Analysis of Shape-Memory-Alloy Fiber Interface Strength for Optimization of Self-Healing Composites

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Abstract

Self-healing materials, possessing an innate ability to mend damage and restore structural strength, have tremendous potential to improve safety and reliability, especially in space applications where recovery or manual performance of repairs may be prohibitive, dangerous, or impossible. Self-healing metallic materials developed with Nickel Titanium (NiTi) Shape Memory Alloy (SMA) reinforcement showed a promising prospect for recovering from larger scale damage. However, NiTi is known to form an inert oxide (TiO_2) surface layer that is extremely hard to attach to. In this research, to promote better strength between the fiber and matrix, TiO_2 surface layer has been removed by etching the NiTi wires in an inert environment and a pull test has been performed to evaluate the resulting change in adhesion strength between the fiber and metallic matrix. The experimental investigation of these interface fracture scenarios will enable the efficient design of composite materials.

1. Introduction

Spacecraft and aircraft can incur damage from fatigue, impacts, and overload events. Damage to aerospace structures can be hard to detect or repair and results can be catastrophic. Structural integrity and weight are primary concerns in flight vehicle structures to ensure safety and efficiency. Self-healing materials will fundamentally change way structures are designed by altering the relation between fracture, damage, and failure resulting in a new generation of light weight aircraft and spacecraft. Self-healing materials will change structure to be light weight, more efficient, more durable, and safer. It will enable structural repair in service, especially in hard to access locations.

One of the material systems that currently demonstrates the most advanced self-healing capabilities is Nickel Titanium (NiTi) Shape Memory Alloy (SMA) reinforced Bismuth Tin (BiSn) metal matrix composite. While advanced self-healing capabilities have been demonstrated in this material system, testing to date has primarily been demonstrations of self-healing ability, including geometric restoration and near complete strength recovery (Misra, 2013; Salowitz, Misra, Haider, Povolo, & Rohatgi, 2022). Critical properties necessary for engineering design, modeling, and structural optimization have yet to be quantified, specifically the strength of the interface between the NiTi fibers and the BiSn matrix. This is complicated by the native inert TiO2 layer that forms on the surface of NiTi nearly instantly in the presence of oxygen (air). Processes have been created to remove this TiO2 layer, but the interface strength between NiTi and BiSn has not been measured in either situation.

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1.1 Motivation. Self-healing materials, possessing an innate ability to mend damage and restore structural strength, will create a paradigm shift in the way structures are designed and analyzed by altering the definition of 'failure' resulting in lighter weight, more efficient, and more durable vehicles (White, et al., 2001). Structural Integrity and weight are key considerations in the design of aerospace vehicles and structures. Unnecessary structural weight can cause cascading increases in weight thought a flight vehicle, e.g 1 lb of extra structural weight in a large rocket can increase the overall weight of the rocket by more than 200 lbs (Bruhn, 1973). Structural failure can result in loss of life or inability to complete a mission.

Traditional design techniques to address these issues include design factors, redundancy, and damage tolerant design. To ensure safety, these techniques are combined with regular inspection, maintenance, and limited design life. Inspection and maintenance in modern aerospace structures require costly downtime. Further, spacecraft operating far from earth cannot be repaired if a failure occurs. Self-healing materials have the potential to be used in most structural components including frames, skins, heat shielding, and even electrical connections (solder joints). The potential range of applications will require a variety of different self-healing materials and capabilities. However, self-healing materials are in their infancy, therefore research is seeking to develop and understand fundamental capabilities and properties.

1.2 Background. Self-healing materials seek to reduce structural weight, down time, maintenance cost, and failure through the integration of a capability to mend damage while in service, preventing the accumulation of damage that can result in structural failure.

In the past two decades, there has been significant research into self-healing materials that have an innate ability to repair damage. This research has resulted in different types of self-healing materials employing different healing mechanisms (Salowitz, et al., 2018). Self-healing materials can generally be categorized as autonomous or non-autonomous and homogeneous or heterogeneous (Kilicli, Yan, Salowitz, & Rohatgi, 2018):

