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Author
Vecchio, K S

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Synthetic Multifunctional Metallic-Intermetallic Laminate Composites

Kenneth S. Vecchio

The field of material microstructure design targeted for a specific set of structural and functional properties is now a recognized field of focus in materials science and engineering. This paper describes a new class of structural materials called metallic-intermetallic laminate (MIL) composites, which can have their micro-, meso- and macro-structure designed to achieve a wide array of material properties and tailored to achieve specific functionalities. The superior specific properties of this class of composites makes them extremely attractive for high-performance aerospace applications, and the fabrication method for creating MIL composites allows new embedded technologies to be incorporated into the materials, enhancing their functionality and utility.

INTRODUCTION

The field of material microstructural design to achieve a set of targeted mechanical and functional properties has become a mainstay of new material development strategies. Structural materials, which by their very nature are intended to carry mechanical loads in service, can be designed to provide additional performance-enhancing functions through tailoring of meso-, micro-, or nano-structures. Structural materials with these performance-enhancing capabilities have been termed "synthetic multifunctional materials."[1] Structural composites, by their multiphase nature, offer many opportunities for the design of performance-enhancing multifunctional materials. Recently, a new class of structural materials has been developed at the University of California, San Diego, termed metallic-intermetallic laminate (MIL) composites.[2] The goal of this materials development effort was to extrapolate upon the positive engineering properties exhibited by hierarchical multiphase complex natural composites, such as mollusk shells,[3,4] to design and synthesize multifunctional composites to optimize specific structural properties while facilitating low-cost, designable, and functional microstructures.

Biological systems often exhibit a wide array of multifunctional materials and offer great biomimetic motivation to develop synthetic multifunctional materials. Mollusk shells are known to possess hierarchical structures highly optimized for toughness. The two mollusks that have been studied most extensively are Haliotis rufescens (abalone) and Pinctata (conch) shells. Considering the weak constituents the shells are made from—namely calcium carbonate ($CaCO_3$) and a series of organic binders, the mechanical properties of these shells are outstanding. Their tensile strength varies between 100 MPa and 300 MPa and fracture toughness between 3 MPa and 7 MPa-m$^{1/2}$. $CaCO_3$ has corresponding strength and toughness values of 30 MPa and <1 MPa-m$^{1/2}$, respectively.[5–9] These mollusks owe their extraordinary mechanical properties to a hierarchically organized structure starting with single crystals of $CaCO_3$, with dimensions of 4–5 nm (nanostructure) and proceeding with bricks with dimensions of 0.5–10 μm (microstructure, Figure 1a), and finishing with layers of ~0.2–0.5 mm (mesostructure, Figure 1b).

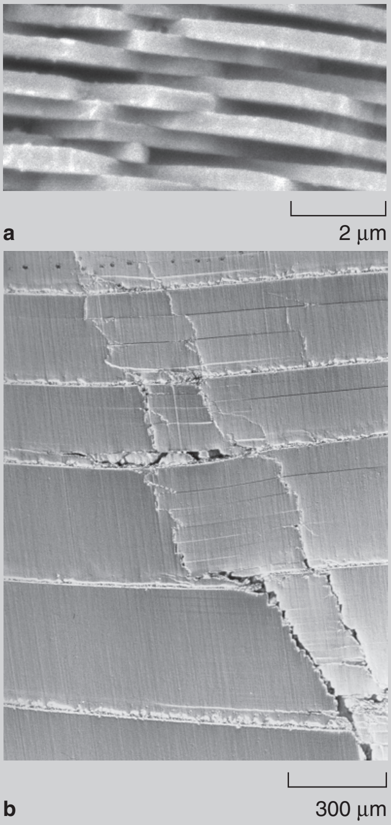


Figure 1. (a) An SEM micrograph of the fracture surface of an abalone shell showing the individual hexagonal aragonite tiles comprising the microstructure. (b) An optical micrograph of the mesoscale laminate structure of the abalone shell in a bend fracture sample showing the crack deflection achieved in this multi-layered material.

Building on the laminate microstructure design found in shells, Ti-Al_3Ti MIL composites have been produced to mimic these structures from elemental titanium and aluminum foils by a novel one-step process utilizing a controlled reaction at elevated temperature and pressure.[2] The novelty of this fabrication process lies in the fact that it is performed in open air and produces a fully dense laminate composite. Figure 2 shows an illustration of the processing setup for fabrication of the MIL composites using a simple open-air heated platen press. The thickness of the original titanium and aluminum foils is chosen to ensure that the entire aluminum layer is consumed upon reaction with the adjacent titanium layers. Such a layering scheme results in a composite with alternate layers of Al_3Ti (to mimic the hard $CaCO_3$ layers in shells) and residual titanium (to mimic the tough protein layers in shells). The thickness of the final layers is dependent upon the thickness of the original aluminum and titanium foils. This process is highly flexible since metal/alloy foils other than titanium can be used individually, or in combination, within the same composite, to produce their respective metal/metal-aluminide combinations. For example, MIL composites using iron-based, nickel-based, and cobalt-based alloys as the starting metal layer (instead of titanium) have been successfully fabricated using the described technique. The MIL composites produced by this method are not hierarchical structures in the manner that natural shells are, but are rather two-dimensional laminate structures. In these structures, the scale of the layering can be controlled, tailored, subdivided, and compositionally altered to achieve desired properties and functions.

