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Identifying Opportunities in the Development of Ceramic Matrix Composite (CMC) Materials for Armor Applications

by Jeffrey J Swab and Emil J Sandoz-Rosado

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14. ABSTRACT

The purpose of this effort was to summarize the history of ceramic matrix composites (CMCs) for armor and capture the current state of the art in fiber-reinforced CMCs and ceramic fibers to identify potential opportunities future research in CMCs for armor applications.

15. SUBJECT TERMS

ceramic matrix composites, CMC, ballistic performance, fiber-reinforced ceramics, ceramic fibers

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Contents

List of Figures

List of Tables

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1. Introduction

1.1 Background on Ceramic Matrix Composites (CMCs) for Armor

The inherent high hardness of ceramic materials such as alumina (Al_2O_3), silicon carbide (SiC), and boron carbide (B_4C) make them integral components in a variety of protections systems for Army vehicles and personnel. Unfortunately their inherent sensitively to flaws (i.e., brittleness) limits this potential especially in regard to multi-hit ballistic performance. Attempts have been made over the past several decades, with varying degrees of success, to improve the performance of the ceramic by modifying the design of the protection system. This includes changes to the backing material, the adhesive used in laminated systems, the geometry of the ceramic as well as different methods to confine and retain the ceramic in a state of compression (Gooch 2002). At the same time research continues within the ceramics community to develop stronger and tougher ceramics through grain boundary engineering, microstructural tailoring, and the incorporation of second phase materials to create CMCs. The second phase in creating CMCs typically has been in the form of a platelet/particulate, whisker or long, continuous fiber. More recently carbon nanotubes (CNTs) have been examined. Fracture toughness improvements have been minimal with platelet/particulate or whisker additions and there are still many questions surrounding the impact of CNTs on toughness. However, the integration of long continuous fibers has significantly increased fracture toughness and resulted in new CMC applications in space vehicles, components for high-temperature gas turbine engines, and for brake systems (Krenkel 2005). The most common of these CMCs are comprised of carbon, SiC, Al_2O_3, or mullite (Al_2O_3-silicon dioxide [SiO_2]) fibers, and these same materials also serve as the primary matrix material.

As a result of these new applications CMCs are more readily available, manufacturing processes for both the fibers and the CMCs continue to mature, and new fiber and CMC materials are under development. Novel fiber technologies are also being developed, including boron nitride nanotubes (Niguès et al. 2014) that have been shown to exhibit high inter-layer friction, which is a desirable characteristic for a fiber.

2. Findings

2.1 CMCs for Armor

Over the past half century there have been several reports and papers published that provided a review of lightweight ceramic materials under consideration for armor applications (Stiglich 1968; Wong and Berman 1971; Viechnicki et al. 1989, 1991; Gooch 2002). These publications have focused on monolithic ceramics and how to maximize the benefits of these ceramics in armor systems with minimal discussion or information on CMCs.

The report by Stiglich (1968) mentions only one "composite" an "Al clad B_4C" and the only discussion about fibers is the placement of boron fibers into an epoxy sheet that could then be built up to make a ceramic backing material or possibly as a strike face material with fine thickness gradations. The status report by Wong and Berman (1971) contained the following single paragraph on CMCs:

> Fiber-reinforced ceramic armors have also been considered and efforts made to determine physical, mechanical, and ballistic properties. Investigations at the Franklin Institute and the Air Force Materials Laboratory have been concerned with continuous matrices of Al_2O_3 and MgO-Al_2O_3 reinforced with either sapphire whiskers and filaments or Nichrome-type wires. Meanwhile, industry and other agencies including Goodyear Aerospace Corporation [Kolarik RV. Development of a 14.5 mm, BS-41 composite armor system. Goodyear Aerospace Corp. (Contract DAAG 46-68-C-0115), 28 June 1968-18 Mar 1970 (confidential report)], and the Army Materials and Mechanics Research Center have evaluated various graphite fiber reinforced ceramics. To date, the experimental results have been mixed and inconclusive. Nevertheless, this class of materials still exhibits a high potential as a source for lightweight armor materials.

A chapter (Laible 1980) on ceramic composite armor makes no mention at all of any CMC materials, but 2 publications by Viechnicki et al. (1989, 1991) provide the most details and indicate that CMCs are more developmental than their monolithic counterparts. These 2 publications show that CMCs are of interest because of their potential to reduce collateral damage around the impact site, which can lead to improved multi-hit capabilities. (Multi-hit performance can be achieved with monolithic ceramics by designing the armor system using individual ceramic plates that are sufficiently isolated from each other to reduce damage propagation into adjacent plates while still providing the necessary overall protection level.) The following specific ceramic composite materials are briefly discussed: titanium carbide containing 15% Ni; Al_2O_3 containing SiC whiskers; borosilicate glass containing a high volume (60–70%) of either a graphite or SiC fiber; titanium diboride (TiB_2) containing either B_4C or SiC particulates; and a suite of Al_2O_3 materials made via the LANXIDE[*] process, which uses the controlled oxidation of liquid aluminum to form an Al_2O_3 matrix with residual aluminum plus the addition of ceramic particulates, whiskers or fibers. An example of this would be a composite of Al_2O_3/aluminum with aligned SiC fibers. The LANXIDE process was successful in fabricating pieces containing ceramic particulates, but fiber reinforcement was difficult because the capillary action needed for molten aluminum infiltration was impeded (Scott 2016).

