon
  (planned)

Generation of boron carbide and B-C-N nanocrystals. Incorporation into TAC matrix
  (planned)

Effect of Boron and Nitrogen Doping on Mechanical Properties and Thermal Stability TAC and BCN/TAC composite coatings
  (planned)

Roundtable with NASA and industry on applications of C-based nanostructured crystalline coatings in structural and propulsion systems.
  (planned)

New directions…

Fig. 1 – Chart showing the status of the two parallel tracks in being followed in the development of new carbon-based nanostructured coatings. The tracks are mainly driven by the complementary nature of the two fabrication strategies being pursued, i.e., Microwave Plasma Chemical Vapor Deposition (MPCVD) and Pulsed Laser Deposition (PLD).
Figure 1 presents a sequential chart showing how these tasks that are being carried out in parallel. The first specific tasks we addressed were therefore the investigation of the thermal stability of nanocrystalline diamond films deposited by MPCVD and the setting up of the PLD facility. In the following sections, we describe the activities, findings and achievements accomplished in the course of performing these tasks (Tasks 1a and 2a in Fig. 1, which are now complete). Mr. Mevlut Bulut, a full-time graduate student in the UAB Physics Program, was assigned to this project and has performed the aforementioned tasks. This seed grant as well as its associated cost sharing funds have provided full support for this graduate student. This student is now developing a thesis entitled “B-C-N nanostructured materials.” His involvement in the setting up of the new PLD laboratory has exposed him to instrumentation development early in his Ph.D. This combination of setting up a new facility and being involved in materials research using state-of-the-art instrumentation provides for a good educational impact of our program.

Activities and findings

In the next few sections we describe succinctly the research activities and findings obtained in the first year of this program. Topics include results on the thermal stability of nanocrystalline diamond films grown by Microwave Plasma Chemical Vapor Deposition (MPCVD), the installation and commissioning of our new NSF-funded Pulsed Laser Deposition (PLD) Facility that will be used in the next stage of this project and the publications and presentations in the period.

On-going and future activities are also delineated in the area of carbon-based nanostructured composite coatings by PLD as well as in boron-doped nanocrystalline diamond coatings by MPCVD.
Open-air thermal stability of diamond coatings is crucial for some technologically important applications, like industrial abrasives and cutting tools, which are subjected to significant heating under operational conditions. Although various groups have reported nanocrystalline diamond coatings with good mechanical properties, the open-air thermal stability of these nanophase materials has not yet been investigated. In this work, the thermal stability of nanocrystalline diamond films grown on mirror-polished titanium alloy substrates by Microwave Plasma Chemical Vapor Deposition technique was studied. Films used for this study were deposited using microwave plasma from a mixture of pure methane, hydrogen and nitrogen gases. Average substrate temperature during the deposition was 850°C. Samples with a 3-µm film thickness were annealed for an hour in open-air atmosphere at different temperatures between 200°C and 800°C. In order to investigate the evolution of the structural and mechanical properties depending on the annealing temperature, X-Ray diffraction and Raman spectra from each sample were taken before and after annealing. The Raman feature near 1150 cm$^{-1}$ was used as a probe of the nanocrystalline diamond content of the coatings. The surface roughness of the samples was also measured following the annealing treatments. The hardness and Young’s modulus values were obtained using a nanoindenter. The results of this study show that nanocrystalline diamond films are highly stable below 400°C with no significant change in mechanical properties. Samples annealed between 400°C and 600°C, however, exhibit values of hardness and Young’s modulus lower by as much as 40% compared to unannealed samples. Above 600°C delamination and graphitization effects were observed in the coatings.

**Deposition conditions and basic characterization**

Ti6Al4V alloy substrates were used for Microwave Plasma Chemical Vapor Deposition (MPCVD). The substrate surfaces were mirror-polished before the coating.
The MPCVD process was carried out using a mixture of three different gasses: hydrogen, nitrogen and methane at a total pressure of 125 Torr used at the following flow rates:

- Hydrogen 500 sccm
- Nitrogen 8.9 sccm
- Methane 88 sccm

During the deposition the microwave power was 800 W, and the average substrate temperature was 850°C as measured by a two-color optical pyrometer. Sample generated in this process were then subjected to annealing at various temperatures. Samples were kept annealed at 200°C, 400°C, 600°C, and 800°C for an hour. Heating up the samples to these temperatures and cooling down to room temperature were realized by a 20°C /min ramp rate.

Figure 2 shows optical images of samples annealed at different temperatures. Even a casual inspection of these images reveals the essence of our results. Samples annealed at 200°C and 400°C show optically homogeneous coatings with no obvious changes with respect to as-deposited samples (not shown). The heterogeneous appearance of the sample annealed at 600°C, however, clearly suggests a major change in the coating morphology. The sample annealed at 800°C once again displays a homogeneous appearance but markedly different in optical texture as compared to the samples annealed below 400°C.