The composition, physical, and mechanical properties of the MIL composites can be varied and tailored within the thickness of the composite by simply varying the individual foil compositions, thicknesses, and layering sequence. The fabrication of MIL composites using this approach has several key advantages that make it ideally suited for the production of commercially scalable structural materials as well as microstructures designed for specific functionalities. First, since the initial materials utilized are in the form of commercially available metallic foils, the initial material cost is reasonably low compared to many of the exotic material processing routes that are commonly pursued in small-scale research environments. This also means that a wide array of compositions can be ready produced, although this paper will focus on the Ti-Al system because of its high specific properties.

Second, the use of initially ductile metallic foils enables the layers to be formed into complex shapes. This opens the door for non-planar structures, such as rods, tubes, shafts, and cones, as well as simple machining of individual foils for complex, three-dimensional (3-D) structures and near-net shape forming of parts. The use of initial metallic foils also allows the individual foils to be machined to contain cavities and pathways facilitating the incorporation

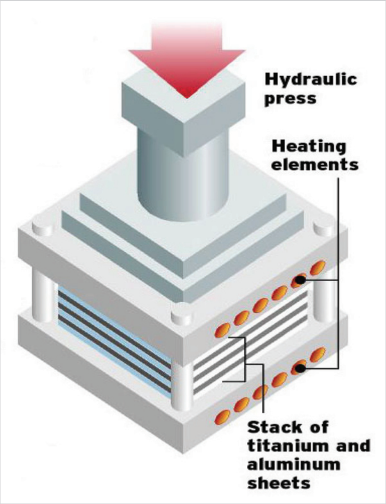


Figure 2. An illustration of metallic-intermetallic laminate composite heated using platen press apparatus for fabrication of planar laminates. Complex platen designs can be used to fabricate 3-D, near-net-shape MIL composites in the same one-step, open-air operation.

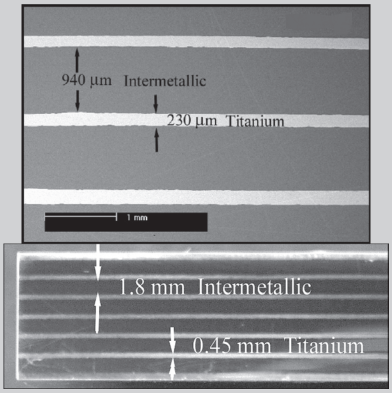


Figure 3. The microstructures typical of Ti-Al_3Ti MIL composites.

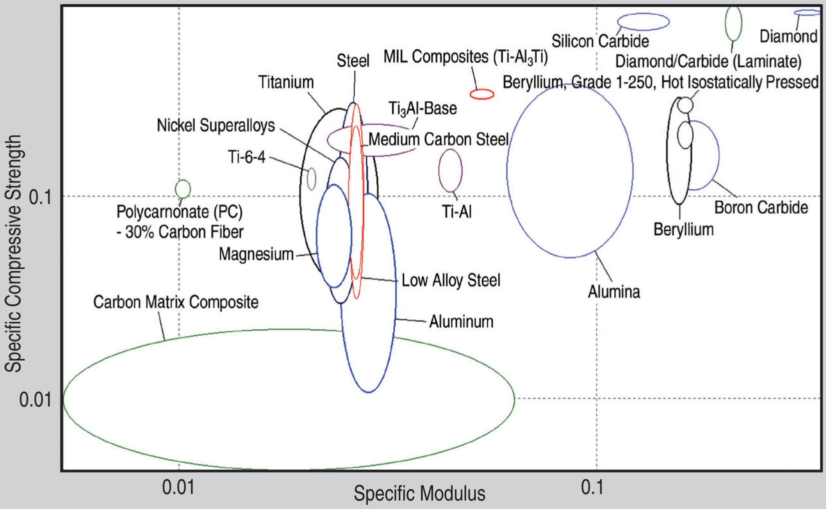


Figure 4. A materials property map comparing specific compressive strength versus specific material stiffness.