A study by Lillo et.al (2003) examined SiC containing a “bone-shaped” SiC whisker in a SiC matrix. The composite had reduced properties and ballistic performance, as measured by depth of penetration, was poor. The mass efficiency was approximately 3.8 compared to 7 for a commercially available, armor-grade SiC. The low properties and performance were attributed to density, which was about 5% lower than the commercial SiC.

Neither of the most recent reviews (Gooch 2002; David et al. 2009) mention CMCs for armor applications. The former review focuses on ballistic requirements, design factors related to the incorporation of ceramics into the armor system, and some of the applications of ceramic armors based on the companies who have produced the ceramic. The latter review discusses materials ranging from ballistic fabrics to ceramic armor to laminated composites and integral armor for current and future body armor applications. This review also discusses nanomaterials and future design concepts, including the use of CNTs in woven fabrics and polymers. There is no mention of any CMC materials being considered for this application.

The US Department of Defense produced a composite materials handbook (MIL-HDBK-17, now called Composite Materials Handbook). Volume 5 of this handbook is dedicated to CMCs. The latest version of Volume 5 is dated 17 June 2002 and it contains a section titled “Impact Behavior”, but unfortunately this section, as well as many others, is empty and labeled as “Reserved for future use.”

An analysis of the fiber-reinforced SiC market by Garshin et al. (2012) includes a discussion of the potential use of fiber-reinforced CMCs in protection systems. They conclude that overall the volume of goods made of ceramic composite materials will steadily rise by 8%–10% each year, that the Liquid Silicon Infiltration(LSI) method has the greatest potential for producing cost-effective

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[*] Lanxide Corp. Newark, Delaware.

ceramic composites and that the main applications are where high temperatures, chemical attack, or abrasive loads are encountered. Garshin et al. (2012) also conclude that “the commercial potential of ceramic composite materials is most fully realized in the following applications: . . . protective equipment for individual and collective use.” Unfortunately, they do not provide any specifics or support for this portion of their conclusion.

2.2 Ballistic Test Information

A search of the technical literature uncovered very few publications that discuss fiber-reinforced CMCs for impact protection or provide impact performance data on this class of materials. Glass reinforced with SiC fibers was discussed by Rawlings (1994) where it was shown that the cracking features were modified by the SiC fiber reinforcement but that the cracking was not drastically different from what is observed on an impacted monolithic ceramic or glass. Danko et al. (1995) reported impact information on a silicon nitride/hexagonal boron nitride (Si_3N_4/BN) fibrous monolithic ceramic. The material was formed following a patented process (Coblenz 1988) that develops a fibrous texture in conventional polycrystalline ceramics, but this material is not technically a fiber-reinforced ceramic. Specimens were tested against 2 hardened steel 7.62-mm threats—the Soviet armor piercing machine gun round at 1731 ft/s and the AK-47 armor piercing round at 2337 ft/s. Perforation was complete against both threats, but there was limited delamination and no cracking in the 25.4-cm radius around the hole and the outline of the perforation was square instead of round. The author uses these latter observations as an indication of a material with multi-hit capability. It is indicated in the Danko et al. paper that Los Alamos National Laboratory agreed to team with Advanced Ceramics Research, Inc. (the lead authors) to conduct further research on this material, but there is no published evidence of any additional research being conducted or that any other monolithic ceramics with a fibrous texture, have been examined for impact resistance.

A ceramic-coated flexible material for improved stab resistance was reported by von Niessen and Gadow (2002). This material was either an aramide fabric (Twaron CT 710, Twaron Products, Wupertal, Germany) or a mullite fiber fabric (Nextel 720 from 3M, Minneapolis, MN, consisting of 85% Al_2O_3 and 15% SiO_2) coated with a 100-µm layer of Al_2O_3 or titanium dioxide (TiO_2) using air plasma spray process. The coated Twaron fabric was 5 times more stab resistant than the uncoated Twaron fabric.

Silicon nitride reinforced with SiC fibers was examined to provide small-scale impact protection for space stations against strikes by meteoroids and orbital debris (Tamura and Mutou 2005). The material was tested in the velocity range of 2.2 to

3.6 km/s using 1-mm-diameter aluminum alloy spheres. As expected the fragments from the composite were much smaller than the fragments from a comparable monolithic Si_3N_4.

