Commercially scalable, single-step polymer-derived reaction bonding synthesis of refractory ceramics

By Boris Dyatkin and Matthew Laskoski

The U.S. Naval Research Laboratory reports on its polymer-derived ceramics synthesis approach, which relies on blends of metals and monomer resins to synthesize near net shape refractory metal carbides, borides, and nitrides using a single-step in situ reaction bonding method.

The unique essence of the "refractory ceramic" class of materials lies in the first word of the term: refractory. Its origin stems from the Latin *refractarius*, which, directly translated, means "stubborn."

This stubbornness most commonly applies to behavior of materials in extreme thermal environments. Refractory ceramics melt at very high temperatures of over 2,500°C.[1] However, these materials often demonstrate stubbornness in multiple categories. They are among the hardest available engineering materials, and they also readily withstand corrosion, whether by caustic chemicals or oxidizing air molecules at elevated temperatures. Many of these "stubborn" materials also readily deflect or absorb ionizing or neutron radiation from nuclear fuels.

As our technological demands grow, the harsh environments that these ceramics must readily withstand will shift from obscure extremes hypothesized for future generations of applications and into regularly experienced conditions that will require materials engineering solutions. Transoceanic passenger flights that complete their journeys in less than an hour will need engines that withstand supersonic air flows and heats of combustion. Multiple-use space vehicles that ferry astronauts back and forth between Cape Canaveral and the International Space Station will demand heat shields that endure fiery re-entries. Our thirst for rare earth minerals and oil will require deployment of drill bits and cutting tools that—without breaking—pierce miles of Earth's crust. Refractory ceramics stand out as a material solution that demonstrate required performance and endurance in the face of these challenging environments.

Binary, covalently bonded, nonoxide ceramics that incorporate transition metal Group IV and V elements from the periodic table offer the optimal combination of refractory properties. These ceramics include metal carbides, metal borides, metal nitrides, and metal silicides. They have attracted interest since the middle of the 20th century, but their use and development has proceeded intermittently in fits and starts since then.

Their bond strengths ensure that the melting points of these refractory materials fall in the 2,500–3,900°C range (Figure 1). While these ceramics adopt a broad range of cubic, hexagonal, and rhombohedral structures, their close-packed lattices ensure these materials maintain excellent strength and hardness of well over 200 GPa. Absence of weakly bonded oxygen in these materials also strengthens the materials' resistance to oxidation. Finally, the covalent nature of bonding behavior in many of these ceramic polymorphs facilitates electronically conductive behavior and even thermoelectric properties.[2]

Although such a wide array of useful properties in such a broad material family is incredibly attractive, several important roadblocks have, to date, precluded their implementation in many perfectly suited engineering systems. Economic and efficient manufacturing stands as the biggest challenge these materials face. Metal carbide powders, for example, are produced via carbothermal reduction of metal oxides and graphite at over 2,000°C. Subsequently, hot pressure sintering compacts those powders into dense monoliths—again, at 2,000°C—and while under over 1 GPa applied pressure. These compaction systems require significant energy inputs to operate, are unwieldy and unsafe, and cannot handle high throughput capabilities. Moreover, weeks of tooling often follows the sintering process in order to carve compacted formless monoliths into engineering parts with precise geometries and sharp angles.

Recent insights into spark plasma sintering have implemented pulsed electric current through ceramic greenbodies to efficiently and rapidly compact them into ceramics.[3] These approaches reduce lead times, yet remain at a small scale:

to date, they cannot produce vehicle-scale heat shields or engine cowls. Polymer-derived approaches, which compact metalorganic molecules into desired shapes and carbonize and pyrolyze them into ceramics, can yield ceramics at much lower temperatures (1,000–1,400°C).[4] However, available chemistries primarily limit this pathway to polysilanes (or similar molecules) that can only yield silicon-based ceramics (e.g., SiC, Si_3N_4, SiO_2). If other ceramics, such as titanium- or hafnium-based refractory composites are desired, silica formers, metal salts or oxides, and copolymers with oxygen groups must be included in the preceramic blend. All of these pathways embed chemical impurities in the resulting ceramic composite and inhibit their mechanical and thermal properties.