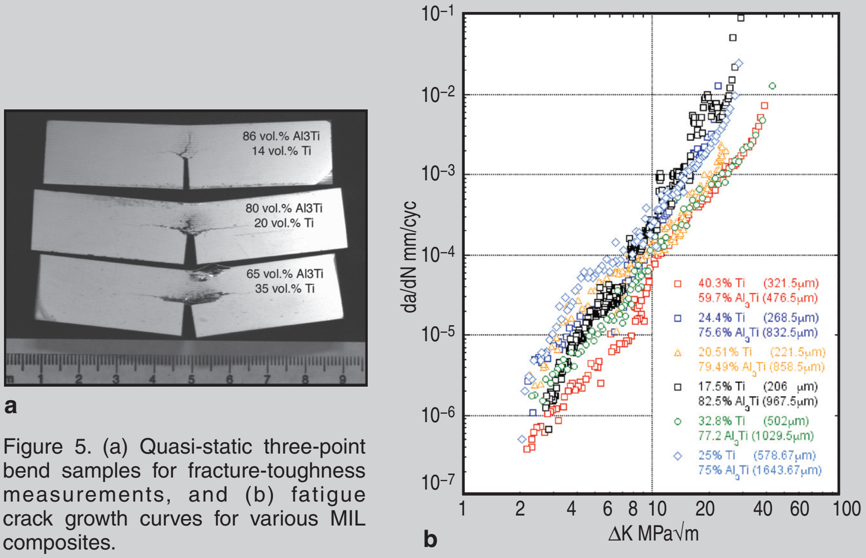


Figure 5. (a) Quasi-static three-point bend samples for fracture-toughness measurements, and (b) fatigue crack growth curves for various MIL composites.

of embedded functionalities, such as passive damping[5] or sensors, prior to processing.

Third, the processing conditions, in terms of temperature, pressure, and atmosphere are very modest. Processing temperatures, in the case of aluminum-foil-containing samples, are below 700°C and the processing pressures are below 4 MPa.[2] Perhaps the most remarkable feature of the processing of these MIL composites is that the processing is carried out in open air, and no special inert gas or vacuum chamber facilities are necessary. The combination of these processing features makes the processing method itself low cost, allows for complex shape fabrication, and is amenable to computer control.

Finally, the microstructure of the MIL composites is determined by the foil thickness and composition and the processing condition. Since the material make-up is based on the selection of the metal foils, it is possible to completely tailor the microstructure from one surface to the other. In addition, the physical and mechanical properties of the MIL composites can be tailored by selection of the foil composition and thickness, making the MIL composite material system ideally suited for engineering the microstructure to achieve specific performance goals.

Of the various possible aluminides in the Ti-Al system, the formation of the intermetallic Al_3Ti is thermodynamically and kinetically favored over other aluminides when reacting aluminum directly with titanium. This preferential formation of Al_3Ti is fortuitous as its Young's modulus (216 GPa) and oxidation resistance are higher, and the density (3.3 g/cm^3) lower than that of the other titanium aluminides such as Ti_3Al and TiAl.[10] The high compressive strength and stiffness of Al_3Ti (and intermetallics, in general) result from their high bond strength. However, intermetallics are brittle at low temperatures due to the limited mobility of dislocations (and paired superdislocations with anti-phase boundaries), insufficient number of slip or twinning systems, and/or very low surface energy resulting in little or no plastic deformation at crack tips. For example, Al_3Ti is extremely brittle at room temperature and has a very low

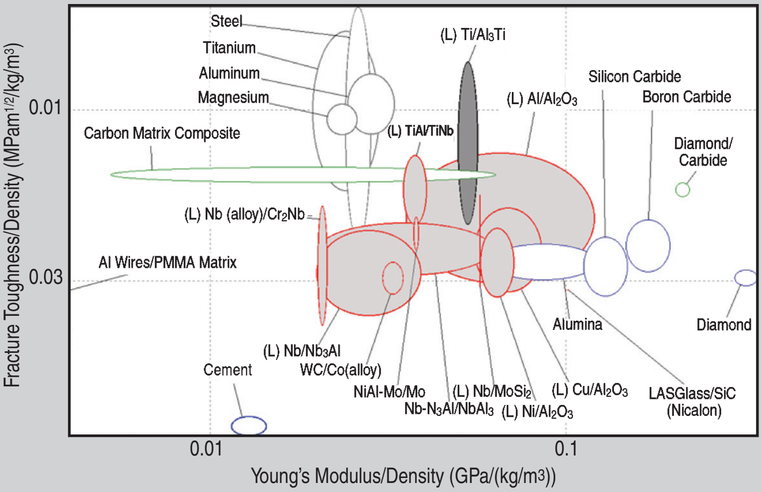


Figure 6. A specific-fracture-toughness versus specific-modulus property map for an array of structural materials. Plot includes MIL (Ti-Al_3Ti) composites (dark gray colored) and other laminate systems (identified by (L) and outlined in red), metals, alloys, and composites.

