DESIGN OF LIQUID-ASSISTED SELF-HEALING METAL-MATRIX COMPOSITES

By

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To my family & friends who have supported me on my adventures
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<tr>
<td>$1\sigma$</td>
<td>One standard deviation</td>
</tr>
<tr>
<td>$^\circ$C</td>
<td>Degrees Celsius</td>
</tr>
<tr>
<td>$\varepsilon_f$</td>
<td>Strain to failure</td>
</tr>
<tr>
<td>$\sigma_a$</td>
<td>Applied stress</td>
</tr>
<tr>
<td>$\sigma_y$</td>
<td>Yield stress</td>
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<tr>
<td>ACP</td>
<td>Active corrosion protection</td>
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<tr>
<td>$A_f$</td>
<td>Austenite finish temperature</td>
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<tr>
<td>Ag</td>
<td>Silver</td>
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<tr>
<td>Al</td>
<td>Aluminum</td>
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<tr>
<td>$A_s$</td>
<td>Austenite start temperature</td>
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<tr>
<td>at%</td>
<td>Atomic percent</td>
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<tr>
<td>Au</td>
<td>Gold</td>
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<tr>
<td>Avg.</td>
<td>Average</td>
</tr>
<tr>
<td>B</td>
<td>Boron</td>
</tr>
<tr>
<td>Bi</td>
<td>Bismuth</td>
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<tr>
<td>BN</td>
<td>Boron Nitride</td>
</tr>
<tr>
<td>CCC</td>
<td>Chromate conversion coating</td>
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<tr>
<td>Ce</td>
<td>Cerium</td>
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<td>cm</td>
<td>Centimeter</td>
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<tr>
<td>Co</td>
<td>Cobalt</td>
</tr>
<tr>
<td>Cr</td>
<td>Chromium</td>
</tr>
<tr>
<td>CSIRO</td>
<td>Commonwealth Scientific and Industrial Research Organization</td>
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<tr>
<td>Cu</td>
<td>Copper</td>
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<td>DOE</td>
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<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
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<td>Energy dispersive spectroscopy</td>
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<td>Eutectic gallium indium</td>
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<td>Gigapascal</td>
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<tr>
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<td>Hafnium</td>
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<tr>
<td>ICP</td>
<td>Inductively coupled plasma</td>
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<td>In</td>
<td>Indium</td>
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<tr>
<td>KSC</td>
<td>Kennedy Space Center</td>
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<td>La</td>
<td>Lanthanum</td>
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<td>Li</td>
<td>Lithium</td>
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<td>MDPL</td>
<td>Materials Design and Prototyping Laboratory</td>
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<td>Mr</td>
<td>Martensite finish temperature</td>
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<td>Mg</td>
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<td>MMC</td>
<td>Metal-matrix composite</td>
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<td>Mn</td>
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<td>Mo</td>
<td>Molybdenum</td>
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<td>MPa</td>
<td>Megapascal</td>
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<td>Ms</td>
<td>Martensite start temperature</td>
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<td>Symbol</td>
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<td>N</td>
<td>Nitrogen</td>
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<td>NASA</td>
<td>National Aeronautics and Space Administration</td>
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<td>Ni</td>
<td>Nickel</td>
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<td>NiTi</td>
<td>Nickel-titanium shape memory alloy</td>
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<td>NSF</td>
<td>National Science Foundation</td>
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<td>RE</td>
<td>Rare-earth</td>
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<td>Siemens</td>
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<td>Sulfur</td>
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<td>Shape memory alloy</td>
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<td>$T_{\text{room}}$</td>
<td>Room Temperature</td>
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<td>TTT</td>
<td>Time-Temperature-Transformation</td>
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<tr>
<td>UA</td>
<td>Under-aged</td>
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<td>UF</td>
<td>University of Florida</td>
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<tr>
<td>UTS</td>
<td>Ultimate tensile strength</td>
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<td>UWM</td>
<td>University of Wisconsin - Milwaukee</td>
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<td>V</td>
<td>Vanadium</td>
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ADVANCED SCIENCE AND ENGINEERING

Chair: Manuel, Michele Viola
Major: Materials Science and Engineering

Advancements in materials science have enabled components to be fabricated lighter, stronger, and more functional than ever. However, damage mitigation in these materials still limits their usable lifetimes. Recently, materials with the ability to heal structural damage have shown promise as potential novel materials of the future. Within metallic-based systems, metal-matrix composites reinforced with shape memory alloys (SMA) have the potential to demonstrate dramatic capabilities in damage mitigation and repair.

Investigations of liquid-assisted self-healing in metal-matrix composites have centered on developing a high specific-strength matrix possessing a low-melting eutectic for use as the healing material. A systems design approach motivated by a thermodynamic-based methodology was used to determine appropriate matrix alloying elements for improved mechanical properties while maintaining healing capabilities. Initial research focused on improving a Sn-Bi matrix reinforced with commercial NiTi SMA wires. Healing was established at over 94% retained strength post-healing. Recent
developments in aluminum-based alloys have shown potential healing across several systems.

This study will detail methodology used to design the prospective Al-based alloy systems and establish the efficacy of the design approach through prediction of strength, microstructure development, and SMA incorporation into the composite. In addition, mechanical behavior of several binary and ternary matrix alloy composites were investigated to determine how healing is affected by different alloying elements in Al. Advancement of healing behavior in an oxygen-containing environment through reactive element addition was also investigated. Finally, areas to advance future matrix and composite designs will be brought forth.
CHAPTER 1
INTRODUCTION

Motivation

Biological materials such as tissue, bone, and muscle are readily able to heal themselves through complex processes which involve microvascular networks, self-assembling systems, and nanostructures (1). Recent literature has delved into the development of engineered biomimetic or bio-inspired materials for use as structural components (2, 3). One potential aspect of biomimetic materials is the ability to repair damage formed during the material’s application with minimal human intervention (3). This relatively new class of materials has been coined “self-healing materials.” This is an active area of research at universities and government laboratories across the globe (4-9).

Self-healing materials represent a paradigm shift in traditional materials engineering. History is filled with high performance alloys designed to resist in-service changes. With the advancement of self-healing materials, however, there is the ability to shift from the Damage Prevention paradigm to one of Damage Management (10). Within the Damage Prevention paradigm, stronger and/or more ductile materials are created in order to better sustain damage. In Figure 1-1a, Material A represents a typical ductile material exposed to constant loads. While under relatively low stresses, i.e. below the yield stress, the material remains intact. However, with continued exposure to increased loads above the yield stress or high cycles to induce fatigue, damage begins to form. This damage will progress until failure of the component. Material B represents a stronger but brittle material, whereas Material C represents a stronger, more ductile material; both Material B & C were manufactured to resist more
deformation during service. However, all of these materials (A-C) trend in one direction with respect to damage formation: either zero damage or positive damage:

\[
\frac{d(\text{damage})}{dt} \geq 0 \quad \text{for } 0 < t < \text{lifetime}
\]

(Eq. 1-1)

where t represents time.

Figure 1-1: Schematic of the a) Damage Prevention and b) Damage Management material paradigms. For traditional materials in the Damage Prevention paradigm in a), Material A represents a low strength, ductile alloy, B is a higher strength, brittle material, and C a high strength, ductile alloy. For novel self-healing materials in b), Material D represents a material able to heal itself once, whereas E is a material able to repeatedly heal itself. Adapted from van der Zwaag, Sybrand. 2007. Self-Healing Materials: An Alternative Approach to 20 Centuries of Materials Science (page 4 and 6, Figures 1 and 2). Springer, New York.

Self-healing materials, on the other hand, represent the Damage Management paradigm where the damage is controlled in such a way that it can be reversed. Material D in Figure 1-1b represents such a self-healing material. Here, the damage realized by the material during service is able to be reversed. Thus, self-healing materials are instead represented by Equation 1-2 during a healing cycle:

\[
\frac{d(\text{damage})}{dt} < 0 \quad \text{for } t_i < t < t_{i+\Delta t}
\]

(Eq. 1-2)
where $t_i$ represents the initial time and $t_{i+\Delta t}$ is the change in time required for healing. An ideal self-healing material is represented by something more akin to Material E; repeated healing over time to ensure damage in the material never reaches the failure point.

This reversal of damage is unlike what is found in traditional engineering materials that lie in the Damage Prevention paradigm, which only utilize higher strength or more ductile materials to prevent material failures. These new self-healing materials all possess similar requirements, including a healing trigger, mobile atoms for the healing mechanism, and crack surfaces being in close contact (7, 10). These requirements reveal that prospective self-healing materials are more than a material, but are instead a self-healing system similar to biological systems.

The White and Sottos groups at the University of Illinois were the first to exhibit appreciable self-healing within a polymer-matrix system in 2001 (11). In the decade following, several more groups also began research across different materials classes including polymers, ceramics, and metallic systems. Several review articles have been written covering all the different aspects for healing in polymer systems (8, 12, 13) and healing in ceramic/cementitious systems (14-16), in addition to textbooks on these topics (6, 17, 18). A review of self-healing in metallic systems has not been completed at this time.

**Potential Applications**

Applications for self-healing materials can be found in the aeronautics and space industry (4). Due to the demanding requirements for materials in aerospace applications, materials are designed with extra safety factors in order to handle the extreme environment. This leads to over-design of the component. However, if
designers are able to shift to a Damage Management paradigm, this would allow the
reduction of volume and mass from components as the materials would enable healing
of the structure without over-designing the part through high safety factors or having to
replace the component.

One specific example would be meteorite damage on satellites. During service, space debris and meteors continually cause damage to spacecraft to such an extent that mission operations can be significantly degraded (19). Due to the extreme costs associated with space travel, replacement of these damaged components is difficult. Therefore, self-healing materials would be prime candidates to ensure continuation of the mission.

Another example of applications of self-healing materials would be for space exploration using rovers on planet surfaces. In 2006, one of the wheels on the Mars rover Spirit stopped functioning properly (20). And in 2012, the landing of Curiosity on Mars was highly publicized because of the new landing system utilized (21). If the landing did not go smoothly, it was probable the rover would have crash landed, breaking required components, and been unusable. These cases show the potential for self-healing materials to be exploited for components in systems which require significant time and money in order to replace.

Deep sea applications are another potential opportunity for self-healing metals to be utilized. The depth and extreme pressures ensure that component repair is extremely difficult. However, an increase in pressure has been found to enhance healing (22) and thus it is a potential area to investigate. Brinker Technologies has started investigations using so-called “platelets” to seal links in undersea umbilical lines
(23). This technology is analogous to the human body sending platelets and clotting tissue to a wound using the vast vascular network known as our circulatory system. As described by van der Zwaag (10), material “systems” may be the future of self-healing.

It is composite systems which will drive the viable application of self-healing metals; graded microstructures for increased toughness and wear resistance, dispersed compounds for increased strength, coatings for high temperature capabilities, vascular networks consisting of liquid delivery systems via hollow tubes (or the even the designed microstructure itself) with shape-memory reinforcements for crack size reduction. These multifunctional systems will help us realize a world of the future where a fender-bender on your car can be fixed by using a heat-gun to heat up the affected area, causing the metal to resume is previous shape and therefore restore the car’s previous form.

**Document Outline**

This document will seek to understand the underlying mechanisms affecting healing in a metal-matrix composite (MMC) system pairing a solid-solution strengthened matrix exhibiting non-continuous eutectic phase with nickel-titanium (NiTi) shape memory alloy (SMA) reinforcements. First, a review of the current topics in self-healing metals will be discussed. Next, an investigation is presented on a prototype tin-bismuth (Sn-Bi) composite system to elucidate how healing is affected by the connection between matrix and the wires in addition to how the pressure applied at the crack during a healing cycle changes post-healing mechanical properties. To advance MMC technology, a methodology is detailed to expand potential matrix alloys into higher strength materials – specifically aluminum (Al) –based alloys. Experiments involving potential binary alloys to serve as matrix materials lead into the design of a high-
The next section investigates ways to improve healing in air via introduction of reactive elements to induce chemical reactions at the interface. Finally, a summary of the work is completed before future areas of development within liquid-assisted self-healing composites are detailed.
CHAPTER 2
BACKGROUND

Self-Healing in Metallic Systems

In 1967, an article appeared in *Time* discussing the “self-healing” capabilities of the recently developed TRIP steels, which use a martensitic phase transformation to blunt small cracks (24). Since 1993, the Olson group at Northwestern has been working to incorporate self-healing characteristics into their iron (Fe)-based metal-matrix composites for structural applications (25, 26). However, self-healing in metallic systems has been relatively uninvestigated compared to polymeric and ceramic systems because of several disadvantages compared to other material classes: 1) stronger metallic bonds, 2) small atomic volume, and 3) relatively slow kinetics due to low diffusion rates of metals (3). Stronger metallic bonds mean the healing material requires higher activation energy in order to initialize the healing process. Unlike polymers which possess large atomic volumes, metal alloys are much smaller and thus it is more difficult to accumulate enough material to fill a crack. Also, low diffusion rates means healing reactions are slower. Despite these drawbacks, various examples of healing in metals have been documented in literature.

Self-healing in metallic systems can be grouped into two general types: solid-state and liquid-assisted healing (27). Solid-state healing is associated with dynamic precipitation for creep and fatigue crack suppression and coatings to reduce corrosion. Liquid-assisted healing has been demonstrated in metal-matrix composites for structural use and in electrical applications. Each of these types will be broken down into the one of two classes – autonomous and non-autonomous (Figure 2-1). Autonomous healing is
only present if there are no outside influences, e.g. heat or light, to trigger the healing process (7).

Figure 2-1: Schematic showing research areas for solid-state and liquid-assisted self-healing in different metallic systems

**Solid-State Healing in Metallic Systems**

Solid-state healing can be found in both structural metals and coatings. For structural materials, research has been focused upon autonomous self-healing through precipitation at high energy surfaces such as grain boundaries, dislocations and voids (28). Much of the research is focused on healing creep and fatigue damage in aluminum (Al) alloys and steel. This precipitation process reduces the maximum flaw size and thus solid-state healing of microscale defects is feasible for structural metals.

**Dynamic Precipitation in Aluminum Alloys**

Al alloys have been utilized as structural materials following age hardening heat treatments since precipitation reactions were first detailed in 1911 for an Al, copper (Cu), and magnesium (Mg) alloy (29). The basis for solid-state self-healing has been the result of similar research by collaborators at the Commonwealth Scientific and Industrial Research Organization (CSIRO) in Victoria, Australia investigating dynamic precipitation.
in under-aged (UA) Al-Cu-Mg-based alloys (9, 28, 30-35). Earlier work was performed by Ringer et al. (36), Wang et al. (37), and Skrotzki et al. (38). In the UA condition, supersaturated solutes are available to undergo dynamic precipitation throughout the matrix during creep or fatigue loading. A commercial alloy with manganese (Mn) additions, Al 2024 (Al-4.4Cu-1.5Mg-0.6Mn), in the UA condition during a creep test also displayed improved properties, including doubling the time to failure, delay of tertiary creep, and increase in strain at failure (30). The healing process was found to be a thermally activated process which corresponds to the Cu and Mg pipe diffusion in an Al matrix (39-41). Results from other studies have suggested the beneficial effects of under-aging may be applied to fatigue failures as well, since the pipe diffusion rate of Cu in Al is still $10^6$ times faster than vacancy diffusion even at room temperature (32).

While dynamic precipitation has the potential to delay fatigue crack initiation and the onset of crack propagation in Al alloys, Wanhill (42) detailed several limitations. First, healing is limited by a maximum allowable flaw size for repair. Second, the amount of solute able to be precipitated results in another limitation, once the alloy reaches peak aging, dynamic precipitation is nullified. Finally, the major hurdle for in-service use of self-healing Al alloys is due to most failures in being initiated by surface defects. Because of oxidation issues and other surface effects, the current self-healing technology for Al alloys would be inadequate to heal surface flaws. Despite these concerns, current research is focused on the significance of the volume changes occurring during healing (28).

**Dynamic Precipitation in Fe-based Alloys**

Shinya and colleagues (43-53) have lead research successfully improving creep properties through autonomous self-healing in heat-resisting austenitic stainless steels.
Creep fracture is known to be the result of nucleation, growth, and coalescence of creep-induced cavities along grain boundaries. Most high-strength heat-resisting steels show this type of failure mechanism (49). Creep cavities grow through diffusion along surfaces and grain boundaries. Sulfur (S) contamination especially increases this rate due to its low melting point, thus increasing the surface diffusion rate (54). However, removal of S through additions of cerium (Ce), a reactive rare-earth element, or titanium (Ti) allows boron (B), Cu, and nitrogen (N) to preferentially segregate to creep cavity surfaces.

This has shown that segregation of B or Cu and the precipitation of BN to the creep surfaces greatly decreases creep growth, thereby improving overall mechanical properties in modified type 304 and 347 stainless steel (modifications include additions of Ce, Ti and/or B). This autonomous healing is accelerated at the elevated testing temperatures, first filling the creep cavity and then blunting creep cavity progression. Therefore, by decreasing the largest defect size within the material, the material life-span is increased.

In addition to the issues raised regarding self-healing in Al alloys, dynamic precipitation for creep prevention in steels suffers from another issue; the self-healing ability of the modified steels does not prevent creep cavities from forming, it only hinders their growth. With time, more cavities will be created and cause ultimate failure despite the healing capability of the steel alloys.

**Reactive Element Coatings**

Self-healing for corrosion protection has been used extensively since the addition of large amounts of chromium (Cr) (>11%) was added to steel to form a protective oxide (55). Recent research has centered on passivation of metal surfaces using chromate-
based coatings for corrosion protection, especially in alloys; articles detailing potential “self-healing” properties can be first found in literature no later than the early 1950s (56). In the decades following, advancement of chromate conversion coatings (CCC) continued into new chemistries, processes, and applicable metals available for coating; a thorough review was completed by Kendig and Buchheit (57). Unfortunately, the mobility of Cr\(^{6+}\) in biological systems and reactivity with oxidation mediators, being linked with DNA damage and lung cancer, and has lead to the regulation and elimination of CCCs and other Cr-based chemicals across numerous industrial processes (58).

