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RPPR Final Report
as of 28-Jan-2022

Agency Code: 21XD

Proposal Number: 77315EGRIP **Agreement Number: W911NF-21-1-0018**

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Report Date: 14-Mar-2022 Date Received: 13-Jan-2022
Final Report for Period Beginning 15-Dec-2020 and Ending 14-Dec-2021
Title: Dynamic Nanomechanical Tester for Characterization of Advanced Structural Materials
Begin Performance Period: 15-Dec-2020 **End Performance Period:** 14-Dec-2021
Report Term: 0-Other
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STEM Degrees: **STEM Participants:**

Major Goals: The goal of the DURIP proposal was to acquire a nanomechanical test instrument Bruker Hysitron® TI Premier Dynamic with XPMTM and nanoDMA® features and following capabilities:

- Nanoindentation with minimum indent depth less than 50 nm to probe minor phases in the microstructure and thin multilayered graphene films.
- Accelerated property mapping (6 indents/s) to reduce the time required to obtain large volume of data.
- Dynamic mechanical analysis (DMA) to measure elastic and viscoelastic properties of biological materials and gels.

Accomplishments: A dynamic nanomechanical test instrument (Bruker Hysitron® TI Premier Dynamic) with accelerated property mapping (XPMTM) using Berkovich and cube corner probes was purchased with the funds provided under the DURIP Award. The instrument was delivered and installed on May 26, 2021.
The instrument capabilities included:
nanoDMA III® Advanced Testing Capability
nanoDMA III® Optimized One-Dimensional Transducer
Hysitron performech II control Module
XPM, SPM+, V3 Optics
TriboScanner™
in-situ Scanning Probe Microscopy Imaging
Optical Microscope with Color Camera (20X and 50X microscope objectives)
Motorized Translation Staging & Controller
Environmental Isolation Enclosure
Magnetic Sample Holder
Passive Vibration Isolation System
TriboScan v.10 Software Package, TriboIQ
Dedicated Workstation
Feedback Control Package
Equipment Rack Assembly
Diamond Tip (3-sided) for Indentation: Berkovich (142.3-deg) and cube corner (90-deg) indenters
Standard and Calibration Samples

We have also performed nanoindentation experiments on a variety of materials as discussed in the attached pdf document

Training Opportunities: One post-doc, three PhD students and one undergraduate students were trained on the instrument

Results Dissemination: Currently several research projects are in progress as reported in the attached pdf and these results will be disseminated at several conferences and in journal publications. At present some of these results are expected to be presented at the
46th International Conference and Expo on Advanced Ceramics and Composites, Daytona Beach, January 2022 and in 2023. Several manuscripts are also in progress and they will be uploaded to this website upon the availability of the final published article.

Honors and Awards: The PI has received the following awards during this reporting Period:
1, University of Florida Doctoral Dissertation Advisor/Mentoring Award-2020-2021 (Aug 2021).
2, B.J. Lazan Award, Society for Experimental Mechanics (SEM) "for innovative contributions to experimental mechanics and development of in-depth understanding of multiaxial dynamic response of ceramics and soft materials" (Jun 2021)

Protocol Activity Status:

Technology Transfer: Prof, Subhash has interacted with Dr. Chritopher Haines, DEVCOM - ARL, Weapons & Materials Research Directorate, APG and has used this instrument to measure the hardness of several Boron Carbide ceramic specimens (Contract #W911NF-20-2-0265).

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Project Contribution:
National Academy Member: N

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National Academy Member: N

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Signature: Ghatu Subhash
Signature Date: 1/13/22 10:11AM

DURIP Final Report

Project Title: *Acquisition of Nanomechanical Test Instrument with Accelerated Property Mapping for Characterization of Advanced Structural Materials*

Contract/Order No.: W911NF-21-1-0018

Principal Investigator: Ghatu Subhash, University of Florida

Report Date: January 15, 2022

Reporting Period: 15 Dec 2020 – 14 December 2021

Introduction

A dynamic nanomechanical test instrument (Bruker Hysitron® TI Premier Dynamic) with accelerated property mapping (XPM™) using Berkovich and cube corner probes was purchased with the funds provided under the DURIP Award. The instrument was delivered and installed on May 26, 2021.