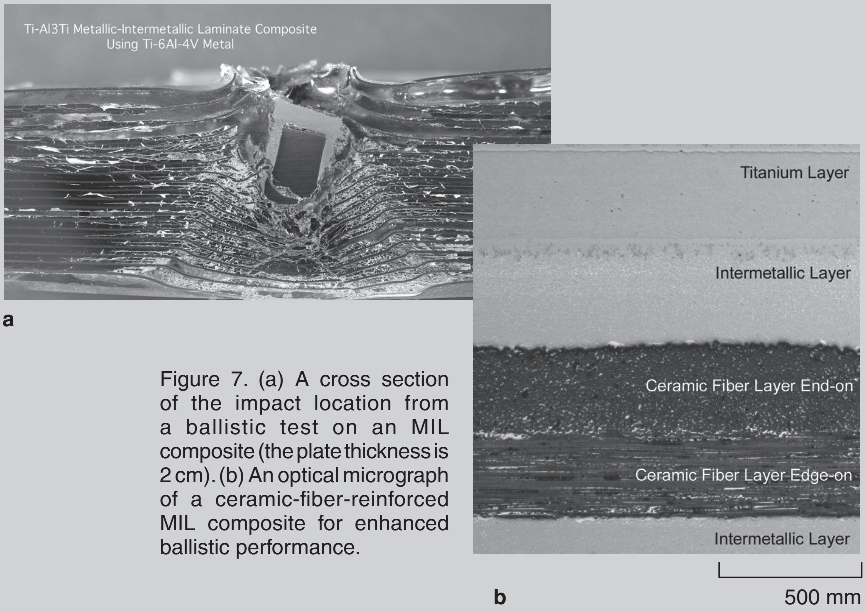


Figure 7. (a) A cross section of the impact location from a ballistic test on an MIL composite (the plate thickness is 2 cm). (b) An optical micrograph of a ceramic-fiber-reinforced MIL composite for enhanced ballistic performance.

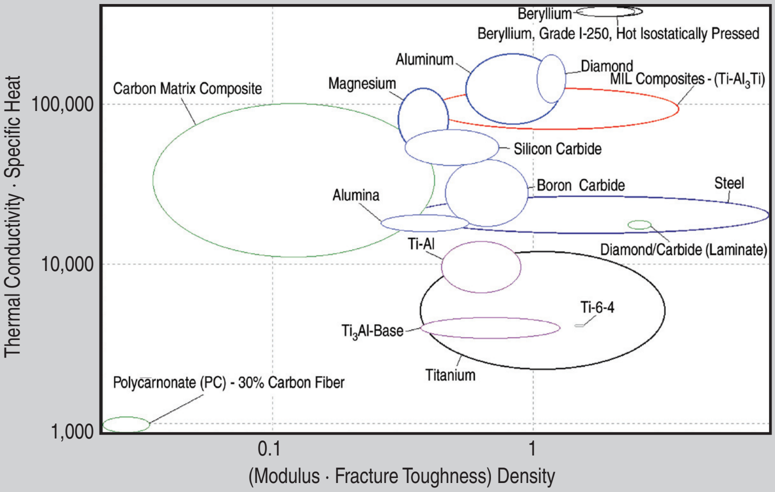


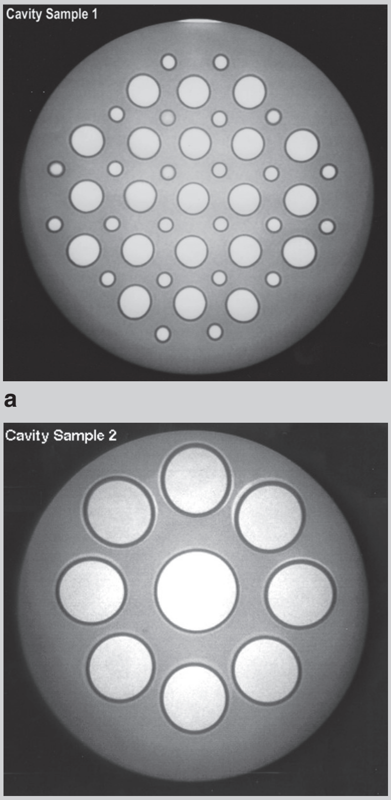
Figure 8. A property map of specific heat capacity and thermal conductivity versus specific modulus and fracture toughness for an array of structural materials. Plot includes MIL (Ti-Al_3Ti) composites (red ellipse), which overlap diamond and aluminum at the lower end of the structural performance range for the MIL composites and lie below beryllium alloys in terms of the thermal properties for a similar specific stiffness/fracture toughness value.

fracture toughness of $\sim 2\ \mathrm{MPa}\sqrt{\mathrm{m}}$.[11]

The unique properties of MIL composites arise from the combination of the high hardness and stiffness of the intermetallic-aluminide phase alternatively layered with the high strength, toughness, and ductility of metal alloys. Figure 3 shows two examples of the microstructure of Ti-Al_3Ti MIL composites with significantly different layer thickness.