In terms of non-chromate corrosion prevention in metals, research can be grouped into three categories: 1) hypervalent transition metals [e.g. molybdenum (Mo), vanadium (V), Mn], 2) transition metal [e.g. zirconium (Zr), hafnium (Hf)] or covalent oxides [e.g. silicon (Si), germanium (Ge)], and 3) rare-earth metal coatings (57). Of these three, only the rare earth (RE) metal-containing coatings have shown promise as “drop-in” replacements for traditional CCCs, both through corrosion prevention and self-healing ability, also known as active corrosion protection (ACP) (59). A review of the rare earth lanthanide series, especially Ce salts, was completed by Bethencourt et al. (60).

The latest research into reactive element additions (e.g. yttrium (Y), lanthanum (La), Zr, Ce) has shown the most positive effects, including slowing scale growth and increasing oxide adhesion (61). The most widely accepted explanations for these reactive element effects are a high oxygen dissociation rate (62) and scavenging of coating impurities (namely S) after deposition (63, 64).
Limitations of self-healing metallic coatings are the continual reparation of the oxide surface protecting the underlying alloy. The loss of matter will slowly reduce the reservoir of the oxide-former, thus further use of the coating will continue to reduce the potential for healing within the coating.

**Liquid-Assisted Healing in Metallic Systems**

Liquid-assisted self-healing has on-going research in both electrical and structural composite applications. For electronic applications, research into autonomous self-healing has been realized through a low melting eutectic alloy of gallium-indium. For metal-matrix composites, the focus has been along two fronts: 1) addition of thin tubes filled with low-melting point alloys which break in-service, allowing for material to flow out and fill a crack during a healing cycle and 2) shape-memory alloy (SMA) reinforcements to enable crack closure during an elevated temperature healing cycle which allows for partial liquefaction of the matrix to enable healing.

**Eutectic Gallium-Indium**

Electrical applications utilizing liquid-assisted healing methods focus on eutectic gallium-indium alloy (referred to as EGaIn). This alloy, Ga-25wt%In, possesses a high electrical conductivity, $3.4 \times 10^4$ S/cm which flows at a critical surface stress (65). Being liquid at room temperature (melting point = 16°C), the alloy readily forms a thin, passivating oxide surface which enables its use in forming metastable, non-spherical structures. Early work using this alloy for electrical applications was conducted by researchers at Harvard University (66, 67).

Researchers at North Carolina State University have developed a self-healing antenna based on EGaIn (68). The antenna is created by injecting EGaIn into micro-channels within poly(dimethylsiloxane) (PDMS), which is used for structural stability.
This composite structure enables the antenna to be mechanically tuned through elongation, while also maintaining flexibility and a radiation range efficiency of 90% from 1910-1990 MHz. The team found the antenna possessed repeatable, autonomous self-healing. When cut with a razor blade, the electrical resistivity was returned to pre-cut values upon the removal of the blade no matter how many times the antenna was cut.

Electrical devices developed by collaborators at the University of Illinois (UI) have also used EGaIn to heal defects (65). They demonstrated autonomous healing in less than one millisecond with over 99% recovery of conductivity using microencapsulated EGaIn layered above patterned gold (Au) lines on a glass substrate. During a crack event, decreasing conductivity of the device to near zero, the EGaIn-filled capsules are ruptured, allowing the liquid metal to flow into the crack and restore conductivity to pre-crack levels. The physical characteristics post-healing, specifically strain and fracture toughness values associated with in-service device application, have yet to be examined.

**Metal-Matrix Composites**

Research into self-healing of metal matrix composites first began at Northwestern University under the direction of Olson. This work was motivated by a hierarchical systems design methodology in an effort to elucidate processing-structure-property-performance relationships (69, 70). Early research consisted of a ferrous matrix aided by continuous SMA reinforcement. The composite, investigated by undergraduate design teams (26, 71, 72), consisted of a ferritic superalloy matrix reinforced with austenitic SMA wires. The austenitic SMA wires consisted of $\gamma'$ precipitates in a face-centered cubic (FCC) $\gamma$ phase.
Further research investigated a different Fe-based self-healing tank for turbine engines. A composition of Fe – 12.55 wt% Ni – 25 wt% Co – 12.5 wt% Cr – 2 wt% Al – 0.9 wt% Ti was investigated (72). The temperature variance between “cold” engine and the running temperature of the engine results in severe cracking during service due to thermal fluctuations. A self-healing composite tank could heal these cracks as the temperature increases because of the clamping force from SMA fibers embedded in the matrix.

The doctoral student overseeing these undergraduate projects, Files, completed his thesis work on an Fe-based B2 NiAl intermetallic superalloy matrix reinforced with austenitic SMA wires (25, 73). His thermodynamically designed Fe-27.6Ni-18.2Co-4.1Ti-1.6Al SMA wires were heat-treated to obtain Ms and As temperatures near room temperature. Up to 5% strain, he was able to demonstrate full recovery of the original length after unloading and heating the SMA wire. His research also showed stable crack growth and crack bridging from the SMA wires in the Fe-based composite. However, during all the Fe-based composite research, complete healing was not realized; poor wettability, intergranular fracture in the SMA wire, and oxidation of the crack interface were blamed.

Despite setbacks in ferrous-based alloys, Files (25) developed a prototype Sn-Bi matrix alloy reinforced with NiTi SMA composites which demonstrated over 80% healing. Further research into a Sn-Bi-In matrix was investigated by another undergraduate team in 1997 and crack closure and healing were realized (74). Because of wettability problems between the matrix and NiTi wires, Bernikowicz (75) focused on knots in the SMA wires to added mechanical adhesion. She also added flux to the crack
interfaces to prevent oxidation during a healing cycle – the composites display 88% recovery of strength. Other student projects investigated incorporation of flux to the matrix to enable in-situ fluxing during a healing cycle (76, 77).

Using both Sn-Bi and Sn-Bi-In based composites, Knapp (78) optimized the liquid fraction in the matrix during healing. He concluded between 15-20% liquid in the matrix during healing balanced structural stability requirements while maintaining enough liquid phase to enable complete healing. Other undergraduate design teams investigated addition of electronic systems to the Sn-based composite systems (71, 79).

Manuel (80) was able to improve healing to over 94% in the Sn-Bi prototype system by coating the NiTi SMA wires with gold to improve adhesion with the matrix. Finite element modeling (FEM) of this self-healing composite system was completed by Burton et al. (81). They demonstrated crack bridging and crack closure from the SMA wires through a one-dimensional constitutive model of the NiTi wires. The model also confirmed the requirement to pre-strain the SMA wires prior to healing in order to create a critical clamping force to enable healing.

An investigation by another undergraduate team to design Mg- and Al-based matrices reinforced with high strength NiTi-based SMA wires for use in self-healing composites was also conducted (82), but samples were not fabricated. However, in Manuel’s thesis (80), she investigated a Mg - 5.7 at% Zn - 2.7 at% Al matrix reinforced with both commercially available NiTi SMA wires and prototype, nanodispersion strengthened SMA wires developed by Jung (83) in his doctoral thesis. The prototype Ni – 32 at% Ti – 3 at% Al – 15 at% Zr wires had similar processing temperatures to those found in the Mg-based composites.
Manuel’s findings show a 160% increase in uniform ductility in the composite and a 40% increase in strength over cast AZ91 commercial alloys (80, 84, 85). Healing behavior was limited due to the oxidation behavior of the Mg alloy in the liquid state, even when samples were vacuum encapsulated during healing heat treatments. However, the strength and thermomechanical models developed will assist with design considerations for future composite development.

A group of researchers at the University of Wisconsin-Milwaukee (UWM) have also investigated healing in metal castings. Initial investigations explored eutectic Sn-Bi infiltrated alumina balloons (86, 87) and an off-eutectic healing model is based on non-homogenous dendrites (88) with only minor success. However, the bulk of the UWM work has focused on filling hollow ceramic tubes with the low-melting alloy and embedded these within an Al matrix to form a self-healing composite (86, 87, 89-92). A crack is introduced into the composite, breaking the ceramic fibers, before the composite is placed into a furnace and heated above the solder melting temperature. Upon cooling, the composite microstructure is investigated. Recently, a composite consisting of 206 Al alloy as a matrix with hollow quartz tubes filled with an 802 Al brazing alloy has shown self-healing potential (87), but bonding behavior was limited between the low melting alloy and the stronger matrix alloys.

**Liquid-Assisted Healing Methodology**

Liquid-assisted healing using SMA reinforcements for crack closure has several advantages over other metals-based self-healing techniques for structural components including faster healing kinetics, the ability to repair large scale defects, and the possibility of repeatable self-healing. The research is based on the concept of crack
healing through partial liquefaction of the matrix material in the presence of a clamping force applied by SMA wires embedded in the matrix.

As shown in Figure 2-2, the composite, consisting of a matrix reinforced with longitudinally aligned SMA fibers, has a crack initiated. The matrix fails but the SMA wires stay intact due to their high strength relative to the matrix. Once the crack spans the entire width, the load is transferred completely to the SMA wires. This induces a local stress-induced transformation at the crack site. Upon removal of the load, two different effects can occur within the SMA wires based on their microstructural state. If in the austenite phase, the wires will be pseudoelastic and immediately revert back to their original (shorter) shape, resulting in crack closure (93). If in the martensite phase, the wires will remain elongated until the composite temperature is raised above their austenite finish ($A_f$) temperature. Concurrently, the increase in temperature creates a partially liquefied matrix, enabling crack filling and matrix softening. This matrix softening enables the removal of plasticity in the composite acquired during fracture as the SMA wires revert to their original length. Subsequently, cooling results in a solidified composite able to realize its pre-cracked strength. A detailed description of the shape memory effect is provided in the following section.

**Shape Memory Alloys**

Shape memory alloys (SMA) benefit liquid-assisted self-healing composites because of their ability to apply a clamping force at a crack interface with elevated temperatures. SMAs are characterized by their ability to recover apparent permanent strains through thermoelastic martensitic transformations (93). The material transforms its crystal lattice through a shearing deformation as a result of cooperative atomic movement in response to applied loads.
Figure 2-2: Schematic of liquid-assisted healing in a MMC reinforced with SMA imbedded wires. Starting at the top at $T_{\text{room}}$, a crack initiates in the matrix. Further propagation causes matrix failure and a stress-induced transformation in the SMA wires. Increasing $T > A_s$ will initiate crack closure from the wires. Further increases will cause a clamping force to push the crack faces together while partial liquefaction of the matrix via low-melting eutectic heals the crack. Cooling enables solidification of the matrix and full functionality.

SMAs possess two basic phases – the cubic, high temperature austenite phase and the monoclinic, low temperature martensite phase (94). There are four characteristic temperatures in all SMAs: 1) martensite start ($M_s$), the temperature at which the material initiates a martensitic phase transformation, 2) martensite finish ($M_f$), the temperature at which the martensite transformation is complete, 3) austenite start ($A_s$), the temperature
at which the material begins transforming from martensite to austenite, and 4) austenite finish (Aᵢ), the temperature at which the austenite transformation is completed. Depending on the starting phase of the alloy, austenite or martensite, the material will exhibit the pseudoelastic or shape memory effect, respectively. A schematic of phase changes in SMAs is shown in Figure 2-3.

Figure 2-3: Schematic of phases present in NiTi-based shape memory alloys. The red circles represent Ti and the blue circles represent Ni. The cycle from 1-3 represents the shape memory effect and the cycle from 4-3 represents the pseudoelastic effect. Adapted from Wayman, C. M., and Duerig, T. W. 1990. “An Introduction to Martensite and Shape Memory,” in Engineering Aspects of Shape Memory Alloys (page 3-20). Butterworth-Heinemann, United Kingdom.

In the Figure 2-3, the austenite phase (in the absence of applied load) can be cooled (1) below its Mᵢ to the twinned martensite phase; this results nearly zero volume or shape change (94). Deformation (2) in the twinned martensite phase causes the twins to reorient along a dominant orientation, becoming detwinned martensite. Heating (3) the detwinned martensite above its Aᵢ temperature causes the reversion to the
austenite phase in the same configuration the material started in. The cycle 1-2-3 is known as the shape memory effect.

It has also been shown an increase in stress within the SMA at a given temperature will result in higher martensite and austenite transition temperatures (93) (Figure 2-4). This is due to the equivalence between temperature and stress in stabilizing the martensite phase (95). Therefore, a mechanical transformation between austenite and martensite is also possible. Looking back at Figure 2-3, if the SMA is in the austenite phase and a load being applied, a stress-induced transformation (4) to martensite will result. When the load is removed (3), the material immediately reverts back to its original austenite shape. This cycle, 4-3, is referred to as the pseudoelastic effect.

![Figure 2-4](image)

**Figure 2-4:** Schematic showing how the transition temperatures ($M_s$ and $A_s$) are changed as a result of applied stresses. Adapted from Wayman, C. M., and Duerig, T. W. 1990. “An Introduction to Martensite and Shape Memory,” in Engineering Aspects of Shape Memory Alloys (page 3-20). Butterworth-Heinemann, United Kingdom.

Both of these behaviors, the shape memory effect and pseudoelasticity, have potential to be utilized to aid in self-healing in metallic components (27).
Shape Memory Alloys in Composites

Prior to their use in liquid-assisted self-healing MMCs, SMA reinforcements garnered significant attention because they have been found to increase the flow stress of the composite (96). Because of their inherent ability to transform shape, SMAs have also found use as reinforcements to enable crack closure (97-99). The role of interfacial debonding was investigated and important factors include composite temperature (100) and martensitic transformations as it relates to interfacial shear stress (101). Early studies of SMA reinforcements in MMCs, especially Al-based matrices, showed similar strengthening and crack-closure characteristics (102-104).

The use of SMA reinforcement inclusion in polymer-matrix composites (PMC) for enhanced healing properties revealed the need for optimization of fiber volume fraction and pre-straining the SMA to decrease interfacial debonding (105). Recently, SMAs have also been used to enable crack closure, thereby increasing crack healing (106). The SMA wires decrease the crack volume, thereby increasing the fill factor of the healing agents utilized in PMC. This is akin to the research in liquid-assisted self-healing in metals with SMA reinforcements.

Summary

There are two major types of self-healing in metallic systems: solid-state and liquid-assisted. Solid-state healing has been investigated for fatigue and creep crack reduction in Al and Fe-based alloys, in addition to being utilized for self-healing coatings. Liquid-assisted healing has found applications in both electrical and composite materials. Solid state healing, however, is limited in applications due to defect size constraints and the reduction of healing material after each heal cycle. Liquid-assisted healing, however, has the advantage of faster healing kinetics due to the liquid phase.
Also, within SMA-reinforced metal-matrix composites, the possibility to heal macro-scale defects is realized using liquid-assisted healing techniques because of the inherent shape-changing abilities of SMAs, making them the best candidate for further development.

While the research at Northwestern advanced the field of liquid-assisted self-healing, it also left several open questions to be addressed regarding the matrix: 1) how can oxidation be mitigated during a healing cycle, 2) the optimum time and temperature for a healing cycle, and 3) how percent liquid affects healing in non-Sn based matrix systems. In regards to the incorporation of SMAs in the composite, the effect of volume fraction of SMA wires on healing as well as the effect of casting and heat treatment on the SMA transition temperatures has also yet to be fully vetted. And finally, the most important question to be addressed, can self-healing be demonstrated in a high strength composite system able to be used as a structural material?
CHAPTER 3
PROTOTYPE SELF-HEALING COMPOSITE

Early work into self-healing metal-matrix composites was based on a prototype system developed by Files (25) and Manuel (80) which consists of a Sn-Bi matrix continuously reinforced with commercially available NiTi shape memory alloy (SMA) wires. This matrix alloy system was selected because it has a low cost, low melting temperature, and good castability. In addition to being part of two doctoral students' thesis work (25, 80), several undergraduate student projects were also conducted to investigate healing within the Sn-Bi composite system (26, 71-77, 79, 82).

This chapter will seek to improve upon this earlier work by investigating whether healing in Sn-Bi can be established while using a mechanical means of attaching the matrix and wires. First, the design methodology for self-healing in a Sn-Bi composite is discussed, which lays the groundwork for the design of future higher strength alloys in subsequent chapters. Second, Sn-Bi composites were fabricated into tensile test geometries and fractured under different heat treatment conditions to demonstrate the effects of crack healing. Next, these composites are compared to Sn-Bi alloy properties to understand the effect of SMA wire inclusion on the mechanical properties. The SMA wire mechanical and thermal properties were also investigated to determine how the healing heat-treatments modify the NiTi wire properties. Finally, an investigation was conducted to determine the clamping force required from the SMA wires to achieve healing in the Sn-Bi matrix.

Design Methodology

Using the thermodynamic modeling software Pandat by CompuTherm, LLC (107), the Sn-Bi phase diagram was calculated using the NIST Pb-free solder database
The calculated diagram was noted to be a simple binary eutectic, and matched experimental results available in the literature.

![Image of the Sn-Bi phase diagram](image_url)

**Figure 3-1**: Calculated Sn-Bi phase diagram using NIST Pb-free solder database (108).

For Sn-Bi alloys, the Sn-rich side of the diagram yields moderately ductile alloys with high castability (55). It can be observed that the composition of Sn – 21 wt% Bi (Sn - 13.1 at% Bi) yields the largest temperature range between the eutectic temperature and the liquidus temperature. A large solidification range yields gradual melting during heat-treatments. This ensures that small fluctuations of temperature are not likely to significantly modify the microstructure during heat treatment. At this composition, it was calculated that at 169°C the alloy would be 20% liquid with the balance being Sn solid-solution phase (Figure 3-2). Therefore, 169°C was utilized as the healing temperature for this composition. It is important to note that previous studies have shown 20% liquid
at the healing temperature results in a balance between enough healing agent, i.e. liquid eutectic phase, while still maintaining structural stability throughout the heat treatment (78). With a fluctuation of $5^\circ C$ above or below $169^\circ C$, it was calculated the percent liquid could fluctuate between only 15.6-25.1%.