The instrument, referred to as the nanoindenter in this document, is used for quantitative nanoscale material characterization, including in-situ scanning probe microscopy (SPM), and nanoindentation to obtain the hardness and elastic modulus of hard and soft materials. The piezo-controlled instrumentation allows for the applications of loads as small as 10 µN, and indentation depths as low as 10 nm. These low loads and displacements allow us to use this instrument to measure features that are too small for micro-scale test methods such as Vickers indentation. For example, a single microVickers indent can require a surface area of diameter ~80-100 µm. This includes the area for the indent and the extent of the plastic zone surrounding the indent. Using the nanoindenter, 400 Berkovich indents could be performed in that same region. Thus, it is possible to use the TI Premier to measure the properties of very small particles or small regions of interest. Due to the precision instrumentation on the device, it can also be used to measure the elastic modulus from the load-displacement curve that is produced during indentation. This feature allows us to measure the elastic properties of very small samples.

The instrument is also capable of performing dynamic experiments, such as nanoDMA (dynamic mechanical analyzer), to obtain the storage and loss moduli of viscoelastic materials. The dynamic Performech II controller, included in this instrument, is also capable of fast property mapping of a sample surface. It's accelerated property mapping (XPM™) mode allows it to perform up to 6 indents per second and quickly obtain a hardness or modulus map of a given region. This feature is beneficial in the testing of composites, to compare the properties of the various phases.

In the seven months since the instrument has been installed at University of Florida, it has been used to test the following four types of materials. The results of these tests are summarized below.

(i) Hard nanostructured spark plasma sintered ceramics
(ii) Hard powder particles prior to sintering
(iii) SiC_f/SiC braided ceramic matrix composites
(iv) Highly oriented pyrolytic graphite (HOPG)

(i) Hard nanostructured spark plasma sintered ceramics

In this project, the nanoindenter was used to measure the hardness and elastic modulus of nanostructured boron carbide (B_4C) samples, prepared using spark plasma sintering. As discussed above, we can measure hardness in smaller areas using nanoindentation, as compared to microindentation. More importantly, the small size of the nanoindents allows us to perform indentations in highly porous samples, where the space between adjacent pores may be less than 40 µm, as seen in Figure 1(b). In these samples, it is very tedious and time consuming to perform (and later identify) the larger microVickers indents, since it is challenging (and often impossible) to find areas without pores. Further, the microindentation would capture the effect of the porous regions as well as the sintered region, whereas nanoindents are small enough to only indent the sintered mass. The nanoindentation hardness and reduced moduli of four nanostructured B_4C disks (plotted in Figure 2) is higher than that reported in literature[1–4] for fine-grained B_4C.

The results of this study, which also includes the strength and characterization of these nanostructured materials, will be presented at the *47th International Conference and Expo on Advanced Ceramics and Composites*, Daytona Beach, January 2023; and will be included in a manuscript titled "Quasi-static and dynamic mechanical characterization of nanostructured boron carbide prepared by spark plasma sintering", which will be submitted to the *Journal of the American Ceramic Society* in late 2022.

(ii) Relating the hardness of hard powder particles to sintered compact hardness

In conjunction with measuring the properties of sintered samples, we are also developing a technique to measure the hardness of hard powder particles prior to sintering. The hardness and elastic moduli of these particles are then compared to their respective values after sintering. As the material properties of a sintered sample are affected by sintering conditions, performing the measurements on the particles prior to sintering allows us to obtain these properties without the effect of sintering conditions. This analysis helps us understand if there is a relationship between the hardness virgin powders and sintered compact.