1) Autonomous self-healing materials activate immediately upon incurring damage and generally have an encapsulated healing agent or a stored energy potential that is released when damage occurs. These materials may have a relatively uniform dispersion or discrete concentrations of healing agents, making them either homogenous or heterogeneous.
    a) Automatic initiation of the healing process removes the need for damage detection but results in a mended structure with any deformations caused by the damage, deformation that itself could be a form of failure.
    b) Healing agents or stored energy are consumables that eventually run out, limiting the number of times self-healing can occur.
    c) Encapsulated liquid healing agents add weight to material but cannot carry tensile or shear loads in their liquid form, reducing strength to weight ratios. This drawback becomes apparent when the strength of healed structures is commonly reported to be greater than that of the pristine structure (healing efficiency > 100%).
    d) Encapsulated healing agents create stress concentrations and fatigue initiation points in the structure.
2) Non-autonomous self-healing materials typically have more organized internal structures, like composite materials, so they are typically heterogeneous but require external activation to initiate healing.

a) Non-autonomous composite structures have demonstrated the potential to achieve the greatest and most complex self-healing capabilities.
b) Structures allow for geometric recovery and multi-stepped healing processes, mimicking the more complex healing found in biological organisms.
c) Knowledge of damage existence is required to activate healing processes, usually through the application of energy in the form of heat, electricity, or light.
d) Advanced capabilities require more detailed micro-mechanical analysis & design.

1.3 Self-Healing MMC. Metal alloys and metal-metal composites (MMCs) have high potential to be utilized in the aerospace industries due to their superior structural properties. However, most research to date has focused on polymeric self-healing materials due to the complexity of high temperature synthesis and precise metallurgical requirement (Alaneme & Omosule, 2015).

Recent research has identified and sought to realize new capabilities in self-healing MMCs. Some of the most advanced and complex self-healing capabilities have been demonstrated in a MMC material system composed of nickel titanium (NiTi) shape memory alloy (SMA) wires reinforcing an off-eutectic bismuth-tin (BiSn) matrix. This NiTi reinforced BiSn composite can resume a predefined geometry after being deformed, mend cracking with near 100% strength recovery and heal without using any internal consumables. The entire NiTi reinforced BiSn MMC is load bearing and doesn't contain significant stress concentrations that can become fatigue crack initiation points.

The ability to restore geometry is due to the shape memory effect observed in NiTi SMA. This property results from the material's ability to undergo a reversible phase transformation between austenite and martensite crystalline structures. Starting from a high temperature state free from mechanical load, NiTi will have an austenite crystalline structure and take on its *parent geometry*. When the temperature is lowered sufficiently, NiTi will progress through the *forward transformation*, taking on a self-accommodated twinned martensite structure and remain in its parent geometry (barring the 2-way shape memory effect). If the NiTi is deformed sufficiently in its martensite state, the martensite structure will detwin and the material will accumulate recoverable strain, which can be significant in magnitude (>5%). When NiTi is re-heated beyond a threshold it will revert to an austenite structure, known as the *reverse transformation*, and try to eliminate the recoverable strain and return to its parent geometry. The specific transition temperatures are dependent on the specific formulation of NiTi but commonly range from sub-zero to a maximum of around 100°C (Lagoudas, 2008; Haider M. , Rezaee, Yazdi, & Salowitz, 2019).

Crack filling and soldering capabilities of this material system are enabled by the off-eutectic BiSn matrix. BiSn has a relatively low melting temperature range with microscopic eutectic regions of the material melting at a temperature of about 160°C and the off-eutectic regions melting at higher temperatures around 175°C (Manuel M. , 2007; Manuel & Olson, 2007; Misra, 2013).

Combined, these materials have demonstrated great potential as a self-healing MMC, but more research needs to be done to understand and optimize the composite structure. The self-healing process of NiTi reinforced BiSn is depicted in Fig 1. If a NiTi Reinforced BiSn self-healing material is deformed and damaged, it can be heated to actuate the NiTi SMA to resume its original geometry, undoing deformations. Continued heating will soften and melt the eutectic regions of the BiSn soldering the matrix back together while the off-eutectic regions remain solid. This system has the advantages of restoring geometry and regaining nearly 100% of its initial strength without using consumables. Conceptually the healing cycle could be repeated indefinitely (Misra, 2013; Salowitz, Misra, Haider, Povolo, & Rohatgi, 2022).