Corman and Luthra (2006) determined the damage tolerance of a variety of CMCs compared to monolithic Si_3N_4, by conducted low-velocity, 116 and 427 m/s, impact tests using 4-mm-diameter steel spheres. These tests were designed to simulate collisions from foreign objects in the turbine engine. The conclusion was the following: “None of the CMC samples tested, with impact energies ranging from the threshold of observable damage up to complete penetration, displayed catastrophic damage, and yet all tests on monolithic sintered Si_3N_4 showed catastrophic failure at both energies tested.”

Boccaccini et al. (2005) tested the impact behavior of a CMC consisting of a mullite matrix containing woven mullite fiber mats (Nextel 720). Tiles, without any backing, were impacted by glass spheres, nominally 10 mm in diameter and weighing 1.4 g, within a velocity range of 77.6–207.5 m/s. Results showed substantial localized damage that is typically observed in similar composites and the material retained some load-bearing capacity even after impact. The authors state that there is limited value of the material being used in ballistic armor applications without any backing material.

The most in-depth analysis of CMCs for armor was work conducted by Heidenreich and colleagues (2003, 2006, 2010). In this series of manuscripts they focused on the development of CMCs for protection against small-caliber threats. A liquid silicon infiltration method (highlighted by Garshin et al. 2012), that was developed to produce carbon-fiber reinforced SiC for spacecraft thermal protection and high-performance brake discs, was used to fabricate carbon-fiber reinforced SiC and biomorphic siliconized silicon carbide (SiSiC) materials. The biomorphic materials are based on low-cost pyrolyzed wooden templates. Their initial testing (2003), against a 7.62-steel core armor-piercing round, showed the biomorphic SiSiC had a single hit ballistic limit of 850 m/s for an areal density of 50 kg/m^2 while the carbon-fiber reinforced SiC exhibited better multi-hit performance since the amount of damage was significantly less in this material. Subsequent testing (2006) compared the biomorphic SiSiC to commercial Al_2O_3 tiles against the same threat. The results showed that the SiSiC had a similar ballistic limit velocity. However, the lower density of the SiSiC (~3 g/cm^3) indicated that it had a ballistic performance comparable to commonly used monolithic SiC materials. Their final publication (2010) in this area focused on changing the SiC of the SiSiC for improved mechanical properties. These materials had a ballistic limit velocity of 930–1056 m/s at areal densities between 36.7 and 38.3 kg/m^3 but they exhibited brittle behavior that limits them to single-hit protection. To improve the potential of multi-hit performance cut carbon fibers were incorporated into some compositions. This addition did not change the ballistic limit velocity, but there was greatly reduced fragmentation indicating potential improvement in the multi-hit capabilities.

2.3 Manufacturers of CMCs for Armor

Very little information on CMCs for ballistic applications is available in brochures or on the company websites. Table 1 from MIL-HDBK-17-5 provides a list of CMC manufacturers (circa 2001) and is presented here. An Internet search was conducted for each manufacturer to see if there was any indication that their materials are presently being evaluated or used for ballistic applications. None of the manufacturers listed have any information on their website indicated that they are developing or using CMC materials for impact/ballistic protection.

Table 1 CMC manufacturers

Albany International Techniweave	Hitco
Ceramic Composites, Inc.	Hyper-Therm
Composite Factory, Inc.	Northrop-Grumman
Composite Optics Inc. Ceramics (formerly a Dow Corning business unit)	Refractory Composites, Inc.
General Electric	Textron, Inc.
Goodrich-Aircraft wheels and brakes division	Ultramet
Hexcel	Synterials
Honeywell Advanced Composites (formerly DuPont Lanxide Composites)	

Examination of a late 1980s brochure from the French company SEP shows that SEP was promoting 2 fiber-reinforced SiC matrix CMCs for ballistic protection. The 2D C/SiC CMC was labeled as SEPCARBONIX and the 2D SiC/SiC CMC was labeled as CERASEP. Both of these materials were designed a standalone components for fragmentation protections or as a support layer in a system using a monolithic ceramic front face to improve multi-hit performance. An Internet search shows that SEP is still in existence, but there is no evidence on their site that they are still conducting research on CMCs for protection applications.

A 2005 brochure from the German company SGL Carbon Group is entirely focused on a “bullet-proof ceramics” labeled as TAVCOR. TAVCOR is a series of carbon-fiber reinforced products for use as armor plating of vehicles, aircraft and ships as well as personnel protection systems. The brochure touts the benefits of these CMCs as multi-hit capability, large plate dimensions, complex geometries, low weight and fewer modifications to vehicle chassis and as having “extraordinary ballistic properties in various applications” and “specially designed to resist ballistic projectiles”. The information in this brochure is not on the current SGL website but they are still developing a carbon fiber-reinforced SiC for ballistic protection. The site indicates that this material is an “innovative material solution for tailor-made high-performance ballistic protection” and the materials can be used in protection systems for military wheeled and track vehicles, helicopters, and ships.