High-char resin: Key to novel polymer-derived refractory ceramics

In 1993, the United States Naval Research Laboratory (NRL) leveraged its longtime research into phthalonitriles, which are thermosets that cure at low temperatures and remain thermally stable at high temperatures,[5] to develop a novel acetylenic monomer resin.[6]

This thermoset is 1,2,4,5 tetrakis(phenylethynyl)benzene ("TPEB"), which is a meltable aromatic polymer that contains solely carbon and hydrogen atoms: $C_{38}H_{22}$. While it is a powder in a neat stage and melts in the 170–200°C range, this resin rapidly cures at 225–250°C and increases its viscosity from about 0.15 Pa·s to over 250,000 Pa·s. Furthermore, as it is heated to over 700°C, TPEB chars but retains a very high carbon yield of over 85%.[7] This polymer has, subsequently, become the carbon source and key functional ingredient in a novel polymer-derived ceramic process.[8]

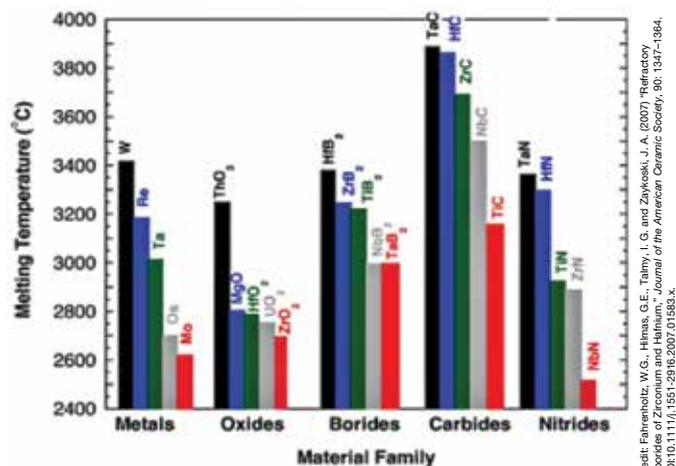NRL's ceramics fabrication approach (shown in Figure 2) blends together this

Figure 1. A comparison of the melting temperatures of the most refractory members of several classes of materials. Several borides, carbides, and nitrides have melting temperatures above 3,000°C and are considered ultrahigh-temperature ceramics.

resin with powders of metals or metal hydrides to yield the two-component homogeneous powder. The subsequent process step then compacts this preceramic into a desired preceramic greenbody shape. This step requires a conventional hand-powered hydraulic Carver press and applied loads of 130 MPa or less.

Depending on the application demands, a broad variety of die configurations—e.g., discs, panels, spheres, cones—guide the form factors and geometries of resulting shapes. NRL has synthesized samples as small as 6 mm diameter discs that were 1 mm thick and as large as 15 cm by 15 cm panels that were over 10 mm thick. The process elastically scales with requested dimensions and is viable for production of even larger components. On the flipside, if the processing requires a powder product, this approach delivers the microscale ceramic powders as well.

In the next step of processing, the greenbodies are placed in a tube or box furnace with flowing inert (argon) gas and are heated up to 1,400–1,500°C. As the TPEB resin cures at 250°C, its exceptionally high viscosity firmly locks and embeds the metal particles in a cross-linked rigid carbon matrix. Subsequently, unlike other polymer-derived processes that rely on thermoplastic carbon sources, no material phase separation or flow occurs in these greenbodies.