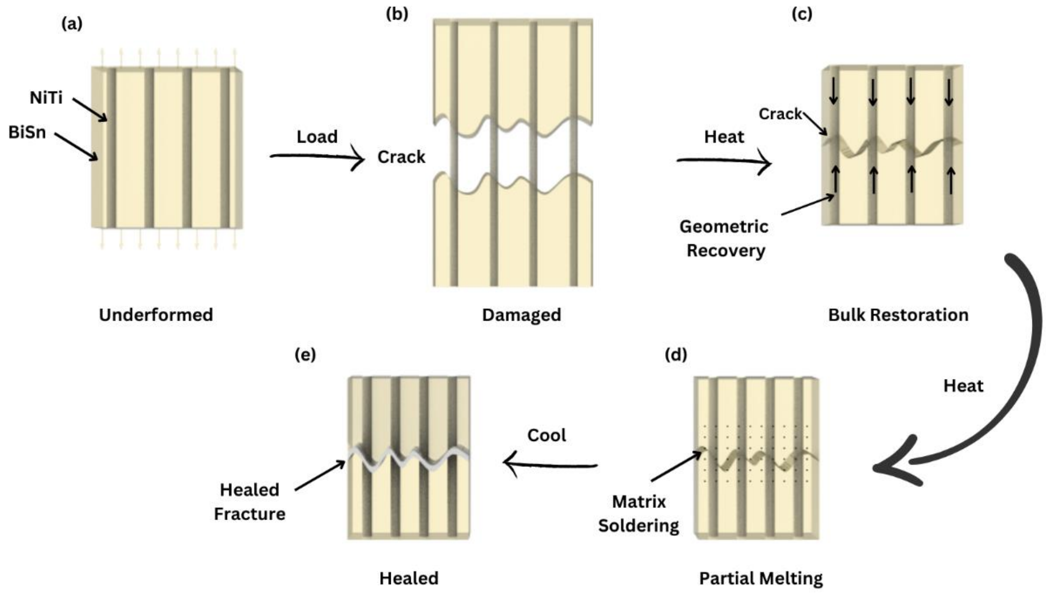

Fig 1: Self-healing process in NiTi reinforced BiSn. a) initial structure b) fracture c) geometric recovery d) soldering e) healed (Haider, Rezaee, & Salowitz, Explorations of Post Constrained Recovery Residual Stress of Shape Memory Alloys in Self-healing Applications, 2021)

1.4 Challenges. In order for fiber reinforced composites to carry and transfer loads, forces and stresses need to be transmitted between the matrix and fibers. The strength of their interface is critical to both the design of composite microstructure (fiber diameter) and the overall strength of the resulting composite material. The importance of this fiber-matrix load transfer is amplified in SMA reinforced self-healing materials, where the fibers themselves can generate internal forces.

Unfortunately, connecting NiTi to other materials and structures is a well-known challenge. In air NiTi forms a native inert titanium oxide (TiO2) surface layer on the order of nanometers thick (Ng, Mahmud, Ahmad, Razali, & Liu, 2022) that is notoriously hard to connect to or remove, resulting in weak interfacial shear strength. This week interface strength is detrimental to the overall strength of NiTi reinforced composites as well as the self-healing capability of the system being investigated.

In prior studies, NiTi reinforced self-healing materials have commonly employed structural anchors for the NiTi to pull against even though it breaks free from the matrix to circumvent this issue. This approach negates potential distributed load transfer between the fibers and matrix of the composite structure along the length of the fibers resulting in a poor composite structure.

Chemical etching in an inert environment has been performed to remove the inert TiO2 surface layer from the NiTi, but the resulting interface strength has not been quantified, therefore any improvement in load transfer and quantitative knowledge thereof required for composite design are missing.

2. Objectives

The objective of this research is to experimentally evaluate the interfacial strength between NiTi fibers and metal (BiSn) matrix in both an unetched state where TiO_2 is present and etched state where TiO_2 has been removed to support design of NiTi reinforced BiSn self-healing composites.

3. Methods

Single fiber composite (SFC) specimens were fabricated using Sn-20% Bi matrix alloy reinforced with a NiTi alloy fiber protruding from the sample. 99% pure Tin and Bismuth were donated by Kohler Company (Kohler, WI) and NiTi Flexinol 90 wires were procured from Dynalloy Inc. (Irvine, CA) with a diameter of 0.508 mm. NiTi wires were cut in length and thermally cycled to acquire their parent geometry at room temperature before being cast in the BiSn matrix. A composition of Sn-20% Bi was selected to support a partial melting temperature of 160-165° C which would be 15 wt% liquid, which is adequate for healing.

Two sets of specimens were created consisting of a single NiTi wire embedded in a block of BiSn:

1) A control set that was synthesized using NiTi wires with their native oxide intact and unetched.

And

2) An experimental set of samples where the NiTi underwent treatments to remove the native TiO_2 layer.