Recently, Lancer Systems, LP, met with the US Army Research Laboratory (ARL) to discuss the possible evaluation of their family of CMCs, labeled CeraComp, for graded lightweight composite armor. There are 3 different CMCs that make up the CeraComp family. All 3 have a silicon oxygen carbon (SiOC) matrix and contain either continuous or chopped carbon fiber or a ceramic fiber as the reinforcement. These materials are currently used in aerospace, industrial, semiconductor, and automotive areas.

2.4 Patents

Table 2 is a compilation of the patents that incorporate fiber-reinforced ceramics in the protection system. To the authors knowledge none of these patents have resulted in a CMC that is being used in an armor system.

Table 2 Patents on fiber-reinforced ceramics for armor

Patent no.	Publication date	Applicant	Title
US5970843	October 26, 1999	Northtrop Grumman Corp	Fiber-reinforced CMC armor
US6135006	October 24, 2000	Northtrop Grumman Corp	Fiber-reinforced CMC armor
US7238414	July 3, 2007	SCL Carbon AG – Germany	Fiber-reinforced composite for protective armor, and method for producing the fiber-reinforced composition and protective armor
US20120055327	March 8, 2012	John Holowczak	Armor systems having CMC layers
US4615935	October 7, 1986	The Boeing Company	Glass fiber-reinforced ceramic perform and method of casting it
EP0376794A1	July 4, 1990	Societe Europenne De Propulstion – France	Protective material with a ceramic multilayer structure

3. Background on Commercial Fibers

Fibers are a critical component to most composite types due to their enhancement of the mechanical properties of the surrounding matrix. “High-performance” fibers typically have high specific i) stiffness (~200 GPa·cm^3/g), ii) strength (~2 GPa·cm^3/g), and iii) toughness (~100 J/g), all of which are critical to the weight-efficient augmentation of composite materials (Pilato and Michno 1994; Papkov et al. 2013). An independent report published in May 2016 predicts that the market for these particular types of fibers is expected to expand at a compound annual growth rate of 8.62% during 2015–2022, increasing by a total of $15.7 billion (Insights 2016). The growth in high-performance fibers is being driven by expanding demand for electric vehicles, aerospace, and defense, which all require lightweight structural composite materials.

Generally speaking, organic fibers attain high performance through the orientation of stiff and strong covalent chain networks along a single axis, whereas the mechanisms for increased toughness are more complicated, and depend on the granular or molecular structure of the respective fiber. Commercial high-performance fibers that are used in composites are generally ultrahigh-molecular-weight polyethylene (UHMWPE), aramid-based fibers such as Kevlar, PBO, glass, boron-based fibers, or carbon fibers. The fiber review detailed that carbon fibers and glass fibers dominate the structural composites markets due to their high stiffness and strength but low-impact resistance, while UHMWPE and Kevlar dominate armor and protection due to their toughness and resilience (Gillespie et al. 2005).

CMCs are used in applications with vastly different operating conditions than traditional polymer-based composites and thus require fibers with different salient properties than the aforementioned polymeric fibers. CMCs are frequently employed in high-temperature (1000 °C+) environments such as gas turbine blades and thus require fibers with good thermal stability, and low creep. The production of ceramics requires high temperatures, prohibiting the use of organic polymeric fibers that degrade below 500 °C and even prohibiting the use of traditional glass fibers that soften or melt below 700 °C (Schawaller et al. 2012). As such, ceramic fibers are frequently used in current CMC applications, despite their low-impact resistance. Ceramic fibers have stiffness and strength comparable to polymeric high-performance fibers, albeit with a higher sensitivity to flaws, and thus lower impact resistance and toughness. Current commercially available CMCs are not optimized to resist the shock of ballistic impact, since both the matrix and the reinforcing fibers have low-impact resistance. Because CMCs are being considered in this review for ballistic protection, major advancement in fiber technology in the past decade will be examined across both inorganic and pure carbon fibers.