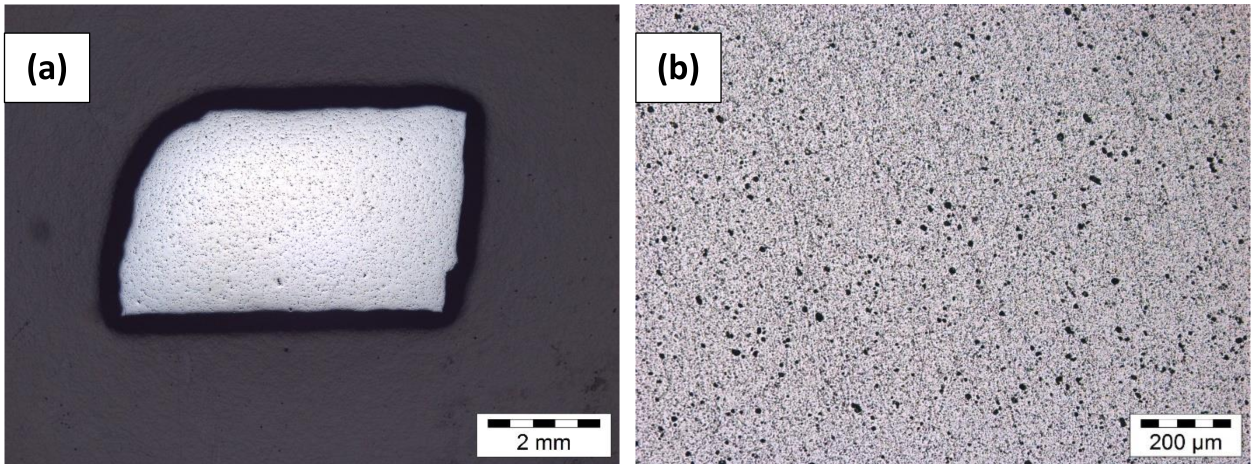

Figure 1: Optical micrographs of nanostructured B_4C sample. (a) Spark plasma sintered fragment mounted in acrylic and polished in preparation for indentation. (b) Higher resolution micrograph showing highly porous structure.