As the material transitions through the 600–750°C thermal processing range, polymer charring removes hydrogens and volatile hydrocarbons from the
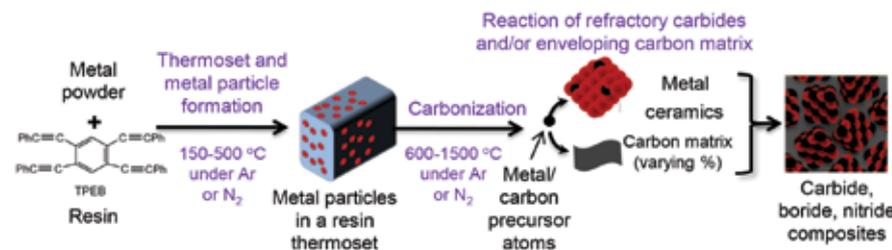
Commercially scalable, single-step polymer-derived reaction bonding synthesis of . . .

Figure 2. Schematic of polymer-derived ceramics synthesis process that implements TPEB resin with a high char yield in a low-temperature, pressureless synthesis route to deliver metal carbides, metal nitrides, and metal borides.

material matrix. Owing to the strong triple bonds in the acetylenic TPEB material, the resin retains a larger mass fraction of its carbon than comparable thermosets during the char process. This carbon, subsequently, reaction bonds with the metals in the 1,000–1,500°C temperature range to form metal carbides. To date, NRL has used it to synthesize titanium carbide (TiC),[9] silicon carbide (SiC),[10] tantalum carbide (TaC),[11] and tungsten carbide (WC).[12] However, practically any transition metal can be incorporated into this process to yield a corresponding metal carbide.[8]

This single-step polymer-derived ceramics process offers several important fundamental advantages. Most importantly, both the cost and processing time are significantly lower than comparable refractory carbide manufacturing techniques; the procedure does not require high temperature sintering and completes end-to-end manufacture in less than 48 hours. The material ingredients are cheap and readily accessible. Metal powders can remain in the micron size and do not require extensive chemical purification, surface treatment, or cleaning prior to use. The polymer precursor can be readily synthesized in large quantities in conventional industrial processing centers. The precursor blending process uses a ball mill, but it does not require excessive grinding and can upscale for simultaneous blending of pounds of preceramic powders. The temperature that facilitates this reaction bonding is 600 degrees lower than that employed in conventional methods and can produce over 75% in energy cost savings.

The reaction bonding process that nucleates metal ceramics from blends of metal atoms and carbons is a rapid kinetic process that has neither a high activation barrier nor a self-igniting exothermic runaway step. The initial preceramics (Figure 3A) convert to the fully densified refractory monoliths (Figure 3B) in a near net shape process. The reaction bonding step negligibly shrinks the solids (< 8% volumetric decrease) and retains the geometric features, such as sharp edges, that had been preset in the greenbodies. The material surface morphology (Figure 3C) shows a homogeneous structure without phase separation or microscale cracking. Leftover free carbon homogenously disperses throughout the ceramic matrix and does not agglomerate into macroscale, structurally weak aggregate phases.

Low temperature processing offers another vital benefit that eludes conventionally sintered ceramics. While high-temperature compaction facilitates densification kinetics and accelerates pore closure in greenbodies, the same processes coarsen crystalline grains of ceramics.[13] Owing to the Hall-Petch effect, resulting dense ceramic monoliths with macroscale grains lose their hardness and strength advantages and become extremely brittle.[14] Moreover, pressureless densification of some ceramics, such as boron carbide (B_4C),

decomposes the ceramic structure into weak constituents above 2,100°C.[15] Low-temperature nucleation of metal ceramic grains from reaction bonded metal and carbon atoms yield nanocrystallites that are narrower than 100 nm across with tight distributions. Moreover, the free carbon polymer byproducts further inhibit grain coarsening.[16]

Versatile routes to novel refractory ceramic nanostructures

Metal carbides are the most intuitive product of the polymer-derived route that reaction bonds metals with the carbon char of the TPEB resin. However, this approach facilitates the formation of other metal ceramics and multiceramic compositions.