4. Inorganic Fibers

4.1 Nonoxide Ceramic Fibers

Silicon carbide (SiC) fibers are one of the more common ceramic fibers used in CMCs. Ceramic fibers comprised of SiC are considered nonoxide, although there can be residual oxygen depending on the quality of the fiber, and generally they have superior tensile modulus and strength compared to oxide fibers (Schawaller et al. 2012). One drawback to nonoxide-based fibers is their susceptibility to oxidative degradation. There are 3 principal types of SiC fibers according to their chemical composition, oxygen content and silicon-to-carbon ratio (Ichikawa 2016). The sequential advancements in the 3 generations of fiber arise from the need to have higher temperature fibers capable of operation at or above 1300 °C. The first generation of fibers, Si-C-O (Nicalon) and Si-Ti-C-O (Tyranno Lox M) both contain over 10-wt% oxygen introduced during their respective curing. While their maximum operating temperature (1100 °C) is low for many traditional CMC applications, these fibers are suitable for consideration in CMCs for hard-armor applications. The second generation of fibers, are SiC (Hi-Nicalon) and Sr-Zr-C-O (Tyranno ZMI), achieving oxygen contents below 1 wt% through exotic processes such as electron beam irradiation curing in a helium environment, for improved thermal stability (1500 °C) but marginal operating temperatures due to creep from excess carbon (1150 °C). Third generation fibers (Hi-Nicalon Type S, Tyranno SA, and Sylramic) achieve stoichiometric ratios of silicon-to-carbon, and thus have reduced creep, by pyrolizing the precursor fibers in hydrogen gas, which removes excess carbon. Because the major advancements in these fiber types are high-temperature operation and creep reduction and the mechanical properties of newer generation ceramic fibers do not shift significantly, fibers with less processing may have adequate performance for CMC hard armors with much less cost associated with manufacturing (see relative properties and costs in Table 3). Furthermore, the role of oxygen and amorphous material regions associated with nonstoichiometric elemental ratios on ductility in these fibers has yet to be investigated. It is possible that fibers with increased oxygen or extra carbon could have better impact resistance than the purified fibers.

Table 3 **Properties and costs for first through third generation commercial nonoxide ceramic fibers. Table data reprinted with permission from Schawaller et al. 2012.**

Trademark	Manufacturer	Curing	Approximate max. production temp. (°C)	Composition (wt%)	SiC grain size (nm)	Average fiber diameter (mm)	Tensile strength (GPa)	Tensile modulus (GPa)	Cost (€ kg^{-1})
Nicalon NL 200/201	Nippon Carbon	Oxygen	1200	Si: 56.5 C: 31.2 O: 12.3	2	14	3.0	220	1000
Tyranno LoxM	Ube Industries	Oxygen	1200	Si: 55.4 C: 32.4 O: 10.2 Ti: 2.0	3–5	11	3.3	187	1200
Tyranno S	Ube Industries	Oxygen	1200	Si: 50.4 C: 29.7 O: 17.9 Ti: 2.0	3–5	8.5/11	3.3	170	1000
Hi-Nicalon	Nippon Carbon	Electron irradiation	1300	Si: 63.7 C: 35.8 O: 0.5	5–10	14	2.8	270	3250
Tyranno ZMI	Ube Industries	Oxygen	1300	Si: 56.1 C: 34.2 O: 8.7		11	3.4	200	1400
Hi-Nicalon S	Nippon Carbon	Electron irradiation	>1500	Si: 68.9 C: 30.9 O: 0.2	100	12	2.6	420	7000

Table 3 Properties and costs for first through third generation commercial nonoxide ceramic fibers. Table data reprinted with permission from Schawaller et al. 2012 (continued).

Trademark	Manufacturer	Curing	Approximate max. production temp. (°C)	Composition (wt%)	SiC grain size (nm)	Average fiber diameter (mm)	Tensile strength (GPa)	Tensile modulus (GPa)	Cost (€ kg^{-1})
Tyranno SA 1/3	Ube Industries	Oxygen	>1700	Si: 67.8 C: 31.3 O: 0.3 Al: 0.6	200	10/7.5	2.8	380	6500
Sylramic	COI Ceramics	Oxygen	>1700	SiC: 95.7 TiB_2: 3.0 B_4C: 1.0 O: 0.3	100	10	2.7	310	8500
Sylramic-iBN	COI Ceramics	Oxygen	>1700	SiC/BN	>100	10	3.0	400	10500