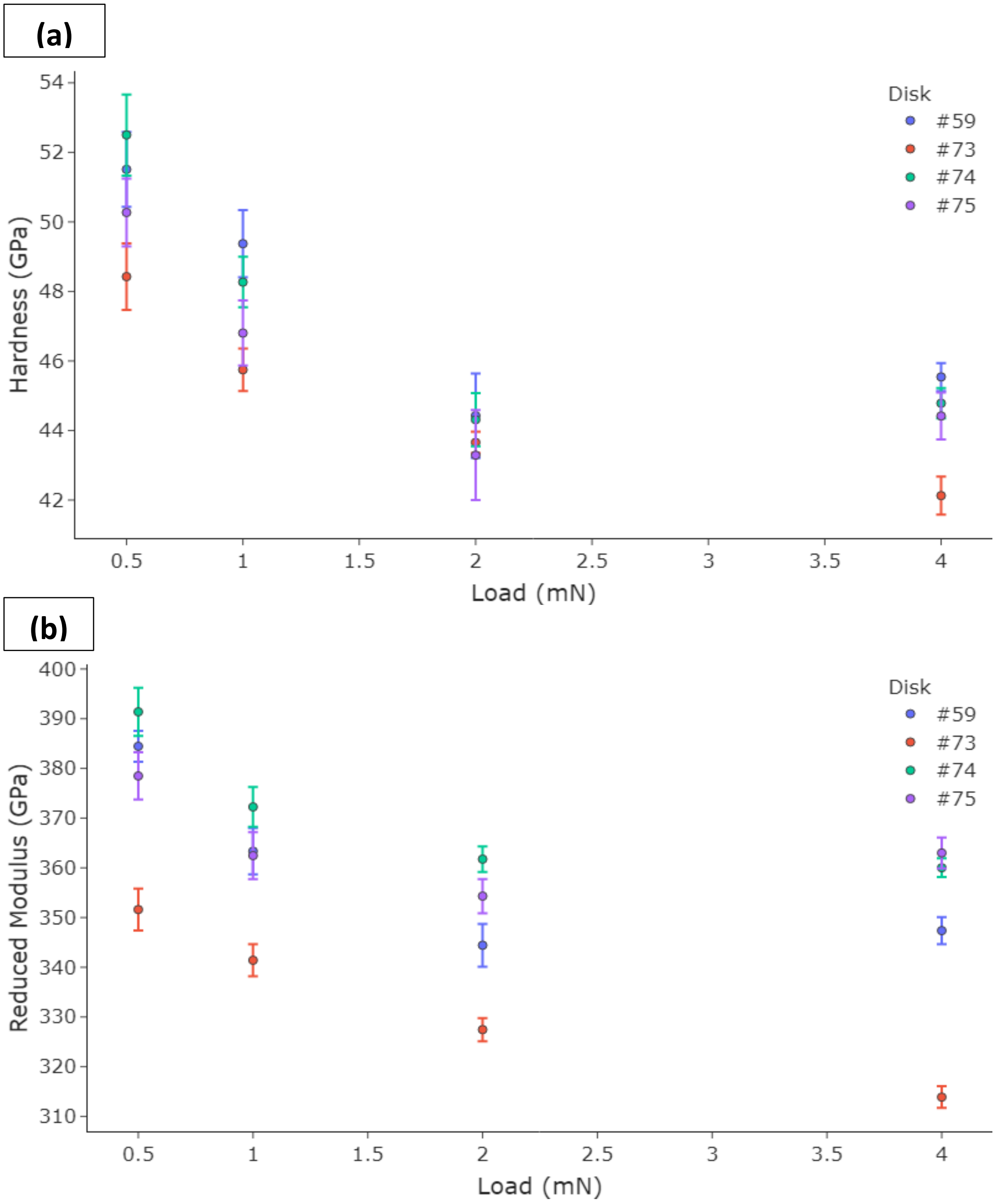

Figure 2: (a) Hardness and (b) reduced modulus of four nanostructured B_4C disks. These values are higher than of the typical range of hardness (32 – 38 GPa) and reduced moduli (340 – 360 GPa) reported for additive-free, fine-grained, spark-plasma sintered B_4C, as published in literature.[1–4]

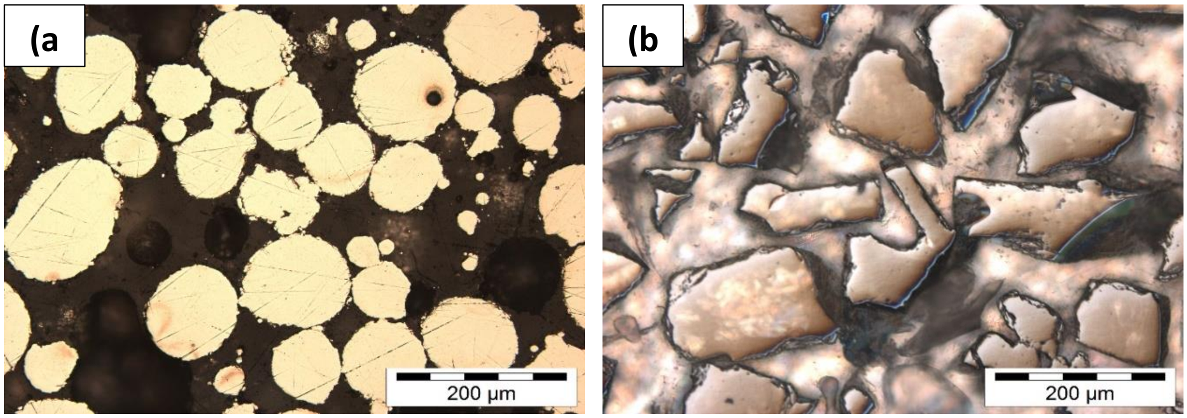

Figure 3: Optical micrographs of (a) M50 steel and (b) SiC powders, mounted in acrylic and polished to a 1 µm finish using diamond media, in preparation for indentation.