Slight modification to the process that yields nanocrystalline titanium carbide (X-ray diffraction data shown in Figure 4A) converts the resulting product into nanocrystalline titanium nitride (TiN). Introduction of nitrogen-rich functional groups into the TPEB structure and execution of the high-temperature synthesis step under flowing nitrogen (N_2) gas (as opposed to argon) yields this refractory ceramic (Figure 4B). Moreover, use of the original, carbon-rich TPEB polymer and N_2 gas delivers a core-shell structure; the resulting ceramic monoliths demonstrate a rigid carbide core and a homogeneous nitride shell that envelops it. NRL has implemented this approach to synthesize niobium carbide/nitride composites (Figure 4C). The interface between the two ceramics is strain-free and seamlessly transitions from one refractory material into another.

The viscous nature of the post-cured TPEB thermoset enables it to function as a binder in an approach that produces a different class of refractory metal ceramics. Preceramic mixtures that include a transition metal, such as zirconium or titanium, blended with boron metal and a small fraction of TPEB yield metal boride monoliths. Zirconium boride (ZrB/ZrB_2) (shown in Figure 4D) or titanium diboride (TiB_2) are examples of these products. In this pathway, the small mass fraction of TPEB embeds the homogeneous blend of boron and the transition metal parti-
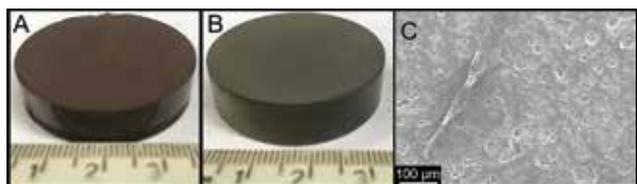

Figure 3. (A) Photograph of a 40 mm diameter preceramic greenbody of boron and TPEB. (B) Photograph of aforementioned greenbody following its conversion into a B_4C monolith at 1,450°C. (C) Electron microscopy analysis of the surface morphology of the B_4C ceramic surface.

cles in close physical contact (to ensure high yield), retains the preceramic near net shape, and forms the free carbon matrix in the formed ceramic (to control grain growth).

Thermal, electronic, and mechanical properties

In addition to low cost and a high degree of customization of synthesis products and resulting material chemistry, the polymer-derived refractory process delivers ceramic composites with different fundamental properties. Subsequently, different refractory carbides, nitrides, or borides can address different technology demands and offer a broad range of breakthrough performances in diverse applications.

To date, engineering studies have evaluated the oxidative stabilities of polymer-derived metal carbides in high-temperature environments, assessed their electronic and superconductive capabilities, and evaluated the influence of their composite structure on their mechanical strength.

One of the hallmark features of refractory carbides are their thermal stabilities and resistance to oxidation at high temperatures. Several polymer-derived ceramics, including titanium carbide (Figure 5A) and silicon carbide (Figure 5B), were heated up to 1,300°C under flowing air in a TGA experiment to assess their performance.

Both TiC and SiC remain stable up to approximately 400°C. Above that temperature, they undergo an exothermic process that peaks at 635°C. Between 400°C and 700°C, due to oxidation of the free carbon and differences in the ceramic structure, TiC loses 0.5% of its mass while SiC loses 8.5% weight percent. Although TiC increases its mass by 21 wt.% during its high-temperature oxidation, no further material erosion of SiC occurs between 700°C and 1,000°C. Further heating up to 1,300°C yields a very slow uptake of weight ($\sim 3.5\%$), which suggests oxidation of the SiC on the surface and the formation of a SiO_2 barrier coating. A similar titania coating forms on the surface of the TiC ceramic. Upon cooling and reheating back up to 1,400°C, neither material changes their

respective masses. This finding underscores the impenetrability of the resulting barrier coating on each material.

Unlike electronically insulating oxide ceramics, metal carbides have tunable electronic transport properties. Depending on the chemical composition and temperature, metal carbides may perform as semiconductors, exhibit metallic-like conductivity, and even demonstrate superconducting capabilities. Polymer-derived ceramics, which feature customized nanocrystalline grains and free carbon inclusions, equally show a range of these behaviors.

Figure 6A shows the temperature-dependent resistivity of silicon carbide. Acting like a semiconductor, its conductivity increases at higher temperatures. It demonstrates a measured bandgap of 0.1 eV, and various defects and lattice deformations in the material matrix all uniquely and significantly influence the electronic structure and densities of states.