4.2 Oxide Ceramic Fibers

The most prevalent commercial ceramic fiber variety is Al_2O_3 or mullite, which is a phase that contains both Al_2O_3 and SiO_2. Oxide ceramic fibers are generally cheaper than nonoxide ceramic fibers, are resistant to oxidative degeneration, but have higher creep and lower thermal stability than nonoxide ceramic fibers (see relative properties and costs in Table 4) (Schawaller et al. 2012, Ichikawa 2016). Some oxide-based ceramic fibers have demonstrated ductility at higher temperature, which could be useful in integration into CMCs for hard-armor applications. Almeida et al. (2015) benchmarked a novel CeraFib75 oxide fiber with Nextel 720 by evaluating elastic and creep properties at temperatures ranging from 25 to 1400 °C. The primary difference in the mechanical performance of the 2 fibers was brought on by the differing Al_2O_3/SiO_2 composition. CeraFib75 is 75-wt% Al_2O_3 and 25-wt% SiO_2, while Nextel 720 is 85-wt% Al_2O_3 and 15-wt% SiO_2 with the former having a larger content of mullite phases, as quantified by X-ray diffraction. The values for elastic modulus and strength for CeraFib75 are 225 ± 25 GPa and 1.42 GPa, and for Nextel 720 the values are 221 ± 16 GPa and 1.65 GPa, as obtained by quasistatic single-fiber tensile test at room temperature. CeraFib75 exhibits very slight softening of elastic modulus as temperature increases, in contrast to Nextel 720, but shows a much higher retention of strength at higher temperatures. At room temperature, Nextel 720 has a higher strength than CeraFib75 likely because of the presence of large defects in the latter fiber, a broader distribution of performance, which can be attributed to the relatively new CeraFib processing line. The superior high-temperature performance of CeraFib75 compared to Nextel 720 as measured by tensile and creep experiments likely stems from the larger presence of mullite in the CeraFib 75 fiber, a phase which is more stable at these temperatures. The high-temperature ductility demonstrated by the CeraFib 75 at 1400 °C is interesting and may indicate a toughening mechanism that could potentially be exploited during impact.

Table 4 Properties and costs for commercial oxide ceramic fibers

Fiber	Composition (wt%)	Diameter (mm)	Density (g cm-3)	Tensile strength (GPa)	Tensile modulus (GPa)	Production technique/ structure	Approx. price (€ kg-1)
3M Nextel 720	Al_2O_3: 85 SiO_2: 15	10–12	3.4	2.1	260	sol/gel, 59 vol% a-Al_2O_3 þ 41 vol% mullite	790 (1500 den) 600 (3000 den)
3M Nextel 610	Al_2O_3: >99	10–12	3.9	3.1	380	sol/gel, a-Al_2O_3	790 (1500 den) 600 (3000 den) 440 (10000 den)
3M Nextel 550	Al_2O_3: 73 SiO_2: 27	10–12	3.03	2.0	193	sol/gel, g-Al_2O_3 þ SiO_2 amorph.	590 (2000 den)
3M Nextel 440	Al_2O_3: 70 SiO_2: 28 B_2O_3: 2	10–12	3.05	2.0	190	sol/gel, g-Al_2O_3 þ mullite þ SiO_2 amorph.	500 (2000 den)
3M Nextel 312	Al_2O_3: 62.5 SiO_2: 24.5 B_2O_3: 13	10–12	2.7	1.7	150	sol/gel, mullite þ amorph. or 100% amorph.	260 (1800 den)
Sumitomo Altex	Al_2O_3: 85 SiO_2: 15	10/15	3.3	1.8	210	polyaluminoxane, g-Al_2O_3	640–720
Nitivy Nitivy ALF	Al_2O_3: 72 SiO_2: 28	7	2.9	2.0	170	sol/gel, g-Al_2O_3	390 (twisted yarn, twists: 10–15)
Mitsui Almax-B	Al_2O_3: 60–80 SiO_2: 40–20	7–10	2.9	not available		unknown, d-Al_2O_3	not available

An oxide/oxide CMC consisting of an Al_2O_3 matrix reinforced with Nextel 720 fibers was characterized using tension, fatigue, and creep experimentation from room temperature up to 1150 °C (Di Salvo et al. 2015). Fracture studies demonstrated that fiber bundle decohesion from the matrix was a limiting factor in the overall mechanical behavior of the material. Fiber pullout occurred with fibers as long as 5 mm being cleanly pulled from the matrix during tensioning, indicating weak bonding between the fibers and the matrix. Computed tomography (CT) scans of the CMC specimens indicated that there was a relatively high volume of porosity existing between individual fibers and fiber tows, leading to stress concentrations and ultimately failure. The role of fiber/matrix interface for ceramics requires a great deal of further study, since fiber delamination and porosity are likely to be a major CMC failure mechanisms during high-rate impact.

5. Electrospun Ceramic Nanofibers

Commercial ceramic fibers (both oxide and nonoxide) are manufactured through 4 production processes defined by how the ceramics are dispersed in preceramic polymer dopes: i) spinning from molecularly dispersed precursors (solution process), ii) spinning from colloidally dispersed precursors (sol/gel process), iii) spinning from dopes containing coarse ceramic particles (slurry process), and iv) spinning from inorganic polymers (precursor polymer process) (Schawaller et al. 2012). While not employed for the commercial production of ceramic fibers, electrospinning has emerged as a method for synthesizing ceramic fibers with diameters down to a few 100 nm (Chronakis 2005). Between 2002, when electrospinning of ceramic fibers was first reported, and a report by Sigmund and colleagues in 2006, more than 20 types of ceramics have been electrospun into nanofibers (Sigmund et al. 2006). Since then, titania (Park et al. 2010), BN (Salles et al. 2010), and SiC nanofibers (Lee et al. 2010) have been synthesized, with the latter showing mechanical properties on par with commercially available SiC fibers albeit with much easier manufacturability owing to the thinner diameter and greater compliance (Chen et al. 2015). Electrospun nanofibers are advantageous to standard fibers because they provide high-surface area per unit mass (better bonding with matrix), can have controlled morphology and surface structure. Electrospun polymeric nanofibers also demonstrate a simultaneous increase in strength and toughness as the diameter of the fibers shrink toward 100 nm, a feat that is impossible for standard fibers above 1 µm in diameter to achieve (for a comparison between standard and electrospun fibers, see Fig. 1) (Papkov et al. 2013). While the mechanisms for toughening polymeric nanofibers through electrospinning differ greatly from ceramic nanofibers, it is possible that mechanisms such as grain alignment and consolidation can be encouraged in ceramic electrospun nanofibers, leading to increased mechanical performance.