Figure 3-2: Phase fractions of Sn – 21 wt% Bi at various temperatures. The heat-treatment temperature of $169^\circ C$ reveals a 20% liquid composition during the healing process. The box signifies the potential area of liquid % should the temperature fluctuate by $\pm 5^\circ C$ during heat-treatment.

**Sn-Bi Matrix Alloy Characterization**

Alloys of Sn – 21 wt% Bi were cast to investigate the matrix alloy mechanical properties. Appropriate amounts of tin (Sn shot, 99.8%, Alfa Aesar) and bismuth (Bi needles, 99.99%, Alfa Aesar) were melted in an open-air furnace at $350^\circ C$ until a liquid solution. The Sn-Bi melt was poured into a graphite mold and allowed to cool. After casting, matrix compositions were verified via inductively coupled plasma (ICP)
spectroscopy (Perkin-Elmer Plasma 3200RL) and found to vary less than 2% from the nominal composition. The tensile bars were placed horizontally into a furnace for 24 hours at 169°C then air-cooled (Figure 3-3). An external thermocouple was utilized to monitor the stability of the furnace temperature. The heat-treatment sets the matrix microstructure to ensure it is comparatively the same before and after a healing cycle.

After air-cooling post heat-treatment, each alloy was polished to a 320-grit surface finish. Tensile testing was completed on an Instron 5582 until failure. Tabulated results of the testing are found in Table 3-1. Graphs of the tensile results can be found in Appendix A.

![Figure 3-3: Representative microstructure of Sn-Bi composite. The dark areas are the eutectic separating the lighter Sn solid solution phase.](image)

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Modulus (GPa)</th>
<th>0.2% Yield Stress (MPa)</th>
<th>Ultimate Stress (MPa)</th>
<th>Failure Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25.9</td>
<td>68</td>
<td>87.5</td>
<td>3.5</td>
</tr>
<tr>
<td>2</td>
<td>23.1</td>
<td>69</td>
<td>90.1</td>
<td>3.3</td>
</tr>
<tr>
<td>3</td>
<td>24.3</td>
<td>67</td>
<td>88.9</td>
<td>2.6</td>
</tr>
<tr>
<td>Avg.</td>
<td>24.4</td>
<td>68</td>
<td>88.8</td>
<td>3.1</td>
</tr>
<tr>
<td>± 1σ</td>
<td>1.4</td>
<td>1</td>
<td>1.3</td>
<td>0.5</td>
</tr>
</tbody>
</table>
NiTi Wire Preparation

The NiTi SMA wires, designated BH-0075 (Ni = 50.6 at% Ti, Ø = 0.18 mm, cold drawn, Memory Corporation) were prepared by vacuum-encapsulating the wires and heat-treating for 3 hours at 500°C. Previous research had shown the as-received, cold-drawn condition of these wires is inadequate for shape memory, therefore a heat-treatment is required prior to casting (80). Since load transfer requires that the matrix be bonded to the NiTi SMA wires, chemically reactivity at the interface is an important criterion. The driving forces for reactivity can be realized using an Ellingham diagram (110). An Ellingham diagram highlighting the constituent phases and elements at the interface are shown in Figure 3-4. It can be seen that the relative stability of TiO$_2$ in comparison to Bi$_2$O$_3$ and SnO$_2$ illustrates the low reactivity between the Sn-Bi matrix and NiTi wires.

![Ellingham diagram](image)

Figure 3-4: Ellingham diagram showing the relative free energy calculations for Sn, Bi, Ni, and Ti. It is shown that any TiO$_2$ formed on the surface of the NiTi SMA wires is unlikely to be reduced by the Sn-Bi matrix. Curves plotted with free energy data obtained from (110).
Previous research has confirmed the poor bonding between the Sn-Bi matrix and NiTi reinforcement (75, 80, 84). These earlier studies mitigated this issue by coating the NiTi wires with a thin layer of gold to improve adhesion with the matrix. However, the present research sought to establish a connection via mechanical attachment, i.e. knots in the wires. Thus, in the area of the wires which would correspond to the grip section of a tensile bar, knots were tied to act as mechanical anchors and compensate for the low chemical bonding between the reinforcement and matrix.

With the NiTi wires prepared, a sub-size tensile bar graphite mold, with measurements based on ASTM E8M: Standard Test Methods for Tension Testing of Metallic Materials (111), with specially designed mold ends to anchor the wires was machined (Figure 3-5a). The mold ends had holes cut through them to enable the incorporation of the SMA wires prior to casting. Appropriate amounts of tin (Sn shot, 99.8%, Alfa Aesar) and bismuth (Bi needles, 99.99%, Alfa Aesar) were melted in an open-air furnace at 350°C until a liquid solution. Three wires were placed into the mold and aligned longitudinally; each wire was clamped on the ends, outside the mold, to prevent the wires from shifting during casting. The Sn-Bi melt was poured over the wires into the mold and allowed to cool (Figure 3-5b). After casting, matrix compositions were verified via inductively coupled plasma (ICP) spectroscopy (Perkin-Elmer Plasma 3200RL) and found to vary less than 2% from the nominal composition. Each tensile bar was then placed horizontally into a furnace for 24 hours at 169°C then air-cooled. An external thermocouple was utilized to monitor the stability of the furnace temperature.

After air-cooling, the virgin composites were polished to a surface finish of 320-grit. Each composite bar was tested in tension using an Instron 5582 mechanical testing
Figure 3-5: Images of mold used in casting metal-matrix composites with SMA wire reinforcements: a) specially designed mold end with holes for wire incorporation during casting and b) entire mold with Sn-Bi matrix cooling after being poured over the wires.

machine (strain rate = 1.0%/min) with an extensometer (Model 3542, Epsilon Technology Corporation) attached to the gauge area. The bars were pulled to complete failure of the matrix while maintaining the integrity of the NiTi wires. Results for the virgin composite testing can be seen in Table 3-2. Curves of the representative stress-strain behavior can be found in Appendix A. The large standard deviations for the strength values are attributed to the poor wetting properties of the Sn-Bi melt on the NiTi wires, which results in poor chemical bonding and thus low load transfer between the matrix and reinforcement (112). This is despite the knots tied into the wires to maintain a mechanical attachment.

The composites were then placed on a steel plate and vacuum-encapsulated. Each was laid horizontally in the furnace and heat-treated again for 24 hours at 169°C. Concurrently, the heat treatment causes the NiTi wires to begin to return to their previous shape and a partial liquefaction within the Sn-Bi matrix to occur. Upon air
Table 3-2: Average mechanical testing results for Sn – 21 wt% Bi matrices reinforced with <0.5 vol% SMA wire reinforcements

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Vf Wires (%)</th>
<th>Modulus (GPa)</th>
<th>0.2% Yield Stress (MPa)</th>
<th>Ultimate Stress (MPa)</th>
<th>Failure Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.31</td>
<td>23.6</td>
<td>71</td>
<td>90.7</td>
<td>4.3</td>
</tr>
<tr>
<td>B</td>
<td>0.37</td>
<td>22.3</td>
<td>59</td>
<td>72.5</td>
<td>5.9</td>
</tr>
<tr>
<td>C</td>
<td>0.40</td>
<td>23.4</td>
<td>57</td>
<td>72.9</td>
<td>1.9</td>
</tr>
<tr>
<td>Avg.</td>
<td>0.36</td>
<td>23.1</td>
<td>62</td>
<td>78.7</td>
<td>4.0</td>
</tr>
<tr>
<td>± 1σ</td>
<td>0.04</td>
<td>0.7</td>
<td>7.6</td>
<td>10.4</td>
<td>2.0</td>
</tr>
</tbody>
</table>

cooling, it was observed the wires had returned back to their original length as the matrix was deformed back to its pre-strained (virgin) length. The composites were tested in tension again. Each composite was found to fail again at the same area as the original crack. The tension results were compared to the previous virgin composite tensile data to quantify the healing efficiency (Table 3-3). Healing is established by comparing the ultimate tensile strength (UTS) of the healed and virgin composite tests via the following equation proposed by Manuel (80):

\[
\frac{UTS_{Healed}}{UTS_{Virgin}} \times 100\% = \% \text{ Healed} \\
\text{(Eq. 3-1)}
\]

Table 3-3: Healing characteristics of Sn-Bi composites

<table>
<thead>
<tr>
<th>Specimen</th>
<th>'Healed' UTS (MPa)</th>
<th>% Heal</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>73.0</td>
<td>80.5</td>
</tr>
<tr>
<td>B</td>
<td>68.2</td>
<td>94.1</td>
</tr>
<tr>
<td>C</td>
<td>49.6</td>
<td>68.1</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>80.9</td>
</tr>
</tbody>
</table>

A representative tensile comparison of specimen ‘B’ is shown in Figure 3-6. Crack healing in a Sn-Bi composite is shown in Figure 3-7. The healed composites were found to retain similar strength values as the virgin composite, but none reached elongations above 1.5%. Using this method for Sn-Bi composite development, it was established that over 94% healing was achievable in <0.5 vol% NiTi reinforced Sn-Bi
composite. These percent heal results were similar to those obtained by Files (25, 73) and Manuel (80, 84).

Figure 3-6: Mechanical testing results of Sn-Bi Composite ‘B’ (Vf wires = 0.37%) in virgin and healed condition. This healed condition was found to retain over 94% of the UTS of the virgin condition.

Figure 3-7: Image showing crack healing in a Sn-Bi composite. The top image is following tensile testing, the bottom image shows the same sample immediately following the healing heat-treatment.
When comparing Table 3-2 to Table 3-3, it was found that the specimens possessing the greater failure strains were also found to obtain a greater healing percent. A schematic showing the different steps during a tensile test and healing as it relates to the NiTi wires is shown in Figure 3-8. In the figure, image A represents the composite as it begins to be pulled in tension by the applied stress ($\sigma_a$) at room temperature ($T_{room}$). This represents the normal length of the SMA wires when in the twinned martensite state. By image B the ductility of the composite has increased the length of the NiTi wires as the wires begin to reorient into detwinned martensite. At this point, a crack begins to initiate within the matrix. After full fracture of the matrix in image C, the load is removed after causing further reorientation of the NiTi into detwinned martensite. In image D, increasing the temperature of the composite above the $A_t$ temperature results in a clamping force exerted on the matrix from the NiTi wires as they revert to their previous shape. This compressive force, paired with softening of the matrix at elevated temperatures, begins to remove the excess length of the composite until the wires reach their initial length. Reducing the temperature back to $T_{Room}$ (which is below $M_f$) transforms the NiTi back into a twinned martensite state.

From a comparison of the results in Table 3-1 for the matrix alloy to Table 3-2 for the composite specimens, it is shown that the modulus and failure strain of the alloys are statistically similar to those in the composite (using a standard t-test with a 95% confidence). However, the alloys possessed strength values greater than the composites (Figure 3-9). This is most likely caused by the lack of bonding between the wires and the matrix.
Figure 3-8: Schematic of changes to the NiTi SMA wires during a composite healing cycle. In A), the stress is applied ($\sigma_a$). Image B) shows lengthening of the SMA wires as a crack initiates in the matrix. Full fracture of the matrix occurs in C), resulting in reorientation of the NiTi to detwinned martensite. Increasing the temperature above $A_t$ in D) results in a compressive force from the NiTi wires as they begin to transfer to austenite. The initial length of the composite is recovered, as cooling of the composite in E) transforms the wires back to a twinned martensite state.

Figure 3-9: Representative tensile results for Sn – 21 wt% Bi alloy ‘2’ compared to the Sn-Bi composite ‘B’ ($V_t$ wires = 0.37%).
NiTi Mechanical Testing

Previous research has shown the thermal and mechanical properties of NiTi SMAs can be modified through heat-treatment (113). Therefore, an investigation was conducted on the NiTi SMA wires utilized for the Sn-Bi composites to determine how the heat-treatments affect the wire properties. Thermal properties to be investigated include the martensite and austenite transition temperatures to confirm the crystal structure of the NiTi wires throughout the healing process. Mechanical properties to be investigated include the plateau stress and the failure stress. The plateau stress is the stress required to transform twinned martensite into detwinned martensite. The failure stress is the maximum stress the SMA wires can reach before wire failure. As the Sn-Bi composites fail within the matrix but the wires remain intact, this stress is an important design factor because the SMA wires must be strong enough to handle the load previously shared with matrix without breaking.

Pieces of the BH-0075 NiTi wire in the as-received condition were placed in to a Perkin-Elmer 8000 Differential Scanning Calorimeter (DSC). Each was cycled 3 times from -50 – 200°C at 10°C/minute to investigate the austenite & martensite transition temperatures of the wire. No transformation was seen in the as-received condition due to the high level of cold work reducing twin boundary mobility, and thus the shape memory effect (94). Therefore, no austenite or martensite start/finish temperatures are reported. Other BH-0075 wires were vacuum-encapsulated in Pyrex tubes and heat-treated for 3 hours at 500°C and then tested under similar conditions. Another set of wires were vacuum encapsulated in Pyrex tubes and heat-treated for 3 hours at 500°C, cooled, and then heat-treated for 24 hours at 169°C before being tested on the DSC to simulate Sn-Bi composite heat-treatment conditions. The average and standard
deviation for 3 wires under each condition are shown in Table 3-4. The transition
temperatures as reported were calculated using the onset method (114). It was found
that the low temperature (169°C) required for healing in the Sn-Bi composite had little
effect on the NiTi wire martensitic transition temperatures.

Table 3-4: The austenite and martensite transition temperatures for heat-treated NiTi
SMA wires

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Transition Temperatures (°C) [Avg. ± 1σ]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A_s$</td>
</tr>
<tr>
<td>500°C for 3 hrs</td>
<td>113.8 ± 0.3</td>
</tr>
<tr>
<td>500°C for 3 hrs, 169°C for 24 hrs</td>
<td>92.3 ± 0.7</td>
</tr>
</tbody>
</table>

Mechanical testing of similarly heat-treated NiTi wires was also conducted.

Similar heat-treatments of the wires were conducted as above and pulled until failure on
an Instron 5582. The plateau stress and failure stress were both noted (Table 3-5). Representitive curves of the tensile behavior can be found in Appendix A. The initial
heat-treatment at 500°C was found to greatly decrease the failure stress, but enabled
the appearance of mobile twin boundaries (113) and thus a martensitic transformation
as shown by the plateau stress. Subsequent heat-treatment at 169°C was found to have
little effect on the plateau and failure stress of the NiTi wires. Representative curves of
the tensile stress-strain behavior can be found in Appendix A.

Table 3-5: Mechanical testing results for heat-treated NiTi SMA wires

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Plateau Stress (MPa)</th>
<th>Failure Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Received</td>
<td>N/A</td>
<td>1491 ± 53</td>
</tr>
<tr>
<td>500°C for 3 hrs</td>
<td>190 ± 5</td>
<td>1183 ± 5</td>
</tr>
<tr>
<td>500°C for 3 hrs, 169°C for 24 hrs</td>
<td>190 ± 5</td>
<td>1163 ± 7</td>
</tr>
</tbody>
</table>
To determine if the casting process had any effect on the mechanical properties of the SMAs, one of the Sn-Bi composites with heat-treated NiTi reinforcements was heat-treated for 24 hours at 169°C and air-cooled, then heat-treated again for another 24 hours at 169°C. This was to match the wire mechanical properties found in a post-healed Sn-Bi composite. The composite was then placed into a solution of 2:1:1 water (H₂O), nitric acid (HNO₃), and hydrochloric acid (HCl) until the Sn-Bi matrix was completely dissolved away leaving only the NiTi wires. Each of the three wires was then pulled in tension until failure. Results are found in Table 3-6 whereas the stress-strain curves can be found in Appendix A. It was determined that the casting process and heat-treatments had little effect on the NiTi wires other than a small increase in the plateau stress.

Table 3-6: Mechanical properties of wires removed from heat-treated Sn-Bi composite

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Plateau Stress (MPa)</th>
<th>Failure Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500°C for 3 hrs</td>
<td>222 ± 10</td>
<td>1187 ± 25</td>
</tr>
<tr>
<td>169°C for 24 hrs (2x)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Pressure Requirements for Healing

In order to quantify the relationship between clamping force and crack healing ability, interface diffusion studies were conducted utilizing a Kovar diffusion couple setup. This work was performed in conjunction with an undergraduate senior thesis by W. Patterson Tuttle (115). Kovar was selected as the material for the diffusion couple jig because it exhibits very low thermal expansion (25-200°C = 5.5 x 10⁻⁶/°C) over the temperature range studied for self-healing in Sn-Bi (116). The Sn – 21 wt% Bi alloy bar was cast and then heat-treated in air for 24 hours at 169°C to set the microstructure. After cooling, pieces were cut from the bar and polished to a 320-grit surface finish. A
slice was cut through the center of the specimen to simulate a crack interface. Both sides of this interface were polished to a 4000-grit finish in order to ensure a smooth contact surface. After polishing, the pieces were loaded into the custom Kovar diffusion couple jigs which minimize pressure effects from the coefficient of thermal expansion caused by the jig itself (Figure 3-10). Pressure was applied to the sample via a torque wrench. The torque wrench was calibrated to yield specific forces at various torque levels, thus allowing for varied pressures to be applied to the Sn-Bi pieces.

![Healed Interface](image)

Figure 3-10: Image of Sn-Bi alloy loaded into the diffusion couple jig post heat-treatment. Note the central interface used to simulate a crack has been healed.