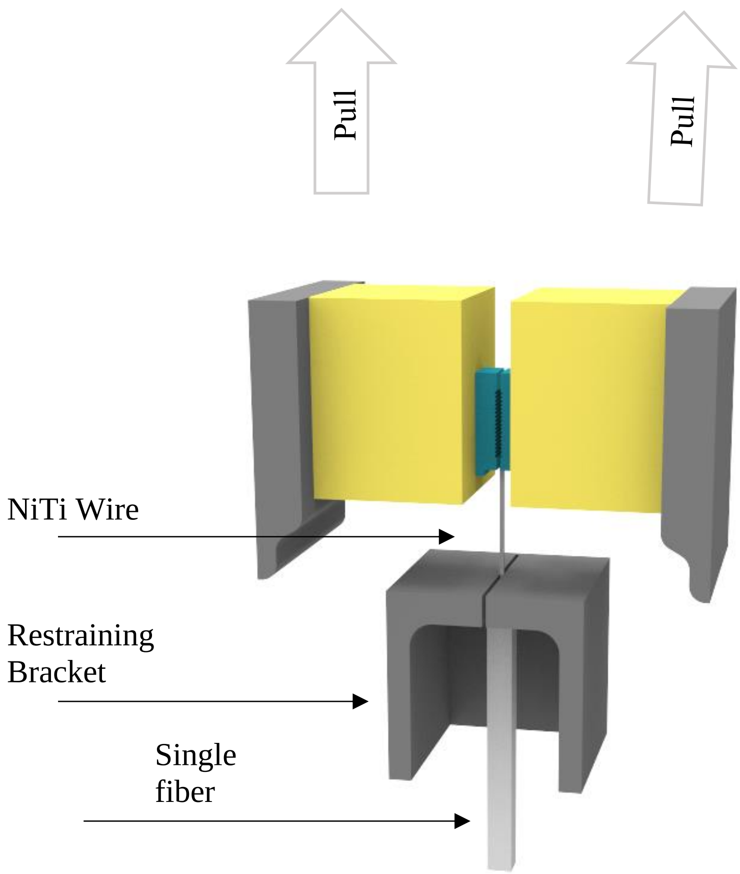

Fig 2: Test setup for single fiber pull test

NiTi wires for the experimental group were etched following the procedure detailed by Coughlin et al. (Coughlin, Williams, & Chawla, 2009; Coughlin J. , Williams, Crawford, & Chawla, 2009) Wires were immersed for 5 minutes in a solution of Hydrofluoric (HF) and Nitric acid (HNO_3) (4.8% HF-10.5% HNO_3) followed by dipping in Phosphoric acid based flux (Indalloy Flux # 2, Indium Corporation of America) and then dipped in molten BiSn to coat them. The procedure was performed in an inert nitrogen environment to prevent re-oxidation. Finally, the coated fibers were cast into the BiSn 'matrix' material. Coughlin et al. conducted a comprehensive investigation on the NiTi etching process and subsequent material interface analysis (Coughlin, Williams, & Chawla, 2009; Coughlin J. , Williams, Crawford, & Chawla, 2009). Misra performed significant metallurgical, microstructural, and elemental analysis around the interface of NiTi wire and BiSn material prepared in the same way and found that an intermetallic layer formed roughly 3 μm thick (Misra, 2013). Moreover, in depth study and the analysis of the interfacial reactions were studied by Coughlin et al. (Coughlin J. , Williams, Crawford, & Chawla, 2009).

Synthesized specimens were loaded into a universal test machine (as shown in Fig 2) for pull testing, where the NiTi wire was clamped to the moving head and the BiSn block was constrained in a custom jig to hold it stationary. Testing was performed to pull out the embedded NiTi fiber from the BiSn matrix under a constant displacement rate of 0.5 mm/min until specimens failed or wires were completely pulled out. Both displacement and force were recorded with video capturing of the entire experiment for better observation of the pull-out phenomena.

4. Results and Discussion

In this experiment, the NiTi fiber embedded in the BiSn matrix was pulled out at a constant rate. Initially, the shear stresses are maximum at the surface where the NiTi enters the BiSn matrix; therefore, this is where failure would initiate (Hsueh, 1990). The applied stress on the NiTi fiber due to axial loading must overcome the interface strength of the fiber and matrix to initiate failure and allow for relative movement. Following the initial fracture, when applied stress exceeds the interfacial frictional stress, further failure can occur throughout the pull test. After complete interface failure, only frictional and sliding forces can exist along the fiber length remaining within the matrix.