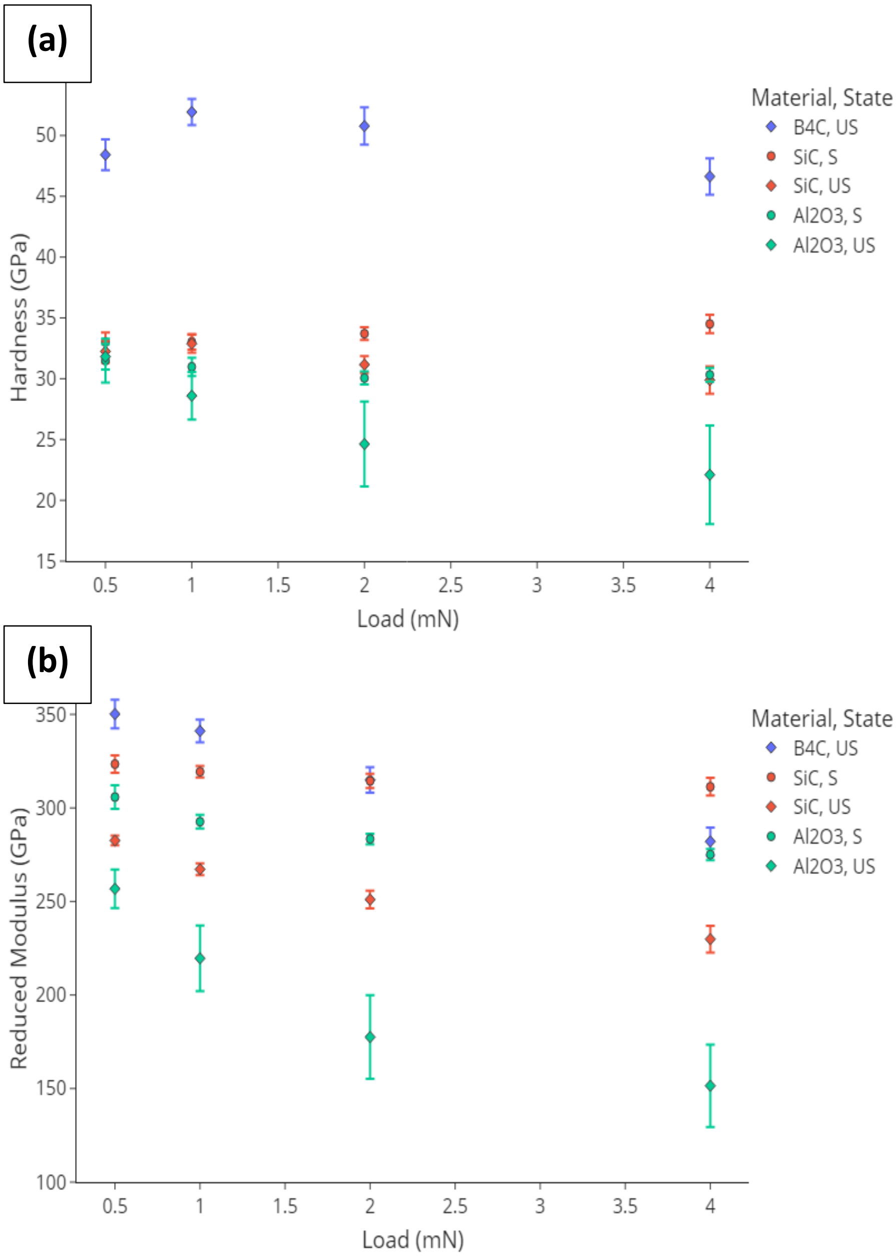

Figure 4: (a) Hardness and (b) reduced modulus of sintered [S] ceramic and unsintered [US] powder samples, obtained via nanoindentation.

However, the typical size of these powder particles is less than 70 µm (as shown in Figure 3) and hence, it is impossible to obtain these properties using microVickers indentation. Nanoindentation is the only viable method available to obtain the properties of these powder particles; and as far as we know, this is the first study to measure the hardness and modulus of individual ceramic powder particles prior to sintering. We intend to develop the technique for the preparation and nanoindentation of hard powder particles and then relate the hardness of these particles to sintered conditions. So far, particles of M50 steel, Al_2O_3, SiC, and B_4C as well as sintered Al_2O_3 and SiC samples, have successfully been mounted, polished, and prepared for nanoindentation. The size and surface structure of two of these samples, after polishing to a 1 µm finish, are shown in Figure 3, and the results for the nanoindentation on ceramics are plotted in Figure 4. The hardness of the sintered samples tends to be higher than that of the unsintered powder at all loads. Next, we will utilize material characterization techniques such as Raman spectroscopy, X-ray diffraction, and Transmission electron microscopy (TEM) to link the properties of the powders and sintered compacts to the microstructural changes occurring during spark plasma sintering. Future work also includes indentation of sintered compacts and powders of B_4C and B_6O.

The results of this study will be presented at the *46th International Conference and Expo on Advanced Ceramics and Composites*, Daytona Beach, January 2022; and will be included in a manuscript titled "Connecting Powder Particle Hardness to Sintered Compact Hardness", which will be submitted to *Ceramics International* in early 2022.

(iii) SiC_f/SiC_m braided ceramic composites

The nanoindenter has been used to measure the hardness and elastic moduli of the constituents of a SiC_f/SiC_m braided ceramic matrix composite (CMC). These composites consist of Hi-Nicalon Type-S SiC fibers, which have a diameter of ~10 µm, that have been densified via chemical vapor infiltration (CVI) with β-SiC matrix as shown in Fig 5(a).

Due to the size of the fiber and matrix, microindentation can only provide a measure of the overall composite hardness and cannot probe individual constituents. However, the nanoscale Berkovich probe allows us to precisely position each indent with sub-micron accuracy using SPM imaging, as shown in Figure 5(b). Thus, nanoindentation enables us to individually measure each constituent's hardness and elastic modulus and characterize the difference between the properties of the SiC fibers and the SiC matrix phases. Indents were performed to depths between 10 – 45 nm and with loads between 1 – 5 mN. The results, plotted in Figure 6, show that the SiC fibers have a lower hardness and modulus compared to the β-SiC matrix, likely due to the presence of turbostratic graphite within the SiC fiber (detected through TEM and Raman spectroscopy).