STRUCTURAL PERFORMANCE ATTRIBUTES

In the case of Ti-Al_3Ti MIL composites, the specific stiffness (modulus/density) is nearly twice that of steel, the specific toughness and specific strength are similar or better than nearly all metallic alloys, and specific hardness is on par with many ceramic materials. An interesting comparison of material properties for the MIL composites can be obtained using a material property map. Figure 4 shows a plot having as the x-axis the specific modulus of a material on a log scale and the y-axis the specific compressive strength on a log scale. In this plot, numerous material locations are shown, and in terms of optimizing these properties (combined compressive strength and stiffness), the upper right-hand corner represents the goal. The location of the MIL composites (red ellipse) is shown to the right (higher specific modulus) of the typical structural metals such as steels, titanium alloys, nickel superalloys, aluminum alloys, and titanium-based intermetallics. The only metallic materials of higher specific stiffness are beryllium alloys. Several ceramic materials are shown, which have higher specific stiffness than the MIL composites, including SiC, B_4C, Al_2O_3, and diamonds. Clearly, the MIL composites possess tremendous potential for structural applications, particularly for demanding, high-specific-stiffness applications.



a

b

Figure 9. X-ray fluoroscope images of the through-thickness of cavities created within the intermetallic layer of a Ti-Al_3Ti MIL composite. The grey circular regions are approximately 13 cm in diameter.

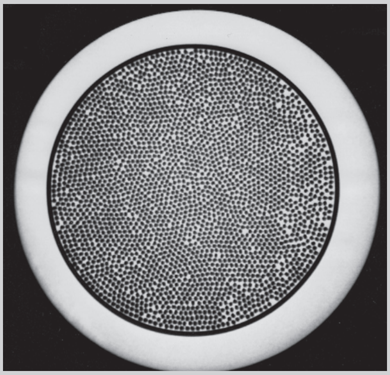
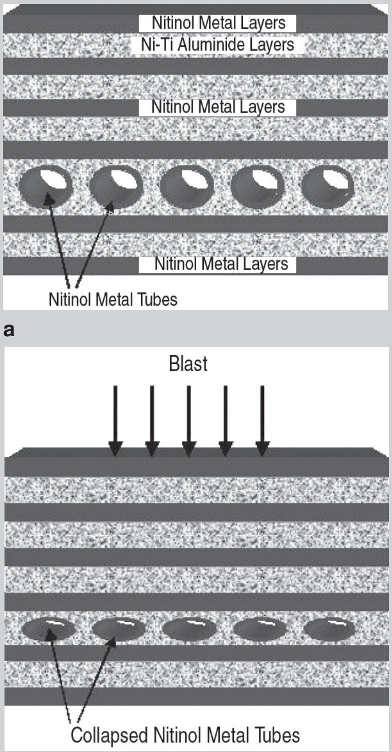


Figure 10. An x-ray fluoroscope image of the through-thickness of a large (10 cm diameter) cavity filled with steel beads created within the intermetallic layer of a Ti-Al_3Ti MIL composite.

The good fracture toughness of the MIL composites is derived from the combination of the highly anisotropic layered structure of the material and the need for crack re-initiation at each successive metal layer. Figure 5a shows an example of the fracture behavior of three different volume fraction Ti-Al_3Ti MIL composites. In samples with as little as 20% remnant titanium, the crack cannot propagate through the samples without being diverted and bifurcated at each titanium metal layer. Figure 5b shows a plot of the fatigue crack growth curves for Ti-Al_3Ti MIL composites having different volume fractions of intermetallic phase. The crack growth curves for these MIL composites closely overlap similar data for monolithic titanium alloys such as Ti-6-4. Since the MIL composites have higher stiffness and lower density than the monolithic titanium alloys with similar crack growth resistance, enhanced performance can be obtained for demanding aerospace applications.

Figure 6 plots the specific fracture toughness vs. the specific modulus of various engineering materials, including the MIL composites (shown by the dark grey ellipse). Several other laminates are outlined in red in Figure 6. It can be seen



a

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Figure 11. Schematic diagrams of MIL composites containing embedded tubes within the intermetallic layers. (a) Initial microstructure, and (b) microstructure with collapsed tubes following blast.

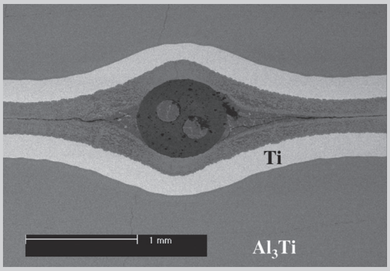

Figure 12. A micrograph of a Ti-Al_3Ti MIL composite containing a ceramic tube filled with two metal wires.

that the Ti/Al$_3$Ti laminate composites have higher specific toughness than other laminate systems and the Ti/Al$_3$Ti specific modulus is surpassed only by the metal/Al$_2$O$_3$ system. Relative to γ-TiAl/TiNb, MIL composites have higher specific fracture toughness and a higher specific modulus for the same volume fraction of the ductile phase. Further, relative to the various metal/Al$_2$O$_3$ systems, the MIL composites have higher specific fracture toughness for the same volume fraction of the ductile phase. Thus, owing to the ease of fabrication of Ti/Al$_3$Ti laminates, low fabrication costs, and their attractive mechanical properties, MIL (Ti/Al$_3$Ti) composites are excellent candidates for engineering applications requiring a combination of low density, high strength, high toughness, and high stiffness.