Each jig and specimen setup was vacuum-encapsulated in a Pyrex tube and heat-treated for 24 hours at 169°C to heal the interface. After air-cooling, the healed composite was pulled in tension via the Instron 5582 mechanical testing machine. Results are shown in Figure 3-11 using the metric defined in Equation 3-1 where the \( \text{UTS}_{\text{virgin}} \) is 88.8 MPa. It is shown 30 MPa of stress is required to obtain the highest post-healing strength – this equates to slightly less than 50% of the room temperature yield strength found in the Sn-Bi alloys (Table 3-3). At greater stresses, the sample deformed and this is thought to have prevented the full compressive pressure from facilitating healing within the sample. It is likely the compressive yield strength of the Sn-Bi matrix was reached at 40 MPa, the highest pressure, which would explain the
deformation of the sample’s shape, as well as the decrease in healing percent. Figure 3-12 shows the healed microstructure of the specimen compressed at 30 MPa.

Figure 3-11: Comparison of tensile results from Sn-Bi pieces compressed at various stresses during healing to simulate the clamping force from SMA wires.

Figure 3-12: Microstructure along interface of healed Sn-Bi alloy compressed at 30 MPa. Note the grain growth across the previous interface line. The black areas are pores likely caused by wedge-type creep cavitation.
As seen in Figure 3-12, pores were evident along the healed interface. When investigating the fracture surfaces of the healed alloys, porosity was found to be present on every sample. The pores were also noted to increase in size (Figure 3-13) but reduced in total area of the interface as the applied stress increased. At 20 MPa, they represented 23.4% of the interface, at 30 MPa, 22.8%, and at 40 MPa 21.4%. Due to the nature of the cavities being present at a fixed stress in elevated temperatures and found at grain boundary triple points, they were determined to be wedge-type (w-type) creep cavities (117). These cavities represent areas of the sample which were not healed, thereby reducing the strength of the interface because less material has joined together, and thus reducing the calculated percent healing due to this reduction in strength. Re-calculating the percent heal while taking this reduction in area into account, the values all increase: 20 MPa = 46.0%, 30 MPa = 106.5%, and 40 MPa = 73.3%.

Figure 3-13: Scanning electron microscopy (SEM) image of the crack face for Sn-Bi alloys healed at a stress of a) 20 MPa, b) 30 MPa, and c) 40 MPa after tensile testing. Note how the size of individual cavities tends to increase with an increase in stress.

Summary

A methodology to design a self-healing metal-matrix composite was described. Sn – 21 wt% Bi composites with < 0.5 vol% of SMA wires were fabricated and found to possess an average of 80% healing, with a high value of over 94% retained strength.
post-healing. These composites were compared to Sn-Bi matrix alloys and statistically found to possess similar mechanical properties. The NiTi wires were investigated to determine how casting and heat treatments varied their mechanical properties. It was found that the healing cycle had only a minor effect on the mechanical and thermal properties of the heat-treated SMA wires. Finally, it was established the SMA wires needed to provide 30 MPa of stress to obtain the greatest healing efficiency in a Sn-Bi matrix.

Due to the weight, strength, and usable temperatures for a Sn-Bi matrix, the above experiments were not intended to establish a Sn-Bi-based composite for industrial application, but instead to serve as a prototype system. This Sn-Bi system assisted in the development of a thermodynamics-based methodology which can be utilized to design greater strength alloys for use as the matrix in a self-healing metal-matrix composite system.

For the next iteration of matrix alloys, several characteristics are desired to enable self-healing MMCs to be utilized for structural applications. First, increase the specific strength of the composite by lowering its overall density and increasing the strength of the matrix. The strength can be increased through using greater strength matrix materials and also through the formation of a chemical bond with the NiTi wires to ensure load transfer. Second, ensure the material has good castability to ensure wetting around the SMA wires. Finally, maintain the high healing efficiency established by the Sn-Bi composite system. The latter point is the most important attribute for future iterations of self-healing MMCs.
CHAPTER 4
SYSTEM DESIGN METHODOLOGY

In light of the positive results found in the Sn-Bi matrix reinforced with NiTi SMA wires as a self-healing composite, further research into higher strength matrix materials was investigated. However, identifying potential matrix alloy systems that can be designed to exhibit self-healing can be a tremendous and tedious undertaking due to the multi-scale effects of the different variables involved. When dealing with systems possessing multivariate interactions, a systematic approach can be used to find the optimal combination of processing steps and microstructures in order to achieve the desired behavior. To facilitate the development of self-healing composites, a systems design approach motivated by thermodynamics was used in determining element selection and processing conditions.

System Design Chart

The design methodology for matrix development utilized for these investigations was based upon systems design method put forth by Jenkins (118). He used flow-block diagrams to describe systems. These diagrams are broken down into sub-systems which can be utilized to organize the overall objective for design. Modifying Jenkins model to illustrate the hierarchical nature of materials fabrication while incorporating the typical processing-structure-properties-performance materials tetrahedron results in a system design chart. System design charts were first developed by Olson at Northwestern University (69, 119-124). Figure 4-1 shows the design aspects for matrix development of a self-healing metal-matrix composite.
Figure 4-1: System design chart for matrix development to be utilized within a self-healing metal-matrix composite

The hierarchical aspect of the systems design chart is shown by having the most important feature higher on the chart in its respective category. The exception is in the ‘Processing’ sub-system, where the hierarchical nature shows the sequence of processing steps for composite fabrication. Each line connecting specific blocks to one another represent specific relationships between the sub-systems. Those lines linking ‘Processing’ and ‘Structure’ sub-systems represent relationships that are thermodynamic or kinetic in nature, whereas between ‘Structure’ and ‘Property’ relationships can be described by empirical or physics based models. This chart will serve as the roadmap which details the direction for alloy design and experimental procedures, and be used to increase efficiency in designing the matrix alloys for use in a self-healing metal-matrix composite.

**Structure-Property Model Development**

The relationships between the ‘Structure’ and ‘Property’ categories shown in Figure 4-1 are physical in nature. The line connecting ‘Composite' with ‘Density’ is given
by the total composite mass \((m_c)\) over the total composite volume \((V_c)\) yielding the total composite density \((\rho_c)\) as shown in Equation 4-1:

\[
\frac{m_c}{V_c} = \rho_c
\]  

(Eq. 4-1)

The relationship between 'Eutectic' and 'Healing Efficiency' is not completely understood at this time. A senior thesis project by Steve Knapp at Northwestern University (78) found that 15-20% eutectic was necessary for healing within a Sn – 21 wt% Bi matrix alloy while still ensuring structural stability. However, it is not known if this will translate directly into other higher strength matrix alloy systems.

The final relationship relates 'Matrix', 'Interface', and 'Reinforcement' to 'Strength'. Using the theory of load sharing within a composite (112), Equation 4-2 shows the volume-averaged loads borne by the matrix and reinforcement in the composite, where \(\sigma = \text{stress}, c = \text{composite}, m = \text{matrix}, f = \text{reinforcement fiber}, \) and \(V_f = \text{volume fraction of the fiber}:\)

\[
\sigma_c = \sigma_m (1 - V_f) + \sigma_f V_f
\]  

(Eq. 4-2)

The interface plays an important role as Equation 4-2 assumes perfect bonding between the matrix and reinforcement. The concept of load-sharing works best during elastic behavior, e.g. prediction of composite yield strength.

A linear superposition proposed by Nembach (125) describes the effects of strengthening contributions to the alloy strength. This includes the strength of the main element \((\sigma_{Al})\), the increase in solid solution strength from alloying elements \((\sigma_{SS})\), and the strength of the eutectic phase \((\sigma_{Eut})\). Thus, the strength of the matrix can be represented by:
where the $k$ exponent is a fit relationship based on modeling and has been found to be $1 < k < 2$. Thus, the total strength of the Al-based composite reinforced with SMA wires can be predicted by the following relationship:

$$
\sigma_c^k = \sigma_{Al}^k + \sigma_{SS}^k + \sigma_{Eut}^k \quad \text{(Eq. 4-3)}
$$

This equation is similar to the one derived by Manuel for Mg-based composite alloys (80).

**Alloy Selection**

To identify matrix alloys with self-healing capabilities, the first step was the base alloy selection. As specific strength is a performance output (Figure 4-1), typical base metals would include Al, Mg, and Ti to obtain high strengths with low weight. However, because a reduction in eutectic temperature is desired in order to keep a low healing temperature, Al and Mg have advantages over Ti because of their lower melting points; 660 and 650°C for Al and Mg, respectively (55). Mg requires special processing due to flammability issues, and was therefore removed from consideration as a base material. Al alloys, in addition to their low density and potential for high strengths, typically exhibit good castability, another beneficial characteristic for fabricating continuous fiber-reinforced composites.

The selection of Al as the base element for the matrix has an added benefit in that it will form a chemical bond with the surface of NiTi SMA wires. Unlike the Sn-Bi matrix, Al$_2$O$_3$ has lower formation energy than either the oxides of Ni or Ti (Figure 4-2). Therefore during casting, the Al melt will reduce the TiO$_2$ on the surface of the NiTi
wires, creating a strong chemical bond, relieving the need to create a mechanical attachment to incorporate the SMA wires (e.g. knotting).

Figure 4-2: Ellingham diagram showing relative positions of Al₂O₃, NiO, and TiO₂ on a free energy scale during the formation of oxides. Curves plotted with free energy data obtained from (110).

With the selection of Al as the main matrix element, the next step is the selection of alloying elements to obtain the eutectic microstructure required for healing. This investigation included alloying elements which would decrease the eutectic temperature in Al-rich alloys to better facilitate efficient healing. The eutectic temperatures of potential alloying elements to Al are shown in Figure 4-3. It is shown that Ge, Mg, Sn, and Zn are the only elements able to reduce the binary eutectic temperatures of Al-rich binary alloys below 500°C.

The alloying elements added to the Al matrix must also be able to improve its yield strength of 12 MPa (55). The thermal cycles inherit in the healing performance
necessitates alloying additions that exhibit good solid solution strengthening. The typical alloying additions to Al that exhibit solid-solution strengthening are shown in Figure 4-4.

![Figure 4-3: Graph showing the eutectic temperature of various Al-based binary alloys. The red line denotes the melting point of pure Al (660°C). Graph plotted from phase diagram data found in (126).](image)

From a comparison of the results in Table 3-1 for the matrix alloy to Table 3-2 for the composite specimens, it is shown that the modulus and failure strain of the alloys are statistically similar to those in the composite (using a standard t-test with a 95% confidence). However, the alloys possessed strength values greater than the composites (Figure 3-9). This is most likely caused by the lack of bonding between the wires and the matrix. Note that Li extends out to 19 at% solute, but that data was not included for clarity. The trend lines were also included to show differences at low atomic percent solute to help guide the eye and does not indicate nor imply a linear strengthening relationship.
Combining the above information, there were four different binary alloys which were deemed appropriate for further consideration: Al-Sn, Al-Cu, Al-Mg and Al-Si. The first alloy that will be investigated, Al-Sn, will explore an alloy system exhibiting the lowest eutectic temperature. Al-Cu and Al-Mg will be studied to investigate the effect of potent strengthening solutes which also decrease the binary eutectic temperature. The final alloy to be investigated will be Al-Si because of its high castability, which is desirable for fabrication of a continuously reinforced composite.
CHAPTER 5
BINARY ALLOY DESIGN

Using the system design chart and the information gathered about binary aluminum alloys in the previous chapter, it was determined to investigate four different binary alloy systems: Al-Sn, Al-Cu, Al-Mg, and Al-Si.

Aluminum-Tin

The first system investigated was Al-Sn because it exhibited the lowest eutectic temperature at only 226°C. As in Sn-Bi, the Al-Sn phase diagram is a eutectic system (Figure 5-1). Because of the large (Sn) + liquid region available for healing in the Al-Sn system, a healing temperature of 250°C was selected. This would ensure any fluctuations in the furnace temperature would not result in the matrix moving into the solid (Al) + (Sn) region of the phase diagram and preventing liquid-assisted healing. At 250°C, a composition of Al – 19.5 at% Sn (51.6 wt% Sn) was calculated to have 20% liquid (132).

Al-Sn Fabrication

Appropriate amounts of Al (Al shot, 99.99%, Alfa Aesar) and Sn (Sn shot, 99.8%, Alfa Aesar) were melted in an open-air furnace at 750°C until a liquid solution. Three NiTi SMA wires, designated BB-35 (Ni – 49.3 at% Ti, Ø = 0.87 mm, Memry Corporation), were laid horizontally in the graphite sub-size tensile bar mold. The Al-Sn melt was poured over the wires into the mold and allowed to cool. Each tensile bar was then placed horizontally into a furnace for 4 hours at 250°C, monitored by an external thermocouple, then air-cooled to set the eutectic microstructure (Figure 5-2). A study was conducted on Al – 19.5 at% Sn and found that only 4 hours were needed to achieve the equilibrium microstructure; further heat-treatment time had little effect.
Figure 5-1: Phase diagram of the Al-Sn system. At 250°C, the composition yielding 20% liquid was calculated to be Al – 19.5 at% Sn (51.6 wt% Sn). Adapted from Al-Sn (Aluminum-Tin) [database on the Internet]. ASM International. 1992 [cited September 2012]. http://products.asminternational.org/hbk/index.jsp.

Figure 5-2: Representative microstructure of an Al – 19.5 at% Sn (51.9 wt% Sn) composite after heat-treatment at 250°C for 4 hours.
Al-Sn Mechanical Testing

After heat-treatment, the Al-Sn composite bars were ground to a 320-grit surface finish before being tested in tension using the Instron 5582 machine at a rate of 1.0%/min. Results of the testing are shown in Table 5-1. Because of the high Sn content, the composites were found to possess low yield and ultimate strengths (less than Sn – 21 at% Bi composites). The tensile graph of sample ‘B’ is shown in Figure 5-3. The ductility of the composite was evident in the sample as multiple cracks began forming along the gauge section, resulting in the dips seen in the tensile data.

Table 5-1: Mechanical testing results for Al-Sn matrices reinforced with <2.0 vol% SMA wire reinforcements

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Vf Wires (%).</th>
<th>Modulus (GPa)</th>
<th>0.2% Yield Stress (MPa)</th>
<th>Ultimate Stress (MPa)</th>
<th>Failure Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.54</td>
<td>49.6</td>
<td>23.9</td>
<td>47.1</td>
<td>5.8</td>
</tr>
<tr>
<td>B</td>
<td>1.51</td>
<td>49.9</td>
<td>23.9</td>
<td>37.0</td>
<td>7.4</td>
</tr>
<tr>
<td>C</td>
<td>1.78</td>
<td>44.2</td>
<td>23.1</td>
<td>39.8</td>
<td>8.6</td>
</tr>
<tr>
<td>Avg.</td>
<td>1.61</td>
<td>47.9</td>
<td>23.6</td>
<td>41.3</td>
<td>7.2</td>
</tr>
<tr>
<td>± 1σ</td>
<td>0.15</td>
<td>3.2</td>
<td>0.5</td>
<td>5.2</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Figure 5-3: Tensile data of Al – 19.5 at% Sn (51.9 wt% Sn) composite – sample ‘B’ after heat-treatment at 250°C for 4 hours.
After initial tensile testing, each composite was placed into a furnace for 4 hours at 250°C to induce healing. Upon removal, large cracks were still evident and healing was not noted to occur. Figure 5-4 shows the extra cracking along the gauge section. These extra cracks did not have an SMA wire passing through them to enable crack closure during a healing cycle. Therefore, a clamping force wasn’t created at these crack sites to assist with healing and the cracks remained open post-healing. Necking was also noted in the samples and was thought to also contribute to the lack of healing. During necking, the deformation is concentrated to the necked region, decreasing the cross-sectional area but still strain hardening the composite. It is thought the concentrated deformation may have caused permanent strains to occur in the SMA wires, decreasing their ability to revert back to their original length and thus complete crack closure to enable healing.

![Matrix Failure](image)

*Figure 5-4: Image of Al – 19.5 at% Sn (51.9 wt% Sn) composite after tensile testing showing cracking in the matrix caused by excess ductility.*

**Aluminum-Copper**

Al-Cu was studied because it had the potential to display high strength increases with increasing solute concentration while simultaneously decreasing the eutectic temperature of the binary system. This is why it was selected over Al-Mn which exhibited greater strength increases per atomic percent solute but lacked the eutectic temperature reduction. Literature has shown compositions below 10 wt% Cu were subject to hot-cracking during casting (133), therefore a composition of Al – 4.5 at% Cu
(10 wt% Cu) was selected. The phase diagram was calculated using Pandat software with the PanMagnesium database (107) (Figure 5-5); it was found to closely match the phase diagram found in literature (134). It was calculated that at the composition of Al – 4.5 at% Cu, the healing temperature would be 566°C for this system. Should fluctuations occur within the furnace, 566°C ± 5°C yields a range of only 18–21.8% liquid (Figure 5-6).

![Figure 5-5: Phase diagram of the Al-Cu system below 40 at% Cu. At a composition of Al – 4.5 at% Cu (10 wt% Cu), a healing temperature of 566°C will yield 20% liquid in the matrix. Calculated using Pandat (107).](image)

**Al-Cu Fabrication**

Al (Al shot, 99.99%, Alfa Aesar) and Cu (Cu shot, 99.9%, Alfa Aesar) were melted in an open-air furnace at 800°C until a liquid and cast into a graphite mold to create an ~30% Cu master alloy. After verifying the master alloy composition via ICP,
the Al-Cu master alloy and more pure Al were melted in an open-air furnace at 750°C until a liquid solution. One NiTi SMA wire, designated BB-35 (Ni – 49.3 at% Ti, Ø = 0.87 mm, Memry Corporation), was laid horizontally in the graphite tensile bar mold. The mold was heated up to 350°C before casting to prevent cold-shuts and air pockets from forming in the as-cast microstructure. The Al-Cu melt was poured over the wire into the mold and allowed to cool. Each tensile bar was then placed horizontally into a furnace for 24 hours at 566°C, monitored by an external thermocouple, then air-cooled to set the eutectic microstructure (Figure 5-7).
Figure 5-7: Representative microstructure of an Al – 4.5 at% Cu (10 wt% Cu) matrix reinforced with NiTi SMA wire after heat-treatment at 566°C for 24 hours and tensile testing. The lack of adhesion between the SMA wire and the matrix is attributed to debonding from mechanical testing.