Temperature-dependent magnetization measurements of polymer-derived tantalum carbide (Figure 6B) highlight the superconducting electronic properties of these ceramics at low temperatures. Diamagnetism onset highlights the transition of the polymer-derived ceramic monolith into the superconducting state that occurs at a temperature of $T_c \sim 10$ K. Resistivity measurements (Figure 6C) further confirm this value. The metal-to-carbon ratio in the precursor blend controls the final stoichiometry of the resulting tantalum carbide and customizes the ratio of TaC to Ta_2C. Since the latter does not exhibit superconducting properties, the polymer-derived ceramic is important for
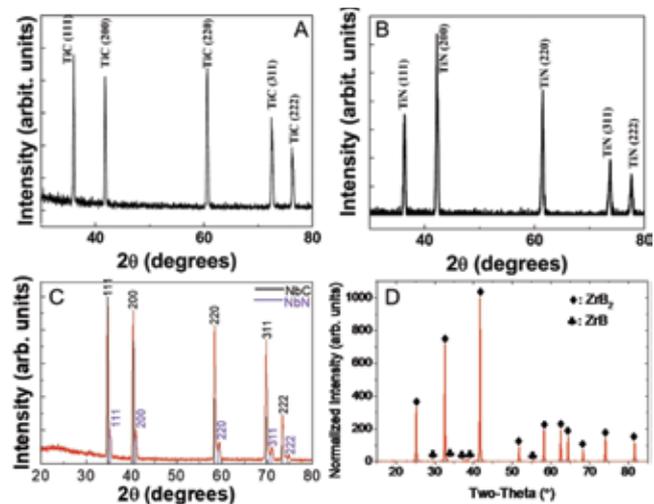

Figure 4. X-ray diffraction analysis of (A) crystal structure polymer-derived TiC ceramic, (B) polymer-derived titanium nitride produced using nearly identical approach, (C) core-shell NbC core/NbN shell, and (D) zirconium boride synthesized from blend of zirconium hydride, boron, and TPEB powder. Source of (A) and (B): T. M. Keller, et al.[9]
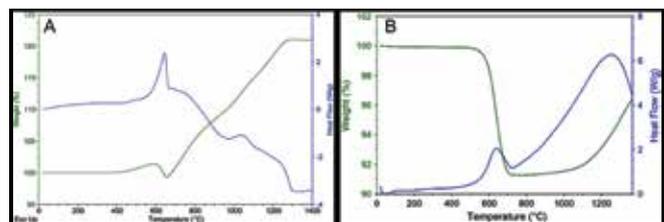
Figure 5. Oxidative study of (A) TiC ceramic and (B) SiC ceramic up to 1,400°C. Source of (A): T. M. Keller et al.[9]; (B): T.M. Keller et al.[10]

synthesis of materials that demonstrate desired electron transport behavior.