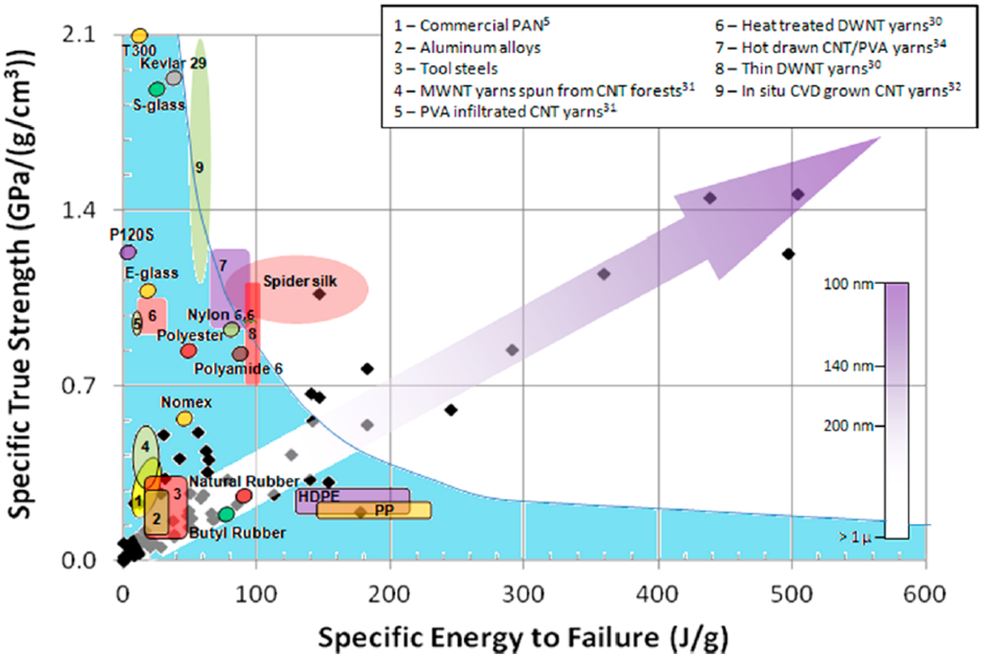

Fig. 1 Specific strength vs. toughness of various fibers, demonstrating that incredibly thin electrospun PAN fibers can disruptively, simultaneously increase strength and toughness (Papkov et al. 2013) (Reprinted with permission from Yuris Dzenis)

6. Carbon Fibers

Commercial carbon fibers have some of the highest specific strength and stiffness of any high-performance fibers and are integral to lightweight structural composites. In particular, the implementation of carbon fiber composites into lightweight automobiles is a burgeoning field, with major automotive companies such as BMW having invested significantly into carbon fiber production for composites in their electric vehicles in the past 5 years (Insights 2016). While the stiffness and strength of carbon fibers is quite high, their impact resistance is low because of the brittleness of carbon-carbon bonding coupled with low-intra-fibular interaction. As a result of low-impact resistance, carbon fibers are not suitable for use in soft-armor applications. Production of carbon fiber is generally from pitch stock (Gillespie et al. 2005) or from PAN fiber (Yusof and Ismail 2012), with the latter production technique accounting for 90% of global carbon fiber production. Creating carbon fiber from PAN precursor requires 4 pyrolysis steps: 1) oxidative stabilization (~200 °C), 2) carbonization (burning off other elements), 3) graphitization (~3000 °C), and 4) activation (~900 °C). The resulting fiber is thermally stable enough to be considered for CMC armor applications, since it can withstand ceramic processing temperatures. Carbon fibers have not been considered for traditional CMC applications because of high-operational temperature requirements (1300 °C+).