**Al-Cu Mechanical Testing**

After heat-treatment, the Al-Cu composite bars were ground to a 320-grit surface finish before being tested in tension using the Instron 5582 machine at a rate of 1.0%/min. Results of the testing are shown in Table 5-2. The Cu addition resulted in composites possessing greater modulus and ultimate strengths than the Al-Sn composites (Table 5-1). Because of the lack of ductility, the 0.2% yield stress was not able to be calculated (Figure 5-8).

Table 5-2: Mechanical testing results for Al-Cu matrices reinforced with 2-2.5 vol% SMA wire reinforcements

<table>
<thead>
<tr>
<th>Specimen</th>
<th>( V_t ) Wires (%)</th>
<th>Modulus (GPa)</th>
<th>Ultimate Stress (MPa)</th>
<th>Failure Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.4</td>
<td>67.6</td>
<td>88.1</td>
<td>0.22</td>
</tr>
<tr>
<td>B</td>
<td>2.2</td>
<td>80.1</td>
<td>104.7</td>
<td>0.2</td>
</tr>
<tr>
<td>Avg.</td>
<td>2.3</td>
<td>73.9</td>
<td>96.4</td>
<td>0.21</td>
</tr>
<tr>
<td>± 1( \sigma )</td>
<td>0.13</td>
<td>8.8</td>
<td>11.7</td>
<td>0.01</td>
</tr>
</tbody>
</table>
Figure 5-8: Tensile data of Al – 4.5 at% Cu (10 wt% Cu) composite – sample ‘B’ – after heat-treatment at 566°C for 4 hours.

Following initial testing, the samples were encapsulated under vacuum and heat-treated again for 24 hours at 566°C. The composites were placed on flat graphite pieces and covered with tantalum foil to prevent oxide from forming along the crack interface which would prevent healing. Following air-cooling, the tensile samples were tested in tension again for healing, but little healing was found (Figure 5-9). Small cracks were still noted on the outer edges post-healing (Figure 5-9c-d). Wire shifting was also noted in the sample (Figure 5-9d), which is likely to be caused by a release of residual stress due to the increase in healing temperature.
Figure 5-9: Image of tensile crack induced in Al – 4.5 at% Cu composite: a) pre-heal top view, b) pre-heal bottom view, c) post-heal top view, and d) post-heal bottom view. Note the wire shifting during heat treatment resulted in a longitudinal crack along grain boundaries in d).

**Aluminum-Magnesium**

Al-Mg was studied because it has the potential of the greatest total strength increases through solid-solution strengthening in binary aluminum alloys (Figure 4-4). The phase diagram was calculated using Pandat software with the PanMagnesium database (107) (Figure 5-10). The diagram nearly matches that found in literature (135), but has the Al₃Mg₂ phase as a line compound with low solubility. Literature values indicate the Al₃Mg₂ phase should be present from 38.5-40.3 at% Mg (135). The composition of Al – 16.6 at% Mg (15.2 wt% Mg) yields the largest freezing range between the eutectic temperature and the liquidus temperature, allowing for a robust
matrix should there be slight fluctuations in the furnace temperature during healing. At this composition, the healing temperature was calculated to be 487°C. Should fluctuations occur within the furnace, 487°C ± 5°C yields a range of only 17–23% liquid (Figure 5-11).

![Phase diagram of the Al-Mg system. At a composition of Al – 16.6 at% Mg (15.2 wt% Mg), a healing temperature of 487°C will yield 20% liquid. Calculated using Pandat (107).](image)

Figure 5-10: Phase diagram of the Al-Mg system. At a composition of Al – 16.6 at% Mg (15.2 wt% Mg), a healing temperature of 487°C will yield 20% liquid. Calculated using Pandat (107).

**Al-Mg Fabrication**

Al (Al shot, 99.99%, Alfa Aesar) and Mg (Mg chips, 99.98%, Sigma Aldrich) were melted in a furnace at 750°C within an argon atmosphere until a liquid solution. One NiTi SMA wire, designated BB-35 (Ni – 49.3 at% Ti, Ø = 0.87 mm, Memry Corporation), was laid horizontally in the graphite tensile bar mold which was heated up to 350°C before casting to prevent casting defects. The Al-Mg melt was poured over the wire into
the mold and allowed to cool. Each tensile bar was then encapsulated under vacuum in Pyrex tubes and placed into a furnace for 24 hours at 487°C, monitored by an external thermocouple. The bars were then air-cooled to set the eutectic microstructure (Figure 5-12). A reaction zone was found at the wire/matrix interface likely caused by a reduction reaction between the matrix and the surface oxide present on the NiTi wire. The depth of this zone found it to be approximately 40μm deep on average.

**Al-Mg Mechanical Testing**

After heat-treatment, the Al-Mg tensile composite bars were ground to a 320-grit surface finish and tested in tension using the Instron 5582 machine at a rate of 1.0%/min. Results of the testing are shown in Table 5-3. Because of the lack of ductility,
Figure 5-12: Representative microstructure of an Al – 16.6 at% Mg (15.2 wt% Mg) matrix reinforced with a NiTi SMA wire after heat-treatment at 487°C for 24 hours. The reaction zone surrounding the SMA wires was noted to be approximately 40μm deep.

The 0.2% yield stress was not able to be calculated (Figure 5-13). While the modulus was similar for each composite, the ultimate stress had a wide range; increasing the volume fraction of SMA wires did not have an effect on the composite strength.

Figure 5-13: Tensile data of Al – 16.6 at% Mg (15.2 wt% Mg) composite – sample ‘C’ – after heat-treatment at 487°C for 24 hours.
Table 5-3: Mechanical testing results for Al-Mg matrices reinforced with < 5 vol% SMA wire reinforcements

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$V_f$ Wires (%)</th>
<th>Modulus (GPa)</th>
<th>Ultimate Stress (MPa)</th>
<th>Failure Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.91</td>
<td>53.6</td>
<td>107.2</td>
<td>0.19</td>
</tr>
<tr>
<td>B</td>
<td>3.97</td>
<td>56.8</td>
<td>62.1</td>
<td>0.11</td>
</tr>
<tr>
<td>C</td>
<td>2.12</td>
<td>52.3</td>
<td>83.3</td>
<td>0.15</td>
</tr>
<tr>
<td>Avg.</td>
<td>2.67</td>
<td>54.2</td>
<td>84.2</td>
<td>0.15</td>
</tr>
<tr>
<td>± 1σ</td>
<td>1.14</td>
<td>2.3</td>
<td>22.6</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Following the virgin composite testing, the samples were encapsulated under vacuum again and heat-treated a second time for 24 hours at 487°C. Following air-cooling, the Al-Mg composites were tested in tension again for healing. Little evidence of healing was found in the composites due to the oxidation of the entire surface (Figure 5-14), including the fracture interface. Despite the use of vacuum during heat-treatment, it appears some oxygen remained to react with the liquefied Al-Mg eutectic phases. Additionally, matrix vaporization was evident by the coating on the Pyrex tubes used during heat-treatment (Figure 5-15). Looking at the microstructure, it was also evident that there was a loss of material during the heat-treatment. Figure 5-16 shows a view of the edge of the composite where an oxide layer formed during heat treatment. It should be noted the black areas are pores where eutectic was thought to have previously occupied; these areas are evident throughout the matrix.
Figure 5-14: Image of Al – 16.6 at% Mg composite a) pre-heal and b) post-heal. Note the black oxide covering the entire surface of the tensile bar after the heal heat-treatment – 24 hours at 487°C under vacuum.

Figure 5-15: Image of Pyrex tubes holding Al-Mg composite after heat-treatment. The black color on the interior surface is likely vaporized magnesium from the liquid eutectic during the heat treatment.
Figure 5-16: Representative microstructure of Al-Mg composite after heat-treatment at 487°C for 24 hours under vacuum. This image is of the sample edge to show the oxide layer that forms, but the pores (black areas) are formed throughout the microstructure. The pores are areas previously occupied by eutectic which is thought to have liquefied during heat-treatment and vaporized.

**Aluminum-Silicon**

The Al-Si system was studied because it represents an alloy system yielding moderate strength increases, a decrease in eutectic temperature, and the binary alloy known to have excellent castability (55). The phase diagram (Figure 5-17) was calculated using Pandat software (107) with the PanMagnesium database, and found to closely match that found in literature (136). Literature has shown compositions below 3 wt% Si are subject to hot-cracking during casting (133), therefore a composition of Al – 3.0 at% Si (3.1 wt% Si) was selected. At this composition, the healing temperature was calculated to be 592°C. Should fluctuations occur within the furnace, 592°C ± 5°C yields a range of only 18–22.6% liquid (Figure 5-18).
Figure 5-17: Phase diagram of Al-Si below 50% Si. At a composition of Al – 3.0 at% Si (3.1 wt% Si), a healing temperature of 592°C will yield 20% liquid. Calculated using Pandat (107).

Figure 5-18: Phase fraction of Al – 3.0 at% Si at various temperatures. The heat-treatment temperature of 592°C reveals a 20% liquid composition during the healing process. The box signifies the potential area of liquid % should the temperature fluctuate by ±5°C during heat-treatment.
Al-Si Fabrication

Al (Al shot, 99.99%, Alfa Aesar) and Si (Si lump, 99.9999%, Alfa Aesar) were melted in a furnace at 850°C and cast into a graphite mold to create an approximately 15% Si master alloy. After verifying the composition via ICP, appropriate amounts of the Al-Si master alloy and pure Al were melted at 750°C until a liquid solution to obtain the desired Al – 3.0 at% Si composition. One NiTi SMA wire, designated BB-35 (Ni – 49.3 at% Ti, Ø = 0.87 mm, Memry Corporation), was laid horizontally in the graphite tensile bar mold which was heated up to 350°C before casting to prevent casting defects. The Al-Si melt was poured over the wire into the mold and allowed to cool. Each tensile bar was placed into a furnace for 24 hours at 592°C and then air-cooled to set the eutectic microstructure (Figure 5-19).

**Figure 5-19:** Representative microstructure of an Al – 3.0 at% Si (3.1 wt% Si) composite after heat-treatment at 592°C for 24 hours.

Al-Si Mechanical Testing

After heat-treatment, the Al-Si tensile composite bars were ground to a 320-grit surface finish and tested in tension using the Instron 5582 machine at a rate of
1.0%/min. Results of the testing are shown in Table 5-4. The Al-Si composites showed moderate yield and ultimate stresses and moderate ductility in relation to the other binary alloys. The failures were found to occur along the eutectic regions as shown in Figure 5-20.

Table 5-4: Mechanical testing results for Al-Si matrices reinforced with 2-3 vol% SMA wire reinforcements

<table>
<thead>
<tr>
<th>Specimen</th>
<th>V % Wires</th>
<th>Modulus (GPa)</th>
<th>0.2% Yield Stress (MPa)</th>
<th>Ultimate Stress (MPa)</th>
<th>Failure Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.26</td>
<td>74.9</td>
<td>38.9</td>
<td>97.2</td>
<td>4.21</td>
</tr>
<tr>
<td>B</td>
<td>2.00</td>
<td>48.4</td>
<td>40.2</td>
<td>83.3</td>
<td>3.18</td>
</tr>
<tr>
<td>C</td>
<td>2.40</td>
<td>63.1</td>
<td>39.0</td>
<td>100.4</td>
<td>4.42</td>
</tr>
<tr>
<td>Avg.</td>
<td>2.22</td>
<td>62.1</td>
<td>39.4</td>
<td>93.6</td>
<td>3.94</td>
</tr>
<tr>
<td>± 1σ</td>
<td>0.20</td>
<td>13.3</td>
<td>0.7</td>
<td>9.1</td>
<td>0.66</td>
</tr>
</tbody>
</table>

Figure 5-20: Representative microstructure in an Al – 3.0 at% Si (3.1 wt% Si) composite after heat-treatment at 592°C for 24 hours showing failure occurring along eutectic regions.

Following the virgin composite testing, the samples were encapsulated under vacuum (in Pyrex lying on a graphite strip and wrapped in Ta foil) and heat-treated a second time for 24 hours at 592°C. Following air-cooling, the Al-Si composites were
tested in tension again for healing. Using Equation 3-1, the percent healing was calculated for the samples exhibiting healing (Table 5-5).

Table 5-5: Healing characteristics of Al-Si composites

<table>
<thead>
<tr>
<th>Specimen</th>
<th>'Healed' Ultimate Stress (MPa)</th>
<th>% Heal</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>88.1</td>
<td>90.6</td>
</tr>
<tr>
<td>B</td>
<td>93.7</td>
<td>112.5</td>
</tr>
<tr>
<td>C</td>
<td>72.0</td>
<td>71.7</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>91.6</td>
</tr>
</tbody>
</table>

New ways to investigate the healing efficiency were also be performed using similar calculations for the elastic modulus (E), \(\sigma_y\), and the strain to failure (\(\varepsilon_f\)). The new healing efficiency calculations are shown in Equations 5-1 to 5-3. The healing efficiencies of the Al-Si composites are shown in Table 5-6. It was found E and \(\sigma_y\) were retained at averages of over 90%, similar to the UTS healing efficiency, and \(\varepsilon_f\) was retained at over 88% on average. These results, paired with the UTS healing efficiencies, show nearly full healing of macro-sized cracks occurred within the Al-Si composite alloys.

\[
\frac{E_{\text{Healed}}}{E_{\text{Virgin}}} \times 100\% = \% E_{\text{Healed}} \quad \text{(Eq. 5-1)}
\]

\[
\frac{\sigma_y^{\text{Healed}}}{\sigma_y^{\text{Virgin}}} \times 100\% = \% \sigma_y^{\text{Healed}} \quad \text{(Eq. 5-2)}
\]

\[
\frac{\varepsilon_f^{\text{Healed}}}{\varepsilon_f^{\text{Virgin}}} \times 100\% = \% \varepsilon_f^{\text{Healed}} \quad \text{(Eq. 5-3)}
\]

It was noted that each specimen showed visible signs of healing (Figure 5-21); i.e. crack size reduction. A comparison between the virgin and healed tensile behavior of specimen ‘A’ is shown in Figure 5-22. All three of the healed composites were found
Table 5-6: Healing characteristics of Al-Si composites using healing efficiency calculations for elastic modulus, yield strength, and strain to failure.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>'Healed' E (GPa)</th>
<th>% E Heal</th>
<th>'Healed' (\sigma_y) (MPa)</th>
<th>% (\sigma_y) Heal</th>
<th>'Healed' (\varepsilon_f) (GPa)</th>
<th>% (\varepsilon_f) Heal</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>80.9</td>
<td>108.0</td>
<td>38.8</td>
<td>99.7</td>
<td>3.57</td>
<td>84.8</td>
</tr>
<tr>
<td>B</td>
<td>59.8</td>
<td>123.6</td>
<td>37.7</td>
<td>93.8</td>
<td>4.08</td>
<td>128.3</td>
</tr>
<tr>
<td>C</td>
<td>40.0</td>
<td>63.4</td>
<td>37.4</td>
<td>95.9</td>
<td>2.30</td>
<td>52.0</td>
</tr>
<tr>
<td>Average</td>
<td>98.3</td>
<td>96.5</td>
<td>96.5</td>
<td>88.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

to retain similar modulus and yield strength values as the virgin composite. For specimen 'B', the greater ultimate strength in the healed composite is attributed to healing a defect which resulted in the premature failure, thereby allowing for a greater ultimate strength post-healing and thus a healing efficiency over 100%. In specimen 'C', the failure in the composite post-healing actually occurred in a different place than the original crack (Figure 5-23). Another crack was initiated on the surface of specimen 'C', (bottom-right side of Figure 5-23) after the initial tensile test in the grip section of the specimen. This crack was not healed during the healing cycle because the crack was opened in an area without a NiTi SMA wire, thus there was no clamping force imparted across the crack. The lack of crack closure prevents the partially liquefied matrix alloy from completely filling the crack, and thus it was prevented from being healed. However, this crack did not serve as the final matrix failure position of the composite specimen.

Figure 5-21: Comparison of the a) pre-heal to b) post-heal tensile bar in an Al – 3.0 at% Si composite reinforced with 2.0 vol% NiTi SMA wire (specimen ‘A’ in Table 5-5).
Figure 5-22: Comparison of the virgin and healed tensile behavior of an Al – 3.0 at% Si composite reinforced with 2.0 vol% NiTi SMA wire. The sample was found to possess 90.6% retained tensile strength post-healing heat-treatment (specimen ‘A’ in Table 5-5).

Figure 5-23: Comparison of the a) post-tensile 1, b) post-heal and c) post-tensile 2 in an Al – 3.0 at% Si composite reinforced with 2.4 vol% NiTi SMA wire (specimen ‘C’ in Table 5-5). The arrow in a) shows the original composite failure and the arrow in b) shows the healed crack in the same location. In c) the oval shows the second failure that occurred during second tensile test.
Increased Volume Fraction NiTi

To study whether increasing the volume fraction of NiTi wires would increase healing, more Al-Si composites were manufactured as above, but with an increased number of NiTi wires. After a heat-treatment of 592°C for 24 hours, the Al-Si tensile composite bars were ground to a 320-grit surface finish and tested in tension using the Instron at a rate of 1.0%/min. Results of the testing are shown in Table 5-7. The new Al-Si composites with nearly double the volume fraction of SMA wires showed more variance in the resultant elastic modulus, yield and ultimate stresses, and strain to failure in relation to the lower volume fraction composites. However, the 0.2% yield strength was found to have increased over 20% on average. The other properties were found to be statistically similar using a t-test with a 95% confidence interval.