STRUCTURAL PLUS BALLISTIC ATTRIBUTES

The specific physical and mechanical properties of the MIL composites make them an attractive material for structural applications. However, the ballistic performance of these materials is also quite impressive, when compared on the basis of areal density for a given threat, against other structural materials. Figure 7a shows a photograph of a cross section through the impact location from a ballistic test on an MIL composite. The sample is a 20% Ti-6-4 and 80% Al$_3$Ti laminate with an initial thickness of approximately 2 cm. This composition produces a sample with a density of 3.5 g/cm^3; therefore, the specific target in this figure would have an areal density of 7 g/cm^2. The penetrator used was a tungsten heavy alloy rod (93W-7FeCo) with a mass of approximately 10 g and initial diameter of 6.15 mm. The penetrator was fired at the target at a velocity of 900 m/s in a normal incidence depth-of-penetration (DOP) orientation. The DOP within the MIL target is less than 1 cm. The demonstrated mechanical properties of the MIL composites make them suitable for structural applications, while the ballistic performance makes them attractive for armor applications, creating a multifunctional (structural + ballistic) material. The ballistic performance of these MIL composites can be further enhanced by the incorporation of harder constituent phases, such as ceramics. Metallic-intermetallic laminate composites have been successfully fabricated using aluminum-based ceramic-particulate-reinforced metal-matrix composites. Also successful has been the direct incorporation of ceramic fibers within the intermetallic layer by layering the ceramic fiber tapes between aluminum sheets prior to reaction sintering of the MIL composites. Figure 7b shows an optical micrograph of a Ti-Al$_3$Ti-Al$_2$O$_3$ fiber-Al$_3$Ti-Ti layered MIL composite. The Al$_2$O$_3$ ceramic fibers are stacked in two layers in a 0–90 orientation within the center of each thicker Al$_3$Ti layer.

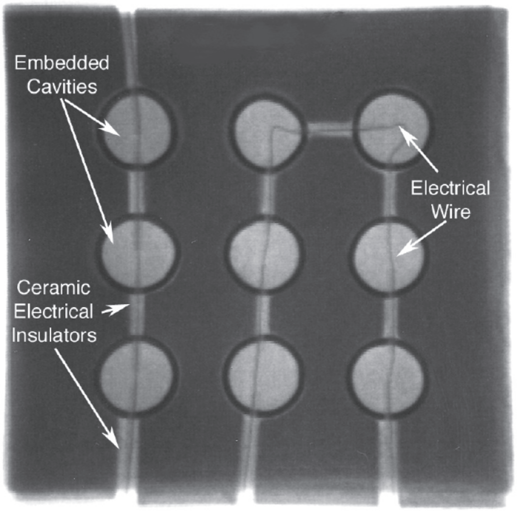

Figure 14. An x-ray fluoroscope image of the through-thickness of cavities, interconnected by ceramic insulators containing wires created within the intermetallic layer of a Ti-Al$_3$Ti MIL composite.

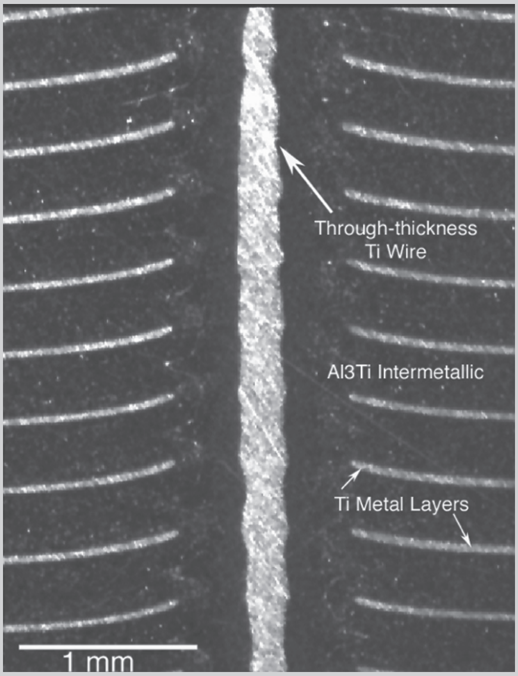

Figure 13. A micrograph showing an example of a through-thickness titanium wire embedded in a Ti-Al MIL composite plate.