Recent advancements in commercial carbon fiber manufacturing include coating the spun PAN precursor fiber (with coatings like silicone oil, fatty acids, etc.) to improve inter-fiber cohesion during the carbonization process yielding a stiffness increase from 219 to 224 GPa, and a strength increase from 2.45 to 3.25 GPa (Yusof and Ismail 2012). Furthermore, catalytic modification of PAN precursor with oxidizing agents, Lewis acid compounds, bases, metal compounds, and acids have resulted in more stable fibers (Yusof and Ismail 2012). More recently, stabilization of the carbon fibers has found to be aided by the tailored surface functionalization of embedded CNTs, yielding higher stiffness and strength, but lower toughness (Park et al. 2015). The scientific research community has focused on extracting superior carbon fiber performance through other synthesis routes and modifications. One group investigated the production of carbon fiber using very high-molecular weight PAN, attaining a final carbon fiber tensile stiffness of 345 GPa and a tensile strength of 4.3 GPa owing to a more homogeneous filament with no core/shell structure because of its comparatively small diameter of 2.5 µm (Morris et al. 2016). Several studies examined the impact of nanoparticulate additives to aid in intra-fibrilar cohesion, with modest increases in performance with the addition of CNTs (Zhang et al. 2009) and graphene oxide (Wang et al. 2016) into carbon fiber precursors. Finally, entire fibers have been synthesized from nanostructures, such as graphene (Xin et al. 2015), which exhibits high-thermal conductivity but relatively low-mechanical properties when compared to commercial high-performance fibers, or CNTs, which produce higher toughness fibers (Xin et al. 2015).

Incidentally, the last publication that covers the mechanical performance of CNT fiber, (Koziol et al. 2007), is coauthored by Philip Cunniff, who summarized the inferior ballistic performance of carbon fibers when compared to polymeric high-performance fibers (Cunniff 1999). While the quasistatic mechanical performance of carbon fibers is excellent, their impact resistance is low due to their brittle fracture behavior, mitigating their performance as a ballistic barrier. As such, carbon fibers should only be considered for CMC armor applications in the event that a technology presents itself that significantly toughens the fibers, especially during impact.

7. Conclusions

The purpose of this effort was to summarize the history of CMCs for armor and capture the current state of the art in fiber-reinforced CMCs and ceramic fibers to identify potential opportunities future research in CMCs for armor applications. The following are the key findings:

- CMCs have been examined periodically over the past 5 decades for armor applications but efforts are few in number and the details are sparse.
- The limited ballistic information available indicates that use of fiber-reinforced CMCs in armor systems can provide some improvement in multihit capabilities, but the single-shot performance is substantially inferior to monolithic ceramics. Platelet/particulate or whisker-reinforced CMCs show minimal, if any, improvement in ballistic performance.
- The primary driver of the fiber-reinforced CMCs market is the aerospace and automotive industries where lightweight, high-temperature structural components are required.
- Ceramic fibers have properties on par with high-performance polymeric fibers.
- No information is available on the impact behavior of ceramic fibers (anecdotally poor). Will this diminish the protective capability of CMCs the same way carbon fibers cannot be used for soft armor?
- No information is available on the required geometries or mechanical properties of a fiber in a CMC for hard-armor applications. Are stiffer or less stiff fibers favorable? Is elongation to failure of 1%–2% adequate? Are CMCs with more fibers (smaller fiber diameter) favorable or are fewer interfaces and thus reduced porosity favorable?
- Based on these findings there is little evidence at this time that any commercially available CMCs perform better than monolithic ceramics during ballistic impact. However, there are no mechanistic descriptions, presently available that explain why monolithic ceramics would be inherently better than CMCs for ballistic protection.
- The potential for improved multi-hit capability of hard armor containing CMCs appears significant and warrants investigation, but limitations in the current processing of CMCs and the impact theory to predict the performance of ceramics during a ballistic event prohibits a comprehensive ballistic evaluation.

- The current manufacturing variability of CMCs commonly leads to the presence of porosity in the final component. This severely limits their ballistic potential but not their use in high-temperature, structural applications. As a result, a project focused on developing CMCs specifically for hard armor is required. Such a project is outside the scope of an internally funded ARL project, because it would require extensive funding and novel CMC manufacturing capabilities. However, a significant external effort, or a meaningful partnership between ARL and a CMC industry leader could lead to advances in CMCs and the creation of hard armors with multi-hit capabilities.

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List of Symbols, Abbreviations, and Acronyms

Al_2O_3	alumina
ARL	US Army Research Laboratory
B_4C	boron carbide
BN	boron nitride
CMC	ceramic matrix composite
CNT	carbon nanotube
CT	computed tomography
LSI	Liquid Silicon Infiltration (method)
Si_3N_4	silicon nitride
SiC	silicon carbide
SiO_2	silicon dioxide
SiOC	silicon oxygen carbon
SiSiC	siliconized silicon carbide
TiB_2	titanium diboride
TiO_2	titanium dioxide
UHMWPE	ultrahigh-molecular-weight polyethylene

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