Table 5-7: Mechanical testing results for Al-Si matrices reinforced with 3.5-4.5 vol% SMA wire reinforcements

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$V_f$ Wires (%)</th>
<th>Modulus (GPa)</th>
<th>0.2% Yield Stress (MPa)</th>
<th>Ultimate Stress (MPa)</th>
<th>Failure Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>4.43</td>
<td>68.7</td>
<td>49.5</td>
<td>108.9</td>
<td>6.24</td>
</tr>
<tr>
<td>E</td>
<td>3.79</td>
<td>73.7</td>
<td>45.7</td>
<td>89.9</td>
<td>2.80</td>
</tr>
<tr>
<td>Avg.</td>
<td>4.11</td>
<td>71.2</td>
<td>47.6</td>
<td>99.4</td>
<td>4.52</td>
</tr>
<tr>
<td>± 1σ</td>
<td>0.45</td>
<td>3.5</td>
<td>2.7</td>
<td>13.4</td>
<td>2.43</td>
</tr>
</tbody>
</table>

Following the virgin composite testing, the greater volume fraction composite bars were encapsulated under vacuum (in Pyrex lying on a graphite strip and wrapped in Ta foil) and heat-treated a second time for 24 hours at 592°C. Following air-cooling, the Al-Si composites were tested in tension again for healing. Using Equation 3-1, the percent healing was calculated for the samples exhibiting healing (Table 5-8).
Table 5-8: Healing characteristics of Al-Si composites with 3.5-4.5 vol% NiTi wires

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Ultimate Stress (MPa)</th>
<th>% Heal</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>35.1</td>
<td>32.2</td>
</tr>
<tr>
<td>E</td>
<td>50.2</td>
<td>55.8</td>
</tr>
<tr>
<td>Average</td>
<td>44.0</td>
<td></td>
</tr>
</tbody>
</table>

It was noted the Al-Si composites with a greater volume fraction of NiTi wires did not heal as well as the lower volume fraction composites. Looking at Figure 5-24, when comparing specimen A to specimen D, the increase yield strength is shown. But the tensile data for specimen E also shows numerous decreases in stress followed by recovery. These decreases were accompanied by a cracking sound during testing and are attributed to debonding between the NiTi fibers and Al-Si matrix (Figure 5-25). The debonding is seen by the decrease in stress at various strains and was accompanied by a cracking sound during tensile testing. This debonding is thought to be the reason for the decreased healing percentages found in the composites with a greater volume fraction of NiTi. Debonding would prevent the wires from pulling the matrix together when as the temperature is increased during a healing heat treatment. It is thought the increased debonding is a result of the extra turbulence during the casting process when the composite is originally fabricated. This extra turbulence could decrease how the molten alloy solidifies around the NiTi wires, therefore decreasing the bond strength at the interface.
Figure 5-24: Virgin tensile behavior of an Al – 3.0 at% Si composite reinforced with either 2.26 vol% or 4.43 vol% NiTi SMA wire. Greater volume fraction composites were shown to possess greater yield strengths, but exhibited debonding under tensile testing.

Figure 5-25: Optical image showing debonding between an Al-3 at% Si matrix and NiTi wire ($V_f = 4.43\%$) following tensile testing.
NiTi Wire Properties

The properties of the NiTi wires were investigated to determine the effects of heat-treatment on their output properties. Pieces of as-received BB-35 wire were placed into a Perkin-Elmer 8000 Differential Scanning Calorimeter (DSC) and cycled from -50 – 200°C at 20°C/minute. The austenitic and martensitic transition temperatures of the NiTi wire were calculated via the offset method (114). Another wire was cut from an as-cast Al-Si composite to determine whether the casting process had any effect on the thermal properties. Other pieces of wire were encapsulated under vacuum in Pyrex tubes and heat-treated either once or twice at 592°C for 24 hours to simulate the heat-treatment of the Al-Si composites before being tested in the DSC. Results of the testing are found in Table 5-9. It was found that the casting process significantly increased all of the NiTi transition temperatures from the as-received condition. The subsequent heat treatment (592°C for 24 hrs) required to alter the Al-Si composite matrix microstructure decreased these values, but the healing heat-treatment (a second cycle of 592°C for 24 hrs) did not significantly change the transition temperatures.

Table 5-9: Average Thermal Properties of NiTi Wires Subjected to Various Heat Treatments

<table>
<thead>
<tr>
<th>NiTi Wire Condition</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A_s</td>
</tr>
<tr>
<td>As-Received</td>
<td>-4.5</td>
</tr>
<tr>
<td>As-Cast</td>
<td>54.8</td>
</tr>
<tr>
<td>592°C for 24 hrs</td>
<td>40.0</td>
</tr>
<tr>
<td>592°C for 24 hrs (2x)</td>
<td>40.0</td>
</tr>
</tbody>
</table>

The phase diagram of Ni-Ti alloys (137) is shown in Figure 5-26, whereas a time-temperature-transformation (TTT) diagram (138) for a nickel-rich Ni-Ti SMA is shown in Figure 5-27. The heat associated with casting is thought to have caused formation of a metastable Ti$_3$Ni$_4$ phase which has been shown to result in increases in martensite and
austenite transformation temperatures (139). Further heat-treatment at 592°C would enable a precipitation of the intermediate Ti$_{11}$Ni$_{14}$ and Ti$_2$Ni$_3$ phases, which would decrease the transformation temperatures (140). The next heat-treatment cycle did not result in shifting these temperatures because the precipitation process requires more time to transform to TiNi and TiNi$_3$ equilibrium phases. Because the Ti$_3$Ni$_4$, Ti$_{11}$Ni$_{14}$, and Ti$_2$Ni$_3$ phases are metastable, they do not show up on the phase diagram shown in Figure 5-26.

![Phase diagram of the Ni-Ti system](http://products.asminternational.org/hbk/index.jsp)

Figure 5-26: Phase diagram of the Ni-Ti system. The composition of the SMA BB wires used for self-healing MMC fabrication is Ni – 49.3 at% Ti. Adapted from Ni-Ti (Nickel-Titanium) [database on the Internet]. ASM International. 1992 [cited May 2013]. Available from: http://products.asminternational.org/hbk/index.jsp.
Figure 5-27: TTT diagram showing aging behavior in a Ti-52Ni alloy. Adapted from Nishida, M., Wayman, C.M., and Honma, T. 1986. Precipitation Processes in Near-Equiatomic TiNi Shape Memory Alloys. Metallurgical Transactions A, Vol. 17A (page 1507, Figure 3).

Next, heat-treated NiTi wires under similar conditions as above were tested in tension to investigate thermal effects on mechanical properties. The samples were pulled on the Instron mechanical testing machine to failure (Table 5-10). As with the thermal properties, the mechanical properties significantly changed with heat treatment, decreasing the plateau stress over 85% and the failure stress by over 20%. However, a subsequent heat treatment to simulate healing of the composite had little effect on the mechanical properties. These results correlate with the thermal properties shown in Table 5-9 also showing little change between the initial heat-treatment and the second one because of the precipitation processes associated with the heat-treatments.
Table 5-10: Tensile Properties of NiTi Wires Subjected to Various Heat Treatments

<table>
<thead>
<tr>
<th>NiTi Wire Condition</th>
<th>Plateau Stress (MPa)</th>
<th>Failure Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Received</td>
<td>492 ± 19</td>
<td>1368 ± 13</td>
</tr>
<tr>
<td>592°C for 24 hrs</td>
<td>67 ± 3</td>
<td>1087 ± 14</td>
</tr>
<tr>
<td>592°C for 24 hrs (2x)</td>
<td>71 ± 2</td>
<td>1091 ± 18</td>
</tr>
</tbody>
</table>

**Binary Alloy Summary**

Of the four different binary systems with potential for self-healing studied, only one matrix, Al-Si, was found to have significant healing. When comparing the different tensile results of the four systems (Figure 5-28), it was noted that Al-Si exhibited uniform elongation without necking. It is thought the moderate ductility allows for transformation in the SMA wires, which is analogous to pre-straining the wires. Modeling of the self-healing process has shown pre-strain in the SMA wires is required in order to obtain the clamping force required for healing (81). The brittle Al-Cu and Al-Mg matrices do not allow this to occur as matrix failure occurred before transformation in the SMA wires began. The necking and multiple cracking in Al-Sn is thought to cause permanent strains in the wires, preventing full shape reversion in the SMA wires, and thus lack of healing. Therefore, it is postulated in order to create a MMC with self-healing capabilities that moderate ductility in a matrix is required to ensure uniform elongation, enabling transformation in the SMA wires, but without necking to cause permanent deformation in the reinforcement.
Figure 5-28: Comparison of the tensile results for different specimens from the Al-Sn, Al-Cu, Al-Mg, and Al-Si composite systems with 1.5-2.5 vol% NiTi wires. Note that only the Al-Si composites were found to heal appreciably.
CHAPTER 6
TERNARY ALLOY DESIGN

Using the system design method for self-healing metal-matrix composite design laid out in Chapter 4 and the information gathered about binary aluminum alloys in Chapter 5, a greater strength aluminum-based ternary alloy system was investigated. The investigation included design of the matrix, fabrication of composites for tensile testing, and healing the fractured composites. The models utilized for design of the matrix and composite were validated through additional testing. Due to issues with lack of ductility, different fabrication methods were investigated in an effort to increase healing.

**Aluminum-Copper-Silicon Matrix Design**

Looking at the investigated binary alloys – Al-Cu, Al-Mg, Al-Si, Al-Sn – self-healing was only found in the Al-Si system, but the greatest strength values were obtained from Al-Cu composites. Literature relates how Cu additions to Al-Si will increase castability (141) and increase solid-solution strength (55), both desirable properties based on the system design chart (Figure 4-1). The ternary phase diagram is known to not form ternary compounds (141, 142). From Chapter 4, it is known both Cu and Si reduce the eutectic temperature of Al (Figure 4-3), in addition to being solid-solution strengtheners in Al (Figure 4-4).

The Al-Cu-Si phase diagram was calculated using Pandat software with the PanMagnesium database (107) (Figure 6-1); it was found be similar compositionally to the phase diagrams found in literature (143, 144), but showed a lower eutectic temperature - 512°C vs 524°C (145). Since the calculated ternary eutectic temperature
was off by over 10°C from the accepted literature value, an experiment was undertaken to investigate whether the difference affected the resultant percent liquid during the healing heat-treatments. First, a piece of cast Al-Cu-Si matrix had its composition checked via inductively coupled plasma (ICP) spectroscopy on a Perkin-Elmer Plasma 3200RL machine and found to vary less than 0.3% from the nominal composition.

The Al-Cu-Si piece was placed into the DSC and cycled 3 times from 400 – 650°C at 10°C/minute to investigate the eutectic and solidus temperatures. Using a technique put forth by Chen and colleagues (146), the percent liquid was calculated for the Al-Cu-Si alloy. Upon comparison to the output from Pandat, the values were found

Figure 6-1: Liquidus projection of the Al-Cu-Si system. The blue lines indicate isothermal lines to indicate the movement of the liquid across different compositions. The lowest melting eutectic point calculated to be 512°C at a composition of Al – 15.0 Cu – 7.3 Si (at%) as indicated by the arrow. Calculated using Pandat (107).
to vary by less than 2% liquid up to 550°C (Figure 6-2). A representative DSC curve can be found in Appendix A.

![DSC curve with Pandat data](image)

**Figure 6-2:** The percent liquid in an Al-Cu-Si alloy comparing DSC data to calculations using Pandat software.

The microstructure of the Al – 4.1Cu – 2.0Si (at%) matrix was also investigated to validate the expected percentage of liquid. Because the heat-treatments used in healing are in the solid + liquid phase region, a strong correlation between percent liquid and percent eutectic in the microstructure is found. Therefore, a cast Al-Cu-Si sample was mounted in acrylic and polished to a final 0.03 μm finish. A Keller’s reagent (147) etchant – 95 mL H2O, 2.5 mL HNO3, 1.5 mL HCl, 1.0 mL HF – was used to increase grain contrast by immersing the mounted sample for 15 seconds. Following etching, the microstructure was imaged and uploaded to ImageJ software. Across several microstructural images, the percent eutectic was calculated to be 21.1% ± 2.3% (Avg. ± 1σ), which encompasses the goal of 20% liquid in the matrix during healing heat-treatment.
Studying the similarities between the calculated Pandat values compared to DSC results, in addition to the percent eutectic being near the 20% goal via microstructural analysis, the thermodynamic-based methodology utilized for this research for the Al-Cu-Si system is validated.

The next step in Al-Cu-Si matrix design was to calculate the isotherm at the ternary eutectic temperature of 512°C (Figure 6-3 for the Al-rich region). Creating a line between the eutectic point and the closest solid-solution Al region, a pseudo-isopleth was calculated (Figure 6-4). Note how closely it resembles the binary phase diagrams calculated in Chapter 5. At a healing temperature of 530°C, it was calculated that a composition of Al – 4.1 at% Cu – 2.0 at% Si (9.0 wt% Cu – 1.9 at% Si) would yield 20% liquid during a healing heat-treatment. Structural stability of the composite during heat-treatment was assured as fluctuation of ± 5°C from the healing temperature resulted in a range of only 18-21% liquid in the matrix (Figure 6-5).

Figure 6-3: Isotherm at 512°C in the Al-Cu-Si system. The dashed line represents the tie line between the ternary eutectic and nearest Al solid solution phase field. Calculated using Pandat (107).
Figure 6-4: Pseudo-isopleth of Al-Cu-Si system along the line from the ternary eutectic point to the closest Al solid-solution phase region. At a healing temperature of 530°C, a composition of Al – 4.1 at% Cu – 2.0 at% Si will yield 20% liquid in the matrix. The left side is at a composition of Al – 16.8 at% Cu – 8.2 at% Si. Calculated using Pandat (107).

Figure 6-5: Phase fractions of Al – 4.1 at% Cu – 2.0 at% Si at various temperatures. The heat-treatment temperature of 530°C reveals a 20% liquid composition during the healing process. The box signifies the potential area of liquid % should the temperature fluctuate by ±5°C during heat-treatment.
Al-Cu-Si Matrix Properties

The mechanical properties of the Al – 4.1 at% Cu – 2.0 at% Si matrix alloy were investigated via tensile testing. Appropriate amounts of Al (Al shot, 99.99%, Alfa Aesar), Cu (Cu shot, 99.9%, Alfa Aesar), and Sn (Sn shot, 99.8%, Alfa Aesar) were melted in an open-air furnace at 750°C until a liquid solution. The mold was heated up to 350°C before casting to prevent air pockets from forming in the as-cast microstructure. The Al-Cu-Si melt was poured into the mold and allowed to air cool. Each tensile bar was then placed horizontally into a furnace for 24 hours at 530°C, monitored by an external thermocouple, then air-cooled to set the eutectic microstructure (Figure 6-6). The results of testing are shown in Table 6-1. Representative curves of the tensile results can be found in Appendix A.

![Representative microstructure of an Al – 4.1 at% Cu – 2.0 at% Si (9.0 wt% Cu – 1.9 at% Si) composite after a heat-treatment at 530°C for 24 hours](image)

Figure 6-6: Representative microstructure of an Al – 4.1 at% Cu – 2.0 at% Si (9.0 wt% Cu – 1.9 at% Si) composite after a heat-treatment at 530°C for 24 hours
Table 6-1: Mechanical testing results for Al-Cu-Si alloys

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Modulus (GPa)</th>
<th>Ultimate Stress (MPa)</th>
<th>Failure Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>66.0</td>
<td>99.0</td>
<td>0.24</td>
</tr>
<tr>
<td>2</td>
<td>84.1</td>
<td>109.3</td>
<td>0.19</td>
</tr>
<tr>
<td>3</td>
<td>78.6</td>
<td>129.9</td>
<td>0.30</td>
</tr>
<tr>
<td>Avg.</td>
<td>76.2</td>
<td>112.7</td>
<td>0.24</td>
</tr>
<tr>
<td>± 1σ</td>
<td>9.3</td>
<td>15.7</td>
<td>0.06</td>
</tr>
</tbody>
</table>

A commercial casting alloy of the similar composition was Al 213.0. This alloy possesses between 6-8 wt% Cu and 1-3 wt% Si. Literature shows a 0.2% offset yield strength in the as-fabricated (F) state and T533 state of 186 MPa and UTS of 227 MPa and 213 MPa, respectively (148). It is thought the Al – 4.1 at% Cu – 2.0 at% Si (9.0 wt% Cu – 1.9 at% Si) investigated in this study had decreased strengths caused by premature brittle failure from the greater eutectic percent, which is typically decreased to a minimum in traditional Al-based alloy systems (149).

Al-Cu-Si Composite Fabrication

To investigate the self-healing capabilities of the design Al-Cu-Si matrix, composites with NiTi SMA reinforcements were fabricated and mechanically tested. Appropriate amounts of Al (Al shot, 99.99%, Alfa Aesar), Cu (Cu shot, 99.9%, Alfa Aesar), and Sn (Sn shot, 99.8%, Alfa Aesar) were melted in an open-air furnace at 750°C until a liquid solution. One or more NiTi SMA wire(s), designated BB-35 (Ni – 49.3 at% Ti, Ø = 0.87 mm, Memry Corporation), were laid horizontally in the graphite tensile bar mold (Figure 6-8). Because the heat of casting was found to induce shifting during the solidification process, the NiTi wires were heat-treated for 24 hours at 530°C to release residual stresses and create a martensitic state in the NiTi wires at room temperature; i.e. activating the shape-memory effect (Figure 1-4). The mold was heated up to 350°C before casting to prevent cold-shuts and air pockets from forming in the as-
cast microstructure. The Al-Cu-Si melt was poured over the wire(s) in the mold and allowed to air cool. Each tensile bar was then placed horizontally into a furnace for 24 hours at 530°C, monitored by an external thermocouple, then air-cooled to set the eutectic microstructure (Figure 6-6).