STRUCTURAL PLUS THERMAL-MANAGEMENT ATTRIBUTES

For applications such as structural heat sinks, a high-performing material must possess the structural attributes described previously in addition to a high specific heat capacity to store the thermal energy and a high thermal conductivity to transport the heat throughout the structural heat sink. Figure 8 shows a plot of the product of thermal conductivity and specific heat capacity (on the y-axis) versus the product of specific modulus and fracture toughness (on the x-axis). The product of specific modulus and fracture toughness was chosen because it represents an optimum for many struc-

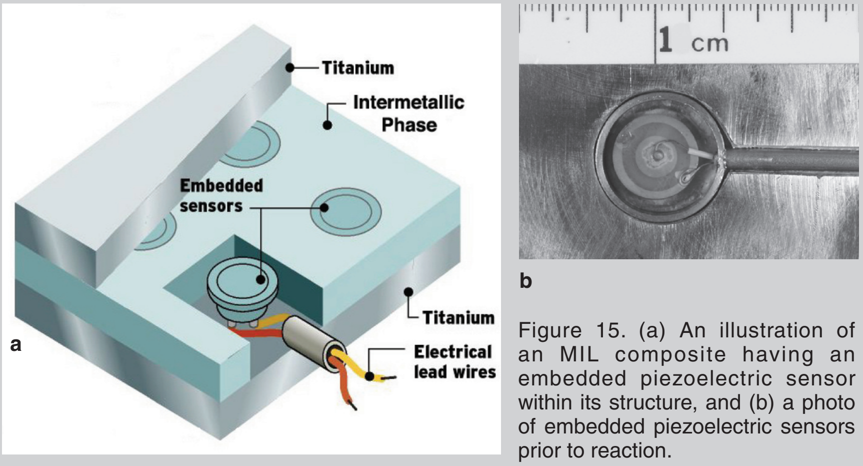

Figure 15. (a) An illustration of an MIL composite having an embedded piezoelectric sensor within its structure, and (b) a photo of embedded piezoelectric sensors prior to reaction.

tural applications wherein high stiffness and high fracture toughness are desired. This combination of properties is usually difficult to achieve considering the highest stiffness materials, such as ceramics, usually possess the lowest fracture toughness. In terms of thermal-management properties, the highest-stiffness materials, such as ceramics, are usually poor thermal conductors, and the high-thermal-conductivity materials such as aluminum alloys and copper alloys have relatively low specific stiffness. The exception to these trends is beryllium alloys, which possess high specific stiffness, high thermal conductivity, and high heat capacity. On the other hand, beryllium alloys have significant drawbacks to their widespread use, such as the limited availability of beryllium, the high cost of beryllium alloys, and the serious health concerns with beryllium manufacturing. As such, alternatives to beryllium alloys for combined structural plus thermal management applications are in great demand. Figure 8 shows that MIL composites are second only to beryllium alloys, in terms of thermal management capacity, for an equivalent structural property level. In terms of thermal management capacity, the MIL composites are only surpassed by beryllium alloys, some aluminum alloys, and diamond. Given the high cost of diamonds and the inability to produce structural components from them, diamonds can be eliminated as a choice. Furthermore, the specific structural performance of MIL composites is nearly three times greater than aluminum alloys, which can be critical for high-performance aerospace applications. As such, Ti-Al MIL composites offer an attractive alternative to beryllium alloys for structural heat sink (multifunctional structural + thermal) applications.

MULTIFUNCTIONAL METALLIC-INTERMETALLIC LAMINATE COMPOSITES

Additional functionalities can be readily incorporated into MIL composites due to the layer-by-layer assembly nature of the materials. Since each layer of the MIL composite starts out as a metal foil, it is possible to create holes and slits in these layers forming open space in individual layers or multiple layers. Within these cavities and slits, additional functionalities can be embedded to further enhance the properties of the MIL composites. The approach follows, to some extent, a multi-layer electronic circuit board methodology with interconnections occurring either within a given layer or between layers, creating a 3-D architecture to the structure of embedded functionalities.

MIL Composites with Meso-Scale Cavities to Incorporate Vibration Damping

By designing cavities within the aluminum layers and filling these cavities with granular material, it is possible to produce MIL composites with tailored vibration damping within the intermetallic layers.[11] Figure 9 shows an example of the presence of these cavities within a Ti-Al$_3$Ti MIL composite. The size, distribution, and location of the cavities within the MIL composite hierarchy can be selected in the material design process by the placement of the cavities within the individual aluminum layers and the placement of these layers within the foil stack. These cavities can be filled with granular materials to serve as particle dampers. Figure 10 shows an example of an MIL composite fabricated with a large cavity filled with steel beads to demonstrate the concept of a particle-filled cavity. Initial damping results have been presented elsewhere.[11]

Enhanced Energy-Absorbing or Fluid-Conduit-Modified MIL Composites

By embedding tubes between various layers of MIL composites, it is possible to incorporate energy-absorbing capacity into these materials, specifically for blast mitigation. These tubes would deform during impact and absorb the incident shock energy. Figure 11 illustrates the concept for this energy-absorbing MIL composite system. In addition, the embedding of tubes within the MIL composites would facilitate the passage of fluids or gases within the structure,