The force vs. displacement curves shown in Fig 3 and Fig 4 present data taken from 4 SFC specimens subjected to the pull test. The total distance traveled by the fiber that was pulled out from the matrix is presented in the abscissa of the plot. It was observed at the outset of the experiment that the fiber was straightening to align with the applied axial load. Following the straightening, initial stresses build up in the free portion of fiber due to initial tension. Due to its small diameter in the free portion relative to the cross-sectional area of the matrix, this tension will result in higher stress relative to the embedded portion of the fiber/combined fiber and matrix. Upon stress generation, the fiber pullout process might diverge in two different directions, mostly due to the strength of the fiber-matrix interface. In the case of weak interfacial strength, the fiber-matrix interface would begin to fail before detwinning of the NiTi, preventing the accumulation of recoverable strain and negating shape memory capabilities. Alternatively, if the interfacial strength is strong, NiTi SMA fibers accumulate recoverable strain due to detwinning upon loading in the free portion of the fiber before interface failure. However, in case of NiTi fiber embedded matrix, a potential elastic strain will occur as the fiber is embedded in the matrix. Material property mismatch between the NiTi and BiSn, i.e., strain to failure, and compatibility require that the NiTi attached to the BiSn remain in the twinned state and break free of the bulk BiSn as it detwins. Again, once the fiber has broken free of the bulk BiSn, only frictional type forces can exist at the interface as the fiber slides out of the matrix.

Fig 3 and Fig 4 present the load-displacement curves for the different samples. As shown in Fig 3, the interfacial strength was weak for unetched samples, with an initial failure force of 15 N. Previous experiments showed that for similar NiTi wires at room temperature, detwinning occurs the force reached 69 N with an equivalent stress of 340 MPa. In the case of the unetched specimen, the interface failed before NiTi detwinning happened and fiber slid out of the matrix with a low load during the entire length pulled out.

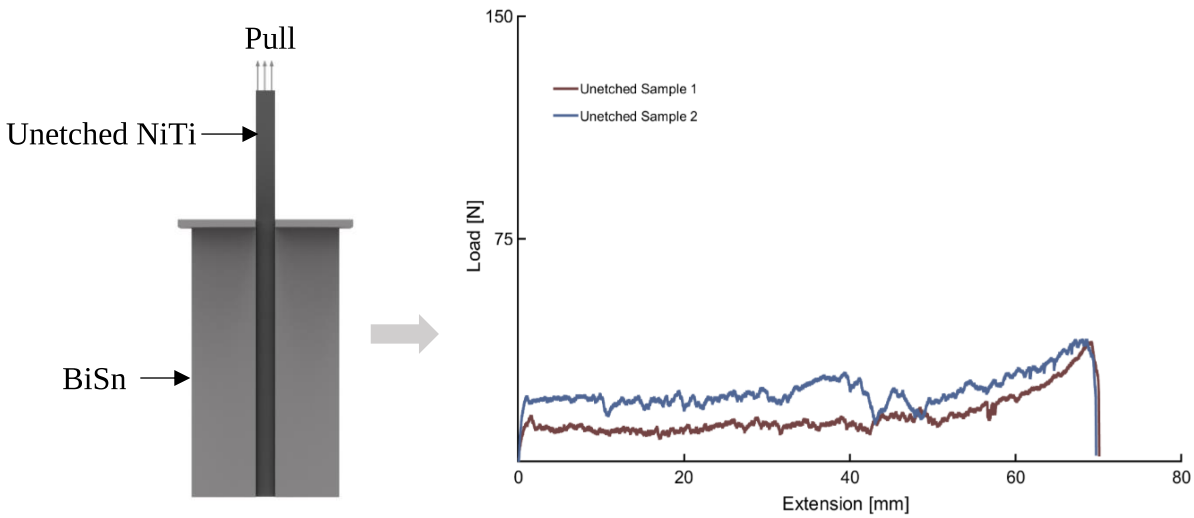

Fig 3: Load vs extension plot from pull test of the composites fabricated by etched NiTi wire and BiSn alloy.