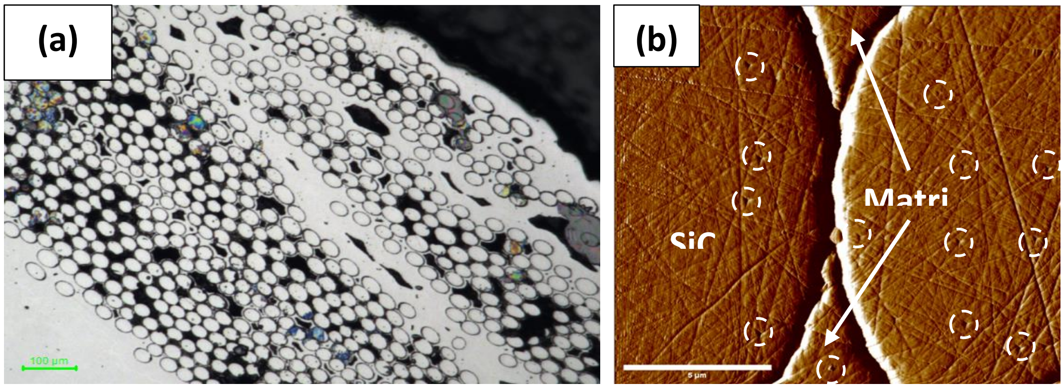

Figure 5: Microstructure of the SiC_f/SiC braided CMC through (a) optical microscopy and (b) scanning probe microscopy (SPM) using the nanoindenter. The high resolution of the nanoindenter image allows for precise positioning of each indent in the fiber or matrix. Few indented locations are shown in dotted circles.

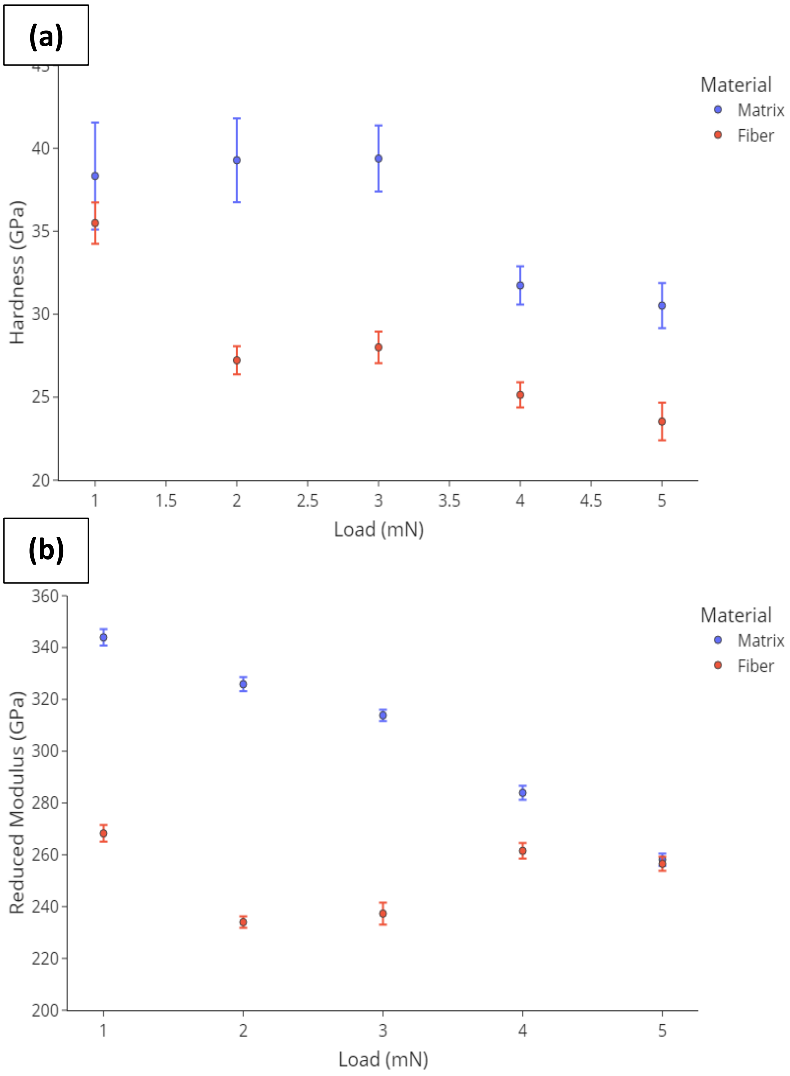

Figure 6: (a) Hardness and (b) reduced modulus of β-SiC CVI matrix and Hi-Nicalon Type-S SiC fiber within the SiCf/SiC braided CMC.