The aforementioned polymer charring process leaves behind microscale pores in resulting ceramic monoliths. These voids contribute to noticeable porosity fractions in the resulting composites, which demonstrate 65–75% densification. Arguably, the polymer-derived single-step approach yields particle-based reaction bonded composite rather than a sintered ceramic monolith. Hardness measurements of TaC highlight this difference. Microscale Vickers hardness values reveal hardness of approximately 143 H_v (1.40 GPa) for tantalum carbide, whereas fully densified TaC typically shows H_v of 1600 (15.7 GPa). Nonetheless, nanoindentation measurements (Figure 7), with values that range between 7 and 15 GPa, exhibit local hardness nearly equal to that of fully densified TaC ceramic. Future processing optimization strategies will aim to densify materials with polymer infiltration and pyrolysis, reaction bonding with metals, and other commercially scalable densification pathways that will reconcile microscale and
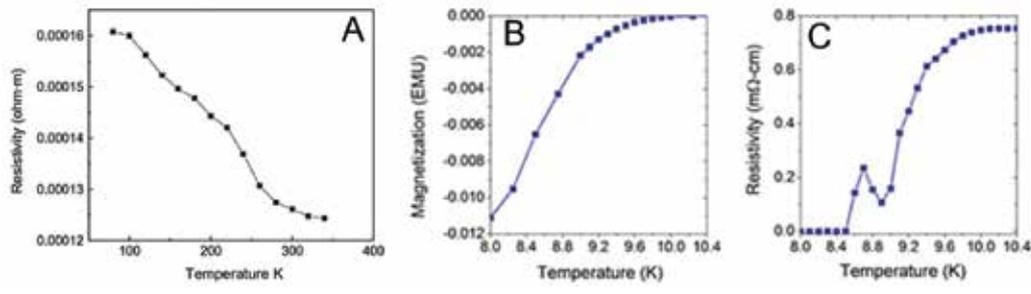
Figure 6. (A) Plot of electrical resistivity as a function of temperature of a solid SiC monolithic disk (2.54 cm in diameter, 0.5 cm thick). (B) Zero field-cooled magnetization versus temperature and (C) resistivity versus temperature of the TaC-nanoparticle comprising pellet. Source of (A): T.M. Keller et al.[10]; (B) and (C): M. Kolel-Veetil et al.[11]
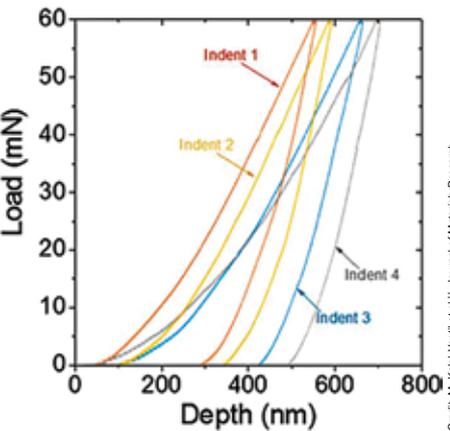
Credit: (A) T.M. Keller et al.[10], *J Mater Sci*; (B,C) M. Kolel-Veetil et al.[11], *Journal of Materials Research*

Figure 7. Nanoindentation curves of TaC-containing pellet as a function of depth of indentation. Source: M. Kolel-Veetil et al.[11]

Credit: M. Kolel-Veetil et al.[11], *Journal of Materials Research*

nanoscale hardness of resulting refractory ceramic composites.

Future materials development

The Advanced Materials section of the Chemistry division at NRL is steadily delivering reports of novel additions to refractory ceramics synthesized via the low cost, single-step polymer-derived pressureless synthesis route, and this trend will continue into the future. Subsequent efforts will provide more insights into the metastable material matrix of charred polymer interspersed with metal atoms, the nature of the chemical reaction bonding between metals, and the kinetics of metal carbide nucleation and their subsequent grain growth at low temperatures. Finally, process improvements and capabilities to additively manufacture these materials will improve their commercial scalability and viability in a broader range of applications.

Looking ahead, the research will focus on the unique ability of this synthesis process to incorporate heterogeneous phases into the ceramic preform and leverage various reinforcement approaches to improve the fundamental material properties of resulting refractory composites. In addition to aforementioned metal carbide/metal nitride heterostructures, which had featured seamless junctions between different ceramic phases, previous efforts had successfully embedded macroscale secondary materials into the preceramic matrices.

Figure 8A shows a silicon carbide disc with chopped carbon fibers, which are several microns thick and about 5 mm long, homogeneously dispersed throughout the monolith. Electron microscopy analysis (Figure 8B) confirms stable interfaces between nanocrystalline metal carbide and graphitic fibers. No microscale fractures or macroscale voids form at junctions of these materials, and the two phases adhere to each other to form properly reinforced ceramic composites.

Other forms of reinforcement may further tune the structure from the bottom up and incorporate multiple phases into the ceramic matrix at the nanoscale level. Multiphase metals, secondary ceramics, and carbon nanostructures can be incorporated into the preceramic blend and reaction bond with the bulk refractory ceramic constituents during synthesis.[17] Subsequently, the nanostructure of the bulk ceramic changes and adopts new fundamental chemical, electronic, and structural properties.