Figure 6-7: Image of graphite tensile bar mold used for composite fabrication

**Al-Cu-Si Composite Properties**

After heat-treatment, the Al-Cu-Si composite bars were ground to a 320-grit surface finish before being tested in tension using the Instron 5582 machine at a rate of 1.0%/min. Results of the testing are shown in Table 6-2. Because of the brittle nature of the composites, the 0.2% offset yield strength is not able to be reported. A tensile graph of Composite 3 is shown in Figure 6-8. The tensile data is compared to the tensile results for one of the Al-Cu-Si matrix alloys. The small drops in stress in the composite data are attributed to debonding between the matrix and NiTi wires. Compared to the Al-Cu-Si matrix alloys in Table 6-1, the composite values are similar when using a t-test with a 95% confidence interval. The apparent decrease in modulus for the composites is attributed to the lower elastic modulus found in the NiTi BB alloys. When heat-treated
for 24 hours at 530°C, the NiTi wires were found to possess an average \( E = 59.4 \text{ GPa} \).

A rule of mixtures calculation can be performed:

\[
E_c = (1 - X) E_m + X E_f
\]

(Eq. 6-1)

where \( E \) is elastic modulus, \( m \) is the matrix, \( f \) is the NiTi fibers, and \( X \) is the volume fraction of the NiTi wires. Using the average value for the matrix (76.2 GPa) Al-Cu-Si specimens in Table 6-1 and the NiTi elastic modulus (59.4 GPa), the calculated average of the composite would be \( E = 75.75 \text{ GPa} \). This decrease in modulus for the composite alloy from the matrix is consistent with the lower elastic modulus of the SMA reinforcements.

Figure 6-8: Representative tensile results of an Al-Cu-Si composite with 2.9 volume percent NiTi SMA wire reinforcements compared to an Al-Cu-Si matrix alloy.

Table 6-2: Mechanical testing results for Al-Cu-Si matrices reinforced with 2-3 vol% SMA wire reinforcements

<table>
<thead>
<tr>
<th>Specimen</th>
<th>( % )</th>
<th>Modulus (GPa)</th>
<th>Ultimate Stress (MPa)</th>
<th>Failure Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.32</td>
<td>71.9</td>
<td>116.9</td>
<td>0.35</td>
</tr>
<tr>
<td>2</td>
<td>2.75</td>
<td>69.2</td>
<td>113.5</td>
<td>0.28</td>
</tr>
<tr>
<td>3</td>
<td>2.89</td>
<td>69.7</td>
<td>116.6</td>
<td>0.32</td>
</tr>
<tr>
<td>Avg.</td>
<td>2.65</td>
<td>70.3</td>
<td>115.7</td>
<td>0.32</td>
</tr>
<tr>
<td>( \pm 1\sigma )</td>
<td>0.30</td>
<td>1.4</td>
<td>1.9</td>
<td>0.04</td>
</tr>
</tbody>
</table>
Additional Al-Cu-Si composites were fabricated in a similar manner, but with increased number of NiTi wires to increase the volume fraction of reinforcements, and thus increase the strength of the composite. A comparison of the tensile properties of composites with increasing volume fraction of NiTi reinforcements is shown in Figure 6-9. It can be seen the increased volume fraction increases the yield strength and modulus, but there appears to be a limit to the increase. It was found that over 9 vol% NiTi in the cast composite sample introduced casting defects (i.e. pores) due to the increase in turbulence from extra wires during fabrication, thus the greatest volume fraction composites failed prematurely.

![Stress vs Strain Graph](image)

Figure 6-9: Comparison of tensile results of an Al-Cu-Si matrix reinforced with increasing volume percent NiTi SMA wire reinforcements

After initial composite testing, the fractured tensile bars were encapsulated under vacuum (in a Pyrex tube laying flat on graphite wrapped in Ta foil) and heat-treated a second time for 24 hours at 530°C to try and induce healing. Following air-cooling, the Al-Cu-Si composites were tested in tension again for healing. However, no healing was detected above 32% as calculated by Equation 3-1; the average healing was typically...
around 10%. Therefore, because of the casting issues with increased Vf of NiTi wires both Al-Si and Al-Cu-Si composites, future matrix development will require better fabrication techniques in order to increase the volume fraction.

When comparing the Al-Cu-Si composite results to Al-Cu and Al-Si composites (Figure 6-10), Al-Cu-Si was found to show the greatest tensile strength of the three compositions. However, it was found the Al-Cu-Si composites were behaving in a brittle manner much like the Al-Cu composites. It is thought this brittle nature is not enabling forward transformation in the NiTi SMA wires, therefore there is not a clamping force during the second heat-treatment to enable higher healing percentages.

![Figure 6-10: Comparison of tensile results of Al-Cu-Si, Al-Cu, and Al-Si matrices reinforced with 2.2-2.4 volume percent NiTi SMA wire reinforcements](image)

**NiTi Wire Properties**

The properties of the NiTi wires (BB-35) were investigated to determine how the heat-treatments for healing affect the output properties. Each wire was placed into a DSC and cycled from -50 – 200°C at 10°C/minute. The austenitic and martensitic
transition temperatures were calculated via the offset method (114). The NiTi wires were encapsulated under vacuum in Pyrex tubes and heat-treated either once or twice at 530°C for 24 hours to simulate the heat-treatment of the Al-Cu-Si composites then placed in the DSC. Results of the testing compared to the previously determined as-received properties (Table 5-8) are found in Table 6-3. As with the 592°C heat treatments, the 530°C heat treatment was found to significantly increase all of the NiTi transition temperatures from the as-received to initial heat treatment. However, a secondary heat-treatment did not significantly change the transitions.

Table 6-3: Thermal Properties of NiTi Wires Subjected to Various Heat Treatments

<table>
<thead>
<tr>
<th>NiTi Wire Condition</th>
<th>A_s (°C)</th>
<th>A_f (°C)</th>
<th>M_s (°C)</th>
<th>M_f (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Received</td>
<td>-4.5</td>
<td>13.2</td>
<td>8.8</td>
<td>-10.0</td>
</tr>
<tr>
<td>530°C for 24 hrs</td>
<td>61.9</td>
<td>72.6</td>
<td>39.7</td>
<td>33.8</td>
</tr>
<tr>
<td>530°C for 24 hrs (2x)</td>
<td>61.4</td>
<td>74.6</td>
<td>40.4</td>
<td>31.8</td>
</tr>
</tbody>
</table>

Next, NiTi wires under similar conditions as above were tested in tension to investigate thermal effects on mechanical properties. The samples were pulled on the Instron mechanical testing machine to failure (Table 6-4). Representative curves showing the stress-strain behavior can be found in Appendix A. As with the thermal properties, the mechanical properties significantly changed with heat treatment, decreasing the plateau stress nearly 75% and the failure stress by over 20%. However, subsequent heat treatment had little effect on the mechanical properties.

Table 6-4: Tensile Properties of NiTi Wires Subjected to Various Heat Treatments

<table>
<thead>
<tr>
<th>NiTi Wire Condition</th>
<th>Plateau Stress (MPa)</th>
<th>Failure Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Received</td>
<td>492 ± 19</td>
<td>1368 ± 13</td>
</tr>
<tr>
<td>530°C for 24 hrs</td>
<td>131 ± 5</td>
<td>1088 ± 30</td>
</tr>
<tr>
<td>530°C for 24 hrs (2x)</td>
<td>130 ± 3</td>
<td>1097 ± 1</td>
</tr>
</tbody>
</table>
Strength Model Verification

Looking at the design aspects found in Chapter 4, one of the major design goals was increasing the specific strength within the matrix alloy. Thus, verification of the strength models used in development of the ternary matrix was conducted.

Solid-Solution Strengthening Model

Using a rule of mixtures method, the strength of the Al-Cu-Si matrix alloy can be predicted by inserting the strength of phases present into the following equation:

$$\sigma_m = (1 - X) \sigma_{(Al)} + X \sigma_{Eut} \quad \text{(Eq. 6-2)}$$

where $\sigma_m$ is the strength of the matrix alloy, $\sigma_{(Al)}$ is the strength of the Al-based solid-solution eutectic strength of the eutectic phase, and $X$ is the phase fraction of the eutectic phase.

As the eutectic phase of Al-Cu-Si alloys is extremely brittle (150), compression testing performed. First, the matrix alloy Al – 4.1 Cu – 2.0 Si (at%) was cast in a similar manner to the above composites, heat-treated for 24 hours at 530°C, and air-cooled. A ternary eutectic composition (as calculated by Pandat) of Al – 15.0 Cu – 7.3 Si (at%) and a solid-solution alloy of Al – 1.85 Cu – 0.74 Si (at%) were also cast; the solid-solution alloy was calculated to have the highest alloying content at the heat-treatment temperature. The solid-solution alloy was heat-treated at 530°C for 24 hours whereas the eutectic alloy was tested in the as-cast condition. Each bar of the three compositions was lathed, cut, and polished to a 600-grit finish to fabricate cylindrical samples for compression testing on the Instron machine at 0.5 mm/min. A comparison of the results is found in Table 6-5.
Table 6-5: Compression Testing of Different Al-Cu-Si Alloys

<table>
<thead>
<tr>
<th>Composition (at%)</th>
<th>0.2% Compressive Yield Stress (MPa)</th>
<th>Compressive Ultimate Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al – 1.85Cu – 0.74Si (Solid Solution)</td>
<td>203 ± 18</td>
<td>494 ± 15</td>
</tr>
<tr>
<td>Al – 15.0Cu – 7.3Si (Eutectic)</td>
<td>365 ± 6</td>
<td>536 ± 26</td>
</tr>
<tr>
<td>Al – 4.1Cu – 2.0Si (Alloy)</td>
<td>267 ± 4</td>
<td>424 ± 9</td>
</tr>
</tbody>
</table>

Inserting in the average values into the rule of mixtures model (Equation 6-2), the predicted matrix alloy yield strength with 20% eutectic phase is only 235 MPa. Compared to the compression data for the Al-4.1Cu-2.0Si alloy, this shows the model under-predicts the total matrix alloy compressive yield strength by 12%. The model, however, completely breaks down for the ultimate strength, as the matrix alloy was found to possess a lower compressive ultimate strength than both the solid solution and eutectic compositions. The predicted compressive ultimate stress is 502 MPa, which is over 80 MPa greater than measured. Therefore, it is posited the yield strength can be generally predicted by the rule of mixtures equation, but not the ultimate strength in this alloy.

Another way to predict the solid solution strength in the matrix is through a strengthening model described by Nembach (125) (Equation 4-3). This model relates how the additive strength of phases relates to the alloy strength through constitutive phase strengthening. Knowing the strength of pure Al (99.9999%) is 12 MPa (55), the increase in solid-solution strength from the 1.85 at% Cu and 0.74 at% Si additions – maximum solubility of the alloys at the 530°C healing temperature – must be calculated.

Utilizing the solid solution strengthening in Al data for Cu and Si (Figure 4-3), it can be seen the strengthening must be predicted using different models; Si by a linear
fit and Cu using the classical Fleischer model (151) (Figure 6-11). The linear model can be found in Equation 6-2, whereas the Fleisher model is shown in Equation 6-3:

\[ \Delta \sigma_y = A \text{ (at\% Si)} \]  

\[ \Delta \sigma_y = B \text{ (at\% Cu)}^{1/2} \]  

(Eq. 6-3)  

(Eq. 6-4)

where \( \Delta \sigma_y \) is the change in yield strength from solute addition and the constants A and B are variable based on data fit. It was found A = 13.88 and B = 20, respectively, and therefore the increase in solid-solution strength from 1.85 at\% Cu and 0.75 at\% Si in Al was found to be 37.5 MPa. This results in the predicted yield strength of between 31.5 MPa for \( k = 2 \) and 49.5 MPa for \( k = 1 \) at the solid-solution composition. Further increases in yield strength can be associated with strengthening from the eutectic phase in the microstructure.

Figure 6-11: Solid-solution strengthening in Al for Cu and Si. The blue line shows a linear fit for the Al-Si data, whereas the red line shows a Fleisher model for the Al-Cu data. Graph plotted with tabulated data found in (127, 130, 131).
As the eutectic tensile yield strength is difficult to determine due to the brittle nature of the material, it is possible to estimate its contribution from the compressive data. Looking at Table 6-5, the compressive yield strength of the eutectic phase is 79.3% greater than the yield strength of the solid-solution alloy in Al-Cu-Si. Therefore, it is postulated that the tensile yield strength of the eutectic phase will also be 79% greater than the tensile yield strength of the solid-solution phase. Previously, the estimated solid-solution strength was found to be 37.5 MPa, therefore the estimated tensile yield strength from the eutectic phase would be 67.1 MPa for use in the model.

Inserting the estimated results just obtained – $\sigma_{Al} = 12$ MPa, $\sigma_{SS} = 37.5$ MPa, $\sigma_{Eut} = 67.1$ MPa – into the Nembach model (Equation 4-3) results in an estimated matrix strength between 77.8 MPa and 116.6 MPa for $k = 2$ and $k = 1$, for an average value of 97.2 MPa. Compared to the strength values obtained for the Al-4.1Cu-2.0Si (at%) found in Table 6-1, this predicted strength falls at the low end of the range found experimentally: 112.7 ± 15.7 MPa. Using the rule of mixtures model (Equation 6-2) and inserting these estimated values – $\sigma_{SS} = 37.5$ MPa, $\sigma_{Eut} = 67.1$ MPa – results in a predicted strength of 104.6 MPa which also falls within the experimental range. Therefore, the prediction of the matrix strength properties via models for the design of a self-healing MMC may be reasonable to use.

**Composite Strengthening Model**

Composite strengthening in a longitudinal, continuous-fiber composite can be estimated using a rule of mixtures model incorporating the individual contributions to strength of the different phases (112). The general equation for strength prediction:

$$\sigma_c = (1 - X) \sigma_m + X \sigma_f$$

(Eq. 6-5)
where $\sigma_c$ is the strength of the composite, $\sigma_m$ is the strength of the matrix alloy, $\sigma_f$ is the strength of the fiber, and $X$ is the phase fraction of the fibers. Using the average values for the Al-Cu-Si matrix UTS = 112.7 MPa (Table 6-1), the plateau strength of the heat-treated NiTi fibers = 131 MPa (Table 6-4), and a fiber volume percent of 2.65%, the predicted composite strength is 113.0 MPa. Compared to the average Al-Cu-Si composite values in Table 6-2, this predicted value falls within 3 MPa of the measured composite strength of 115.7 MPa.

Another predictive model for composite strength (Equation 4-4) combines the Nembach model with the rule of mixtures. Using the values of the estimated matrix strength – between 77.8 MPa and 116.6 MPa for $k = 2$ and $k = 1$ – and the plateau strength of NiTi and volume percent previously stated, the composite strength in the range of 79.2 – 117.0 MPa. Comparing this to the previous results shows that the prediction of strength via the Nembach-based model works best with a value near $k = 1$.

**Internal Stress in SMA Wires**

In her dissertation, Manuel (80) introduced a model to determine the minimum volume fraction of SMA wires required to induce a clamping force at the crack interface during a healing cycle. The model is based on the transformation temperatures of the SMA wires and the compressive yield strength of the matrix at elevated temperatures.

The Johnson-Cook relationship (152) is shown in Equation 6-6:

$$
\sigma_{flow} = \left[ A + B\varepsilon^n \right] \left[ 1 + C \ln \dot{\varepsilon}^* \right] \left[ 1 - \left( \frac{T - T_{room}}{T_{melt} - T_{room}} \right)^m \right]
$$

(Eq. 6-6)

where $\sigma_{flow} =$ flow stress of alloy, $\varepsilon =$ plastic strain, $\dot{\varepsilon}^*$ = normalized plastic strain rate, $T_{room} =$ room temperature, $T_{melt} =$ melting temperature of alloy, and $A$, $B$, $C$, $n$, and $m$
represent material constants. Each set of brackets represents a subset of work-hardening, strain rate, and thermal effects. Because only temperature effects on stress are desired, Equation 6-6 can be simplified to:

\[
\sigma_{\text{flow}} = A \left[ 1 - \left( \frac{T - T_{\text{room}}}{T_{\text{melt}} - T_{\text{room}}} \right)^m \right] 
\]  
(Eq. 6-7)

Because of the nature of the alloys, the eutectic temperature (\(T_{\text{eut}}\)) of the alloy was utilized as \(T_{\text{melt}}\) due to the softening which occurs in a partially liquefied alloy. Thus, the modified Johnson-Cook relationship can be represented by:

\[
\sigma_{\text{flow}} = A \left[ 1 - \left( \frac{T - T_{\text{room}}}{T_{\text{eut}} - T_{\text{room}}} \right)^m \right] 
\]  
(Eq. 6-8)

In an equilibrium condition, there are equal applied forces (\(F\)) when the matrix is being clamped back together by the SMA wires at elevated temperatures (Figure 3-8d). Equal forces equate to normalized stresses (\(\sigma\)) over an area (\(A\)) for the matrix and SMA wires:

\[
F_{\text{SMA}} = F_{\text{matrix}} \quad \rightarrow \quad \sigma_{\text{SMA}} A_{\text{SMA}} = \sigma_{\text{matrix}} A_{\text{matrix}} 
\]  
(Eq. 6-9)

If this relationship is divided by the cross-sectional area, the following relationship is obtained:

\[
\sigma_{\text{SMA}} V_f = \sigma_{\text{matrix}} (1 - V_f) 
\]  
(Eq. 6-10)

where \(V_f\) = volume fraction of SMA wires. During healing, the stress in the SMA wires will be equal to the reversion stress (\(\sigma_R\)) of the SMA wires and the stress in the matrix will equate to the matrix compressive yield stress (\(\sigma_{\text{MCYS}}\)) at elevated temperatures under compression. Thus, rearranging Equation 6-10 will yield:
\[ \sigma_R = \sigma_{MCYS} \left( \frac{1-V_f}{V_f} \right) \]

(Eq. 6-11)

Equation 6-11 shows that the reversion stress of the SMA relates to the compressive yield strength of the alloy through an indirect relationship with the volume fraction of the SMA wires in the composite. Knowing that the flow stress of an alloy is equal to its yield strength while under compression (i.e. \( \sigma_{\text{flow}} = \sigma_{MCYS} \)), the model for optimal volume fraction of SMA wires in the composite is found by inputting the modified Johnson-Cook model (Equation 6-8) into Equation 6-11:

\[ \sigma_R = A \left[ 1 - \left( \frac{T - T_{\text{room}}}{T_{\text{melt}} - T_{\text{room}}} \right)^m \right] \left( \frac{1-V_f}{V_f} \right) \]

(Eq. 6-12)

This model describes the relationship to obtain the optimal volume fraction of SMA wires for a specific matrix alloy. To verify this model, both Al-Cu-Si and Al-Si alloys were investigated to compare results.