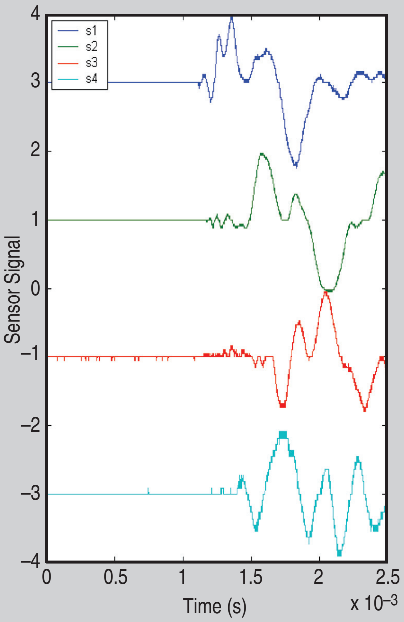

Figure 16. Voltage signals recorded simultaneously from four piezoelectric sensors embedded within the MIL composites following reacting of the plate.

which might be used for heat exchange, fluid transport, or embedded reactions.

MIL Composites with Embedded Sensing Capability

Synthesis of in-plane embedded wires and tubes as electrical and/or optical pathways for damage detection and life monitoring can make these MIL composites truly multifunctional. By creating slots in the aluminum foils prior to MIL synthesis, it is possible to introduce metal wires, metal or ceramic tubes, ceramic tubes containing metal wires, optical fibers, etc. By monitoring the wires or fibers, it is possible to monitor and detect damage within the intermetallic layers. The embedded wires also serve as micro-rebars within the intermetallic layers to further toughen these layers. Figure 12 shows an example of embedded ceramic tubes in the intermetallic layers. The embedded ceramic tube has two wires within it that are electrically isolated from the sample itself.

MIL Composites with Through-Thickness Wires or Tubes

Since metal foils are used as the starting material, it is possible to machine the foils individually or in a group to facilitate fabrication steps. By drilling a hole through the entire foil stack and placing either a wire or tube in the hole, it is possible to create a through-thickness-strengthening feature. Figure 13 shows an example of a through-thickness titanium wire embedded in a Ti-Al MIL composite plate. The location and distribution of these wires can be designed to regulate the balance between through thickness and transverse strength. These wires can also serve as embedded electrical resistors for strain sensors or damage detection. Replacing the wires with tubes provides a method to introduce rivet-type attachment holes and through-thickness fiber optics for imaging or environmental sensing.

Fully Functional MIL Composites

The next step to multifunctional MIL composites having meso-scale cavities and electrical conduits to incorporate sensing devices, such as piezoelectric devices, accelerometers, gyroscopes, and microelectromechanical system devices is to combine the technology of embedded cavities with the concept of embedded electrical pathways. Figure 14 shows an x-ray fluoroscope image of an MIL composite containing a series of cavities with interconnected electrical insulators and a pair of wires running through the cavities. These cavities can also be filled with high-temperature-capable devices such as lithium niobate piezoelectric crystals that can be used for detection of mechanical impulses, or conversely excited electrically to produce mechanical vibration of the material. Figure 15 shows an illustration of an MIL composite having an embedded piezoelectric sensor within its structure and a photo of an actual embedded sensor prior to reaction of the MIL composite. Figure 16 shows the voltage output from four piezoelectric sensors embedded within an MIL composite following reacting of the plate. The responses of the sensors are identical to their responses before embedding in the plate. The signals from this array of sensors have been used to perform impact location determination and through modal analysis of the signals determine the magnitude of the impact force.

CONCLUSION

Metallic-intermetallic laminate composites embody and exploit the concept of synthetic multifunctional materials. They have the potential to perform various other functions, such as thermal management, ballistic protection, blast mitigation, heat exchange, vibration damping, and sensing of various types through embedded devices. The materials are assembled layer by layer, with the functional features incorporated primarily within the intermetallic layers, and interconnections are completed within a given layer and between layers using electrically insulated wires. Strategies need to be developed that would allow the optimal integration of these interconnections while not significantly degrading material properties and performance.

In addition, constitutive and damage evolution models need to be developed that could be integrated into large-scale computer codes to predict the accuracy and effectiveness of performance indices for both properties and functionality.

The development of "rules and tools" for designers to utilize these inherent and embedded functionalities, and their distribution and density within the material, with experimental verification of the models, will lead to greater implementation of these materials in demanding multifunctional structural applications.

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Kenneth S. Vecchio is a professor in the Department of Mechanical and Aerospace Engineering at the University of California at San Diego, La Jolla, CA.

For more information, contact Kenneth S. Vecchio, University of California at San Diego, Department of Mechanical and Aerospace Engineering, La Jolla, CA 92093-0411; (858) 534-6076; fax (858) 534-5698; e-mail kvecchio@ucsd.edu.