This approach provides a unique capability for resulting ceramic composites to overcome current capabilities of bulk ceramics. State-of-the-art refractory metal carbides, nitrides, and borides have finite performance limits that are bound by their respective intrinsic structures. Top-down reinforcement strategies that incorporate additions during high-temperature sintering cannot replicate the degree of homogeneity and seamless bonding that the bottom-up, polymer-derived approach can deliver.

These research efforts will allow the polymer-derived refractory ceramic route to deliver high-performance engineering materials that overcome existing limitations. Despite showcasing high melting points, most ultrahigh-temperature ceramics are prone to failure from thermal shock during conditions of extreme thermal gradients.[18] Under high dynamic mechanical stresses, many mechanically strong and extremely hard carbides develop soft amorphous shear bands, which are as weak as the graphite in a pencil, and retain only a mere fraction of their former strength.[19] Nanoscale reinforcements may, among other factors, facilitate efficient thermal conductivity, increase lattice ductility, and pin dislocations in order to preclude their propagation through ceramic grains.

Commercialization of technology

Since 2017, NRL had partnered with Nanoarmor, LLC, which is a California-based startup that aims to develop and commercialize NRL's polymer-derived ceramic technology. Since then, the two entities have completed several joint development efforts that advanced the technology readiness level of the ceramics, optimized and scaled up key elements of the production process, and identified essential supply line elements that control manufacturing cost and lead times. Nanoarmor has licensed NRL's ceramics technology in order to accomplish these goals.

A core mission of the United States Research Laboratory is the transition of research breakthroughs from basic laboratory studies into targeted applied developments. In turn, these transition efforts advance the readiness level of the technology, scale up manufacturing, and, by leveraging the capabilities of commercial entities, allow the United States Navy and the Department of Defense to integrate novel technology solutions

into its fleet and related operations. The Advanced Materials Section has a strong track record of transitioning its material breakthroughs, particularly in the areas of phthalonitrile composites that withstand high temperatures, into the hands of the warfighter. In addition to delivering important fundamental insights into polymer-derived reaction bonding of refractory carbides and formation of composites, the ongoing ceramics effort stands to benefit both the commercial and military enterprise.

Conclusions

Polymer-derived ceramics synthesis route that implements a high-char thermosetting resin offers a rapid and inexpensive capability to pressurelessly synthesize metal carbides, metal borides, and metal nitrides. The near net shape process, which requires temperatures below 1,500°C, reaction bonds precursors into refractory ceramics with high purities and nanocrystalline grains. The preceramic blend composition tunes the chemistry of the resulting ceramic matrix and allows bottom-up incorporation of reinforcements and structural modifiers. In turn, these control the nanoscale architecture of the resulting material and take advantage of multiphase refractory ceramic composites in order to tailor oxidative stability, mechanical strength, and electronic properties of resulting ceramic structures. The versatility and commercial viability of the process enables it to solve numerous engineering challenges and enable the use of ultrahigh temperature ceramics in a broad range of applications.

Acknowledgements

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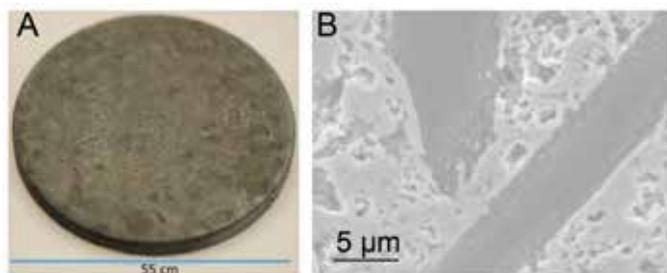
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Figure 8. (A) SiC ceramic composite reinforced with chopped carbon fibers. (B) SEM of fiber-ceramic interface.

Credit: Boris Dyatkin and Matthew Laskoski