The results of this study will be presented at the *46th International Conference and Expo on Advanced Ceramics and Composites*, Daytona Beach, January 2022; and will be included in a manuscript titled "Mechanical Properties of SiC_f/SiC ceramic matrix composites", which will be submitted to *Journal of Nuclear Materials* in early 2022.

(iv) Highly oriented pyrolytic graphite (HOPG)

We have probed the properties of highly oriented pyrolytic graphite (HOPG, sometimes referred to as multilayer graphene) deposited on a nickel (Ni) substrate using the nanoindenter. The thickness of the HOPG deposition is ~100 – 150 nm (corresponding to 300 – 450 graphene layers), while the Ni substrate has a thickness of ~30 µm. The microstructure of this material, obtained with transmission electron micrography (TEM) is shown in Figure 7. An organometallic platinum (Pt) coating is applied to the top of the sample to protect the HOPG from the focused ion beam (FIB) used to prepare the sample for TEM.

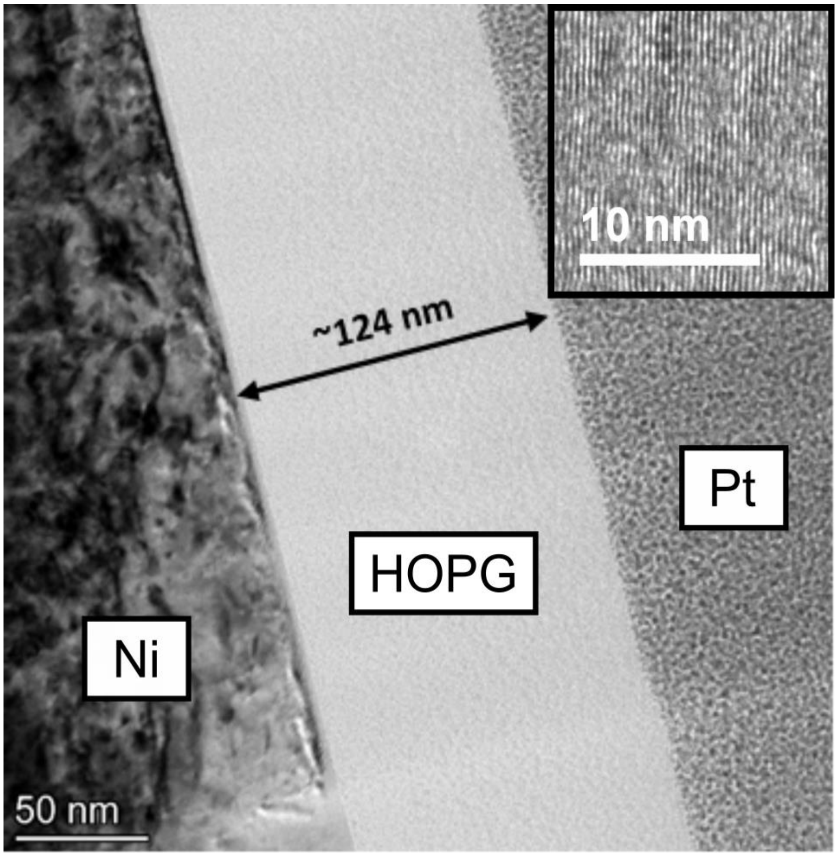

Figure 7: TEM micrograph of an HOPG sample deposited on a Ni substrate. The Pt coating provides protection to the HOPG film during the FIB process. The thickness (124 nm) corresponds to 370 graphene monolayers; the interlamellar spacing is shown in higher resolution with the inset.