**Compression of Matrix Alloys**

To obtain the elevated temperature compressive yield stress of the alloys, Al-4.5Cu-2Si and Al-3Si (at%) bars were cast and heat-treated at 530°C for 24 hours and 592°C for 24 hours, respectively. Pieces were machined according to ASTM E209-00: Standard Practice for Compression Tests of Metallic Materials at Elevated Temperatures with Conventional or Rapid Heating Rates and Strain Rates (153). The samples were tested at a strain rate of \( 10^{-3} \text{ s}^{-1} \) on an MTS 810 Material Testing Machine with an argon-atmosphere furnace attachment. Each sample was tested at various temperatures to determine the compressive yield strength. The raw data for each of the alloys is found in Table 6-6.
Table 6-6: 0.2% Compressive Yield Strength at Elevated Temperatures of Al-4.1Cu-2Si and Al-3Si (at%) Alloys

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>0.2% Yield Strength (MPa)</th>
<th>Al-4.1Cu-2Si</th>
<th>Al-3Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>269</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>157</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>--</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>135</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>21</td>
<td>9.5</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>10</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>530</td>
<td>2</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>550</td>
<td>--</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

The data was plotted on a true stress vs. temperature graph and fitted to the modified Johnson-Cook model (Equation 6-8) with the parameters found in Table 6-7 used to determine fit (Figure 6-12).

Figure 6-12: Elevated temperature compressive yield strength for Al-4.1Cu-2Si and Al-3Si (at%) with an overlaid modified Johnson-Cook model for fit.

Table 6-7: Parameters Used to Model Elevated Compression Testing in Al-4.1Cu-2Si and Al-3Si (at%) Alloys

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Al-4.1Cu-2Si</th>
<th>Al-3Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>270</td>
<td>65</td>
</tr>
<tr>
<td>m</td>
<td>0.7</td>
<td>0.6</td>
</tr>
<tr>
<td>T_{room} (°C)</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>T_{heal} (°C)</td>
<td>592</td>
<td>530</td>
</tr>
</tbody>
</table>
Transformation Temperatures in NiTi Wires

To determine how stress increases would shift the transformation temperatures in the NiTi SMA wires, BB wires were loaded on the Instron 5582 in tension at specific stress values. The wires were previously heat-treated at 530°C for 24 hours to simulate healing temperatures in Al-Cu-Si composites. The wire loaded at the specific stress was then held at the displacement this stress imparted for the remaining portion of the test. The temperature was increased on the wires under tension and the temperature was recorded where transformation in the SMA wires was observed by an increase in stress. The results of the testing are shown in Figure 6-13. The black dots represent the A_s and A_f temperatures as determined previously from the DSC. The linear fit lines were found to increase at a rate of 5.5 MPa/°C. This aligns with previous research which has shown typical rates are from 2.5 – 15 MPa/°C (113).

Figure 6-13: Change in A_s and A_f for NiTi wires heat-treated at 530°C for 24 hours. The black dots are the A_s and A_f temperatures determined by DSC. The linear fit lines were found to increase at 5.5 MPa/°C.
Next elevated temperature testing of the SMA wires was conducted to determine the reorientation/yield temperatures. Olson and Cohen (154) described a stress-temperature dependence for martensitic nucleation. Below a specific temperature and stress state called $M_{s\sigma}$, initial yielding of the wire occurs through a stress-assisted transformation from twinned martensite to detwinned martensite; i.e. reorientation of the martensitic phase. However, above $M_{s\sigma}$, the strain-induced nucleation of the parent phase occurs through a slip; i.e. yielding of austenite. Using BB NiTi SMA wires which were heat-treated at 530°C for 24 hours, elevated temperature tensile testing was conducted on the Instron 5582. Results of the testing can be found in Table 6-8. Overlaying this data on the previously determined $A_s$ and $A_t$ temperatures for similarly heated wires results in Figure 6-14.

![Figure 6-14: Schematic of the stress-temperature relationships for NiTi BB SMA wires.](image)
Table 6-8: Elevated Temperature Tensile Testing of NiTi BB Wires Heat-Treated at 530°C for 24 hours

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>0.2% Offset Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>85.6</td>
</tr>
<tr>
<td>50</td>
<td>108.1</td>
</tr>
<tr>
<td>100</td>
<td>166.8</td>
</tr>
<tr>
<td>150</td>
<td>166.8</td>
</tr>
<tr>
<td>200</td>
<td>140.4</td>
</tr>
</tbody>
</table>

Optimization of NiTi Wire Fraction in Al-Based Composites

Using the previously gathered NiTi stress-temperature data and overlaying the calculated stress in NiTi SMA wires within an Al-4.1Cu-2.0Si (at%) composite using Equation 6-12 results in the data shown in Figure 6-15. It was noted that the minimum NiTi fiber volume percent required was determined to be 55%, meaning the composite would possess more SMA wires than matrix alloy to be effective.

![Figure 6-15: Schematic of the stress-temperature relationships for NiTi BB SMA wires heat-treated at 530°C for 24 hours with the stress in SMA wires found in an Al-4.1Cu-2.0Si (at%) composite with Vf = 55% of NiTi wires.](image)

Similar data was collected for SMA wires incorporated in an Al-3 at% Si composite (Figure 6-16). Here, the volume % of SMA wires was calculated to be 25%.
However, as healing was found in Al-Si composites at less than 2.5 vol% SMA wires, the Manuel model was found to be inadequate at determining minimum SMA volume fractions in Al-based composites. This can be attributed to the assumptions in the model including equal strain and no plasticity in the composite. For composite models exhibiting equal strain, the ends of the reinforcements are fixed to the ends of the matrix and elongation results in equal length changes for both matrix and reinforcement, without sharing an equal stress. However, because of the interfacial bonding, load sharing will occur, which would decrease the stress found in the NiTi wires. Also, plasticity was found to not be negligible in the Al-Si composite with failure strains of nearly 4% on average. The increased toughness in the composite would also decrease the required NiTi volume fraction. Therefore, further investigations into more refined models will be required to optimize the volume fraction of SMA wires in future self-healing MMCs.

Figure 6-16: Schematic of the stress-temperature relationships for NiTi BB SMA wires heat-treated at 592°C for 24 hours with the stress in SMA wires found in an Al-3.0Si (at%) composite with $V_f = 25\%$ of NiTi wires.
Novel Processing Techniques

The healing of the Al-Cu-Si composites did not match the high healing percent results found in Sn-Bi or Al-Si composites. It is thought the lack of transformation of the SMA wires because of the lack of ductility in the matrix alloys prevented a clamping force from occurring during healing. This clamping force has been shown to be required for healing (Chapter 3). Thus, different fabrication techniques were investigated to determine if healing of Al-Cu-Si composites could be improved.

Pre-strain of SMA Wires

Previous research into SMA reinforcement for crack closure in composites had shown the need for pre-straining the SMA wires to ensure a clamping force following a crack event (81, 100). Therefore, an investigation into pre-straining the NiTi SMA wires prior to casting was conducted. First, a NiTi BB wire was heat-treated at 530°C for 24 hours to relieve residual stresses from fabrication and to move $A_s$ transformation temperatures above room temperature. This meant the wires were in the martensitic state at room temperature, and thus the SMA wires would retain any deformation until they were heated above their $A_s$ temperature.

The heat-treated NiTi wires were pulled in tension to 5% strain using the Instron 5582. Each wire was then place into a custom jig designed to hold the wire fast during the high temperature casting and not allow for transformation. Using similar casting techniques to those utilized in fabricating previous Al-4.1Cu-2.0Si (at%) composites, castings were poured with the pre-strained SMA wires. Samples were tensile tested, and healed as previous, but little healing was noted. It was observed that the elongated length of the SMA wires in the pre-strained state was not retained following initial casting, so it is thought the SMA wires returned to their austenitic state during casting.
despite the jig to prevent this. Therefore, pre-staining the wires via different means was continued.

**Hot Compression for Composite Fabrication**

Wrought products are known to have higher mechanical properties than traditional cast products because the deformation processes reduce defects. Therefore, a mechanical means of improving ductility in the Al-Cu-Si composites was investigated in a joint project with another member of the Manuel group, Glenn Bean. First, an alloy of Al-4.1Cu-2.0Cu (at%) was cast into a bar and heat-treated at 530°C for 24 hours to set the microstructure. The bar was cut into thin plates (thickness ~ 1 mm) via electric discharge machining (EDM) at NASA’s Kennedy Space Center (KSC).

Thin NiTi SMA wires (BH), were prepared similar to those for the Sn-Bi composites: heat-treating at 500°C for 3 hours. Two thin plates were then pressed around 3 aligned BH wires at 500°C at a strain rate of $10^{-4}$ s$^{-1}$ to creep the matrix around the wires and pressed further at 530°C at different stresses for varying times. The pressing was completed in an argon atmosphere on the MTS 810 testing machine. A design of experiments (DOE) was completed to determine if time or pressure was most important during the hot-pressing fabrication (Table 6-9).

![Table 6-9: Parameters of DOE for Hot-Pressing Fabrication of Al-Cu-Si Composites](image)

<table>
<thead>
<tr>
<th>Condition</th>
<th>Force (MPa)</th>
<th>Time (hr)</th>
<th>Run Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>8</td>
<td>3</td>
</tr>
<tr>
<td>C</td>
<td>4</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>D</td>
<td>4</td>
<td>8</td>
<td>4</td>
</tr>
</tbody>
</table>

Upon completion of fabrication, each bar was machined to a 320-grit finish and pulled in tension on the Instron 5582 at a rate of 1.0%/minute. Each composite was found to have a SMA vol% between 1.0-1.5%. Results of the virgin tensile testing can
be found in Table 6-10. It was noted the highest yield strength was achieved in a composite pressed at 2 MPa for 8 hours, but the highest UTS and strain to failure was found in a specimen pressed at 4 MPa for 4 hours.

Table 6-10: Parameters of DOE for Hot-Pressing Fabrication of Al-Cu-Si Composites

<table>
<thead>
<tr>
<th>Condition</th>
<th>Vf Wires (%)</th>
<th>0.2% Yield Strength (MPa)</th>
<th>Ultimate Strength (MPa)</th>
<th>Failure Strain (%)</th>
<th>Diffusion Layer Thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.40</td>
<td>89.0</td>
<td>89.5</td>
<td>0.39</td>
<td>2.92</td>
</tr>
<tr>
<td>B</td>
<td>1.37</td>
<td>117.7</td>
<td>119.8</td>
<td>0.45</td>
<td>8.54</td>
</tr>
<tr>
<td>C</td>
<td>1.28</td>
<td>110.5</td>
<td>133.3</td>
<td>0.66</td>
<td>3.59</td>
</tr>
<tr>
<td>D</td>
<td>1.55</td>
<td>N/A</td>
<td>102.5</td>
<td>0.33</td>
<td>8.14</td>
</tr>
</tbody>
</table>

Further microstructural inspection of the cross-section revealed a diffusion layer at the SMA/matrix interface. Using energy dispersive spectroscopy (EDS) analysis, the diffusion was found to be mostly Al and Si into the NiTi wires (Figure 6-17). Results of the total thickness of the diffusion layer into the NiTi wires can be found in Table 6-10. The diffusion layer was found to be strongly dependent upon time, but did not very with changes in stress.

Images of the post- hot-pressing microstructure can be found in Figure 6-18 for specimens with the highest mechanical properties (condition B and C). Note how the grains have grown over the interface between the original two matrix bars. After tensile testing, each bar was healed at 530°F for 24 hours under vacuum, but found to heal less than 15% in terms of strength retention (Equation 3.1).

Another specimen was prepared with multiple plies of SMA wires (4 layers of matrix, 3 plies of wires) was also prepared in a similar manner to Condition B, which exhibited the highest yield strength. The multiple plies resulted in an increase to 1.67 vol% NiTi wires. Tensile testing was completed and a significant increase in strain to...
Figure 6-17: EDS analysis of a representative microstructure of a hot-pressed Al-Cu-Si composites: a) SEM image of the NiTi wire in the matrix, b) SEM image of the area in the red box in a) with the elemental analysis overlaid, and c) elemental analysis showing diffusion of Al and Si into NiTi SMA wire. Cu was not found to diffuse into the NiTi.

Figure 6-18: Microstructure of Al-Cu-Si composites a) pressed at 4 MPa for 4 hours and b) pressed at 4 MPa for 8 hours.
failure was noted (Figure 6-19). Over the 1-ply hot-pressed sample, the strain to failure was increased over 140%, but against a traditionally cast Al-Cu-Si composite (specimen 1), the strain to failure was increased over 210%. When a healing heat-treatment was conducted – vacuum-encapsulated in Pyrex on a graphite sheet covered in Ta foil and heated at 530°C for 24 hours – the 3-ply sample was found to exhibit over 37% healing. This leads to the conclusion that deformation-based fabrication techniques may help increase healing in brittle matrix alloys.

![Graph showing tensile behavior](image)

**Figure 6-19:** Comparison of tensile behavior of a cast Al-Cu-Si composite ($V_f = 2.32\%$), a hot-pressed Al-Cu-Si composite with 1-ply ($V_f = 1.37\%$), and a hot-pressed Al-Cu-Si composite with 3-pies ($V_f = 1.67\%$). The hot-pressed 3-ply composite exhibited an increase of strain to failure of over 140% on the 1-ply specimen and over 210% on the cast specimen.

**Summary**

In an effort to produce a stronger matrix with self-healing potential, an Al-4.1Cu-2.0Si (at%) composite was designed and fabricated. Tensile behavior showed a stronger composite, but lacked the strain to failure required to induce a pre-strain in the
NiTi reinforcements needed to cause a clamping force during a healing cycle. Increases in the vol% of SMA wires yielded greater moduli and strengths, but also lacked ductility. Various strength models used in the design methodology were verified, but a model used to optimize the vol% SMA wires was found to lack robustness for Al-based matrices. Different fabrication techniques were investigated to induce higher failure strains and hot-pressing while at the healing temperature was found to induce bonding across an interface while also increasing the strain to failure. Increasing the vol% through multiple plies resulted in the largest failure strains while also bringing healing of the composite up to over 37% retained strength.
CHAPTER 7
REACTIVE ELEMENT ADDITIONS

Bonding characteristics between liquid phases and solid surfaces is vital to the understanding healing in metal-matrix composites. Surface oxides, however, have been found to decrease the bond strength at the solid/liquid interface. An in-situ fluxing technique inspired by lead-free solder research has shown promise to improve healing capabilities in atmosphere. The method requires a reactive element alloying addition to the matrix composition which possesses a lower free energy of oxide formation than the parent element, thus creating a strong chemical bond across the interface as the reactive element addition reduced the parent element oxide.

This chapter will show how the reactive element addition maintains fracture toughness values measured using the chevron-notch short bar technique after a bonding heat treatment by increasing the bond strength along the interface and deflecting the crack into the matrix. Next, the methodology will be detailed for addition of reactive elements to the matrix alloys used in liquid-assisted self-healing in MMCs.

Interfacial Toughness

Traditional techniques for joining such as welding, soldering, and brazing utilize a liquid phase to bond two or more metallic components. Advanced processing methods, such as liquid phase sintering (LPS) (155, 156) and transient liquid phase bonding (TLP) (157, 158), also inherently use a liquid phase to enable joining of components. Often, the substrate will possess a native oxide surface which hinders the production of a strong bond.

In order to increase the propensity for bonding between the liquid and metal surface, and thus the quality of the bond, fluxing agents are frequently used to
breakdown or chemically reduce the surface oxide layer. This fluxing increases the availability of bonding sites for the liquid to react with the underlying metal as well as increasing the wettability of the surface (159, 160). To simplify this process, in-situ fluxing techniques have been developed utilizing self-fluxing alloys which possess alloying additions to increase wettability and depress the melting temperature (161). Joining in the presence of a reducing environment has also been found to increase the wettability and bond efficiency (159, 162).

Investigations into lead-free solders utilizing rare earth element additions to increase bond strength between metals and oxides have yielded positive results (163-165). It has been proposed that the reason for the increase in bond strength can be attributed to a strong chemical bond created at the solid/liquid interface through reduction of the metal oxide by the rare-earth element addition, which possess a highly negative free energy of formation (164, 166, 167). To expand on this research for self-healing metal-matrix composites, an investigation into the thermodynamic principles of the bonding characteristics was undertaken.

To study the effect of reactive elemental species during bonding, interfacial plane-strain fracture toughness testing via the chevron-notch short bar (CNSB) technique was utilized. The chevron-notch technique has been found to yield reproducible interfacial fracture toughness results (168-170), and will therefore be utilized to obtain a quantitative measure of crack growth resistance at metal/oxide interfaces. Additionally, the short bar technique works well for alloy development because the specimen size is relatively small (10mm x 10mm x 14.5mm), fatigue pre-cracking was not necessary due to the stress concentration and geometry to initiate a
sharp crack at the tip of the chevron-shaped notch (171). Furthermore, knowledge of the crack size is not required to determine the fracture toughness ($K_{IC}$) because the critical point is constant for a specified geometry (168). A schematic of a representative CNSB specimen is found in Figure 7-1.

![Figure 7-1: Schematic of a chevron-notch short bar (CNSB) specimen. Adapted from ASTM Standard E 1304 - 97. 2008. Standard Test Method for Plane-Strain (Chevron-Notch) Fracture Toughness of Metallic Materials (Page 925, Figure 3). ASTM International, West Conshohocken, PA.](image)

**Matrix Design**

To study how reactive elements could improve healing characteristics, phase diagrams of two alloys, one containing a reactive species (relative