![Optical images of samples](image)

**Fig. 2** - Optical images of samples Ti6Al4V alloy substrates coated with a nanocrystalline diamond film. The different fields represent samples annealed at different temperatures as indicated.
We have performed x-ray diffraction measurements on annealed samples to verify the crystallinity of the specimens. Figure 3 shows how samples annealed at 600°C or below still exhibit distinct diamond peaks while the sample annealed at 800°C is dominated by the peaks of hexagonal TiO$_2$ (Fig. 3a). In Fig. 3b, we show an expanded region of the spectra around the diamond peak at $2\theta \approx 44^\circ$. The extinction of this diamond peak at 800°C and the concurrent appearance of the TiO$_2$ indicate the complete loss of the coating at these high temperatures. This is confirmed by parallel Raman measurements carried out on the same samples (inset of Fig 3b) that show the disappearance of the 1150 cm$^{-1}$ vibrational mode of diamond in samples annealed at 800°C.

**Mechanical Properties**

We have also carried out nanoindentation measurements on the annealed samples in order to probe any changes in their mechanical properties as a function of annealing temperature. These results are shown in Fig. 4. Although x-ray diffraction and Raman measurements show the presence of nanocrystalline diamond in samples subjected to annealing at 600°C, hardness data establishes a significant softening of these films. Hardness decreases by as much as 40% as compared to as-deposited coatings or samples annealed below 400°C.

When considered in association with optical images, x-ray diffraction, and Raman data, these results lead to the conclusion that nanocrystalline diamond films deposited by MPCVD are thermally stable up to 400°C. Up to this temperature, films show no significant change in microstructure or mechanical properties under annealing in open air. For temperatures above 400°C-600°C, the coatings soften, compromising their mechanical properties, although their chemical and microcrystalline character remain essentially unaltered. In the 600°C-800°C the coatings oxidize and are lost. It is clear that more detailed experimentation is needed to improve the resolution of the temperature at which softening as well as coating loss occurs.
Fig. 3 - X-ray diffraction spectra showing that the nanocrystalline diamond film is completely lost at 800 °C, and the surface of the sample annealed at 800 °C is covered by an hexagonal TiO₂ layer instead. The inset in part (b) shows Raman spectra that confirm the loss of the coating with at 800 °C by the disappearance of the 1150 cm⁻¹ vibrational mode of diamond.
Fig. 4 – Measurements of hardness (a) and elastic modulus (b) of the nanocrystalline diamond coatings as a function of displacement into the surface after various annealing temperatures.
Installation and commissioning of new Pulsed Laser Deposition facility that will be used in next stage of this project

Overview

We have recently completed the installation of a new Pulsed Laser Deposition (PLD) system in the Department of Physics at UAB. A schematic of the system is shown in Fig. 5. Conventional PLD is combined with a new deposition technique known as Nanoparticle Beam Pulsed Laser Deposition (NBPLD) pioneered by the PI at UAB. This system has been made possible by a Major Research Instrumentation Grant from the National Science Foundation (Award # DMR-0116098). Figures 6, 7, and 8 show recent photographs of our PLD laboratory.

Now that this system is operational, our goal is to simultaneously employ our NBPLD source and conventional PLD (Fig. 5), to create B₈C₄N₂ nanocrystal/amorphous C matrix composites. Because the mechanical properties of these B₈C₄N₂ nanostructured materials are inextricably tied to their nanoscale interfacial chemistry, our goal will be the engineering of chemical states at the nanocrystal/nanocrystal or nanocrystal/matrix interface that may lead to controllable interfacial binding,
Fig. 6 – Pulsed Laser Deposition System installed and operational at UAB

Fig. 7 – Closer view of the Excimer Laser (Lambda Physik LPX305i) used in the system. System performing at a maximum energy of 1.4 J/pulse (KrF; 248 nm; 20 ns pulse duration; max. 50Hz repetition rate)
delivering mechanical properties that could be “tuned” on demand by the processing conditions. We will achieve this by independently tailoring nanocrystal and matrix characteristics to obtain viable interface chemistries for effective mechanical exchange at the nanoscale.

Fig. 8 – Close view of the vacuum system (left) where substrate heater and target holders are mounted. At right, undergraduate student Jennifer Kirchhoff (NSF-funded Research Experiences for Undergraduates UAB Physics Program) and graduate student Hyunbin Kim use pyrometer to calibrate the substrate temperature of the system in preparation for Pulsed Laser Deposition experiments.
Carbon-based nanostructured composite coatings

Overview

Tetrahedral amorphous carbon (TAC) is an amorphous carbon network in which the coordination of carbon is close to four. The properties of TAC films depend strongly on the ratio of sp³ to sp² bonds. Density measurements around 3 g/cm³ have commonly been reported. This material has attracted much attention recently because of its chemical inertness, good thermal stability, optical gap of approximately 2 eV, negative electron affinity (a weak p-type semiconductor) and low coefficient friction. In addition it presents hardness and thermal conductivity comparable to those of diamond. TAC is doubtless a good candidate material for wear resistant coatings and as a matrix for carbon-based nanocomposites with properties tailored for a variety of protective coating applications.