The hardness and elastic modulus of the HOPG deposition was measured as a function of depth of indentation (i.e., contact depth). To obtain this, indents were performed via a "partial unloading" method, illustrated in Figure 8(a), wherein the load on the indenter tip is momentarily reduced at numerous intervals during the loading process. Hence an unloading curve is obtained at several steps during a single indent. This allows for the calculation of hardness and elastic modulus at multiple depths during the indentation process. These tests demonstrate the typical pop-in behavior of lamellar structures, characterized by the abrupt increase in displacement at a constant load during the nanoindentation. This phenomenon, illustrated in Figures 8(a-c), likely corresponds to the abrupt defect (fracture or dislocation) nucleation. Initially, the hardness of the film increases with increasing depth of indentation. However, at some point, the film fractures, and the hardness drops to ~30% of its maximum value. The drop in modulus is less pronounced. As the thickness of the film is less than 150 nm, microVickers indentation does not have the resolution to perform these indents, whereas the nanoindenter can perform indentations as small as 10 nm in depth.

The results of this study will be included in a manuscript titled "Microstructural characterization and nanomechanical properties of highly oriented pyrolytic graphite (HOPG) on metal substrates at room temperature", which will be submitted to *Carbon* in early 2022.

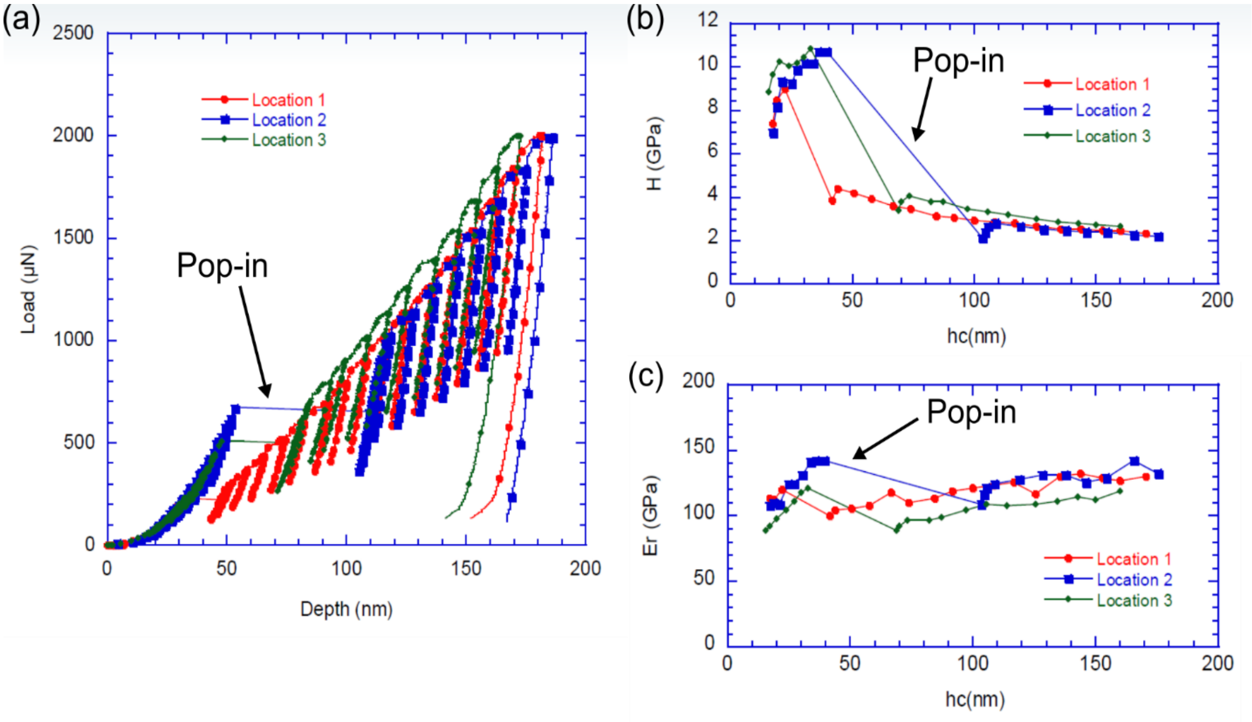

Figure 8**:** (a) Load-displacement curves for the partial-unloading nanoindentation tests performed on a HOPG sample deposited on a Ni substrate. Each color corresponds to a different location on the sample where a single partial unloading test was performed. (b) Hardness and (c) reduced modulus of the three locations as a function of indentation depth. The pop-in phenomenon, labelled in the plots, results in a sudden drop in properties.

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