For etched samples, the load-displacement plots shown in Fig 4 revealed that higher force is required to pull the NiTi fiber out of the matrix than unetched samples, indicating higher interfacial strength between the NiTi and BiSn matrix. The initial load peak before plateauing was five times higher than load observed with the unetched samples. Hence, high stress developed, which caused the detwinning of the NiTi wires. The distinct change in the slope near 69 N is an indication of this change in behavior. As the force increased, increasing stress would initiate interface failure and simultaneously continue detwinning of the fiber as it broke free from the matrix. The results of the unetched fiber not accumulating any recoverable strain, and the etched fibers accumulating recoverable strain were confirmed by measuring the lengths and heating the NiTi above the austenite finish temperature after testing; the unetched samples did not change length, indicating they were still in their parent geometry and no detwinning occurred. The etched samples were observed to be longer after mechanical testing, and shortened when heated indicating that they had accumulate recoverable strain through detwinning during the testing.

A gradual increase in force was observed as the fiber continued to be pulled out of the matrix beyond the point where compatibility would require the fiber to be completely free. This indicates the occurrence of something other than traditional Coulomb friction. An investigation into this gradual increase in force is ongoing.

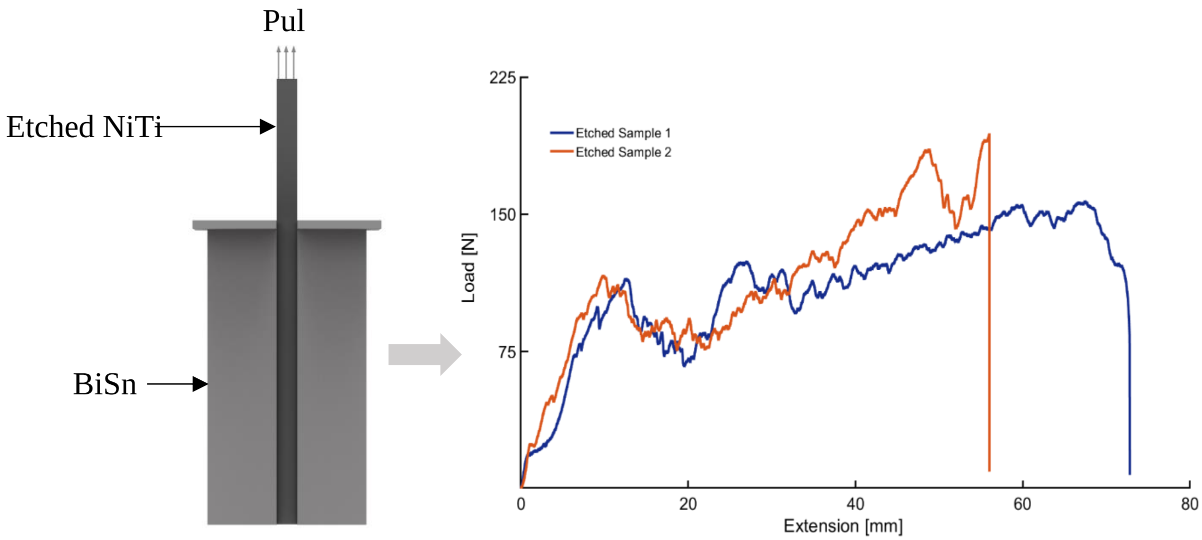

Fig 4: Load vs extension plot from pull test of the composites fabricated by etched NiTi wire and BiSn alloy.

5. Conclusion

In composite materials, load transfer is depended on the interfacial strength between fibers and matrix; hence understanding the interface strength between them plays a crucial role in improving composite performance. For proper, distributed load transfer between the fiber and matrix, the interface strength between the NiTi fibers and BiSn matrix needs to be adequate. This study presents an experiment and analysis to explore the interfacial strength between NiTi wires and BiSn metal matrix composite. Comparative studies of pull tests for both unetched and etched specimens demonstrated that the native oxide that forms on NiTi is detrimental to the strength of its interface with BiSn and potentially other matrix materials in a self-healing composite structure. Removal of this layer resulted in superior in interfacial strength, demonstrated by higher failure strength and different material behaviors. Further investigation is necessary to fully understand the load vs extension behavior. This study will play a significant role in the development of SMA reinforced metal matrix composites by providing essential knowledge of interfacial strength and failure mechanism between fiber and matrix, enabling optimization of wire diameter and advancing the capabilities of self-healing MMCs.

This work is a way forward to a breakthrough toward the greater vision of creating fully autonomous and advanced monitoring systems that integrate structural health monitoring techniques into self-healing materials (SHM^2). SHM^2 is a bioinspired technique that would autonomously detect and locate damage when it occurs, trigger proper healing by inspecting and monitoring for the occurrence of more damage in service and prevent further damage.

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