Synthesis methods

Various techniques have been successful in the production of TAC thin films, including Pulsed Laser Deposition (PLD), Laser Initiated Vacuum Arc Deposition, Plasma Beam Deposition, and Ion Beam Deposition. In a variety of deposition experiments it has been found that sp³ carbon atoms grow mostly in clusters as their concentration does not exceed ~15-30%. However, for sp³ carbon content in the ~25-75% range, most of the additional sp³ carbon atoms do not gather into clusters but rather are dispersed throughout the sp² phase.

In this project we will employ our recently commissioned PLD Facility (described in previous section) to generate TAC coatings. A target of high-purity pyrolytic graphite has been obtained and is currently been installed in our PLD system. We will explore the wide range of PLD deposition conditions and correlate these with the mechanical properties of the coatings obtained.
Characterization methods

Vibrational spectroscopies such as inelastic neutron scattering, high resolution electron energy loss spectroscopies (HREELS), infrared and Raman (UV and visible) spectroscopies, NMR, and transmission electron microscopy-based techniques have been used to characterize TAC thin films. NMR can resolve sp² and sp³ sites and quantify the proportion of sp² and sp³ bonding but requires large or ¹³C enriched samples. Electron energy loss spectroscopy (EELS) gives a direct measurement of the sp² bonding from the 1s → π* peak at 285 eV. However, sp³ sites are not probed directly, as they contribute with the sp² to the step at 290 eV associated with σ* states. Additionally EELS is a destructive and time-consuming technique. Raman spectroscopy is a convenient tool for vibrational characterization of amorphous solids, in which case it represents the phonon density of states (PDOS), weighted by a coupling parameter. However, Raman spectroscopy of diamond-like carbon films, obtained with photons in the visible range, does not appear to provide a good representation of the PDOS. First, the high-frequency stretch modes of sp² carbon atoms are overemphasized due to π-π* transition resonance effect. Secondly and more importantly, the sp² carbon network exhibits resonance enhancement in the Raman cross section since the local sp² carbon energy gap of ~2 eV is comparable with the energy of incident photons. The sp³ carbon atoms do not exhibit such a resonance effect because of the higher local gap of ~5.5 eV. As a result, Raman spectra obtained with visible excitation are completely dominated by the sp² carbon atoms. Raman scattering in the UV region appears to be more promising for vibrational studies. Advantages of using UV over visible photons include the suppression of previously dominant resonance Raman scattering from sp² carbon atoms and the possible increase in the signal from sp³ carbon atom, for which the resonance is expected to be attained. In addition, the overall Raman intensity is proportional to ω⁴, where ω is the frequency of incident photons; this makes the utilization of UV excitation even more advantageous considering the weak Raman signal usually obtained from diamond-like carbon films. Raman spectroscopy provides a more equally weighted view of the vibrational density of states, complementary to techniques such as low energy EELS and inelastic neutron scattering.
Planned research activities

Our current goal is to deposit a TAC films by PLD and systematically study the influence of deposition parameters, film nanostructure and sp³ to sp² ratio on their mechanical properties. The PLD scheme to be used in these depositions is shown in Fig. 9. We will then explore the incorporation of size-selected nanocrystals of different chemical composition and structure into the TAC film. We will first attempt to use our NBPLD source to generate boron carbide nanocrystals and incorporate them into the TAC matrix (Fig. 10). The successful deposition of boron carbide films (B₄C) by PLD has been reported recently, and using our NBPLD source we will attempt to expand this method to the creation of a beam of size-selected boron carbide nanocrystals that can be used to engineer new composites. This approach, combined with careful control of the substrate temperature, may provide a new way of creating B-doped TAC films with improved thermal stability. We will explore this possibility also.

Fig. 9 - Scheme for deposition of tetrahedral amorphous carbon (TAC) using conventional Pulsed Laser Deposition. A variety of TAC films will be deposited and evaluated for sp³ and sp² bonding, mechanical properties and thermal stability.
Fig. 10 - Scheme for the deposition of nanostructured composites coatings comprising size selected boron carbide nanocrystals embedded in a TAC matrix.

Presentations and Publications

(1) “Thermal Stability of Nanocrystalline Diamond Films Grown by Microwave Plasma Chemical Vapor Deposition,” Mevlut Bulut, Shane A. Catledge, Yogesh K. Vohra, Renato P. Camata, 2002 Fall Meeting of the Materials Research Society, Boston, MA, December 2-6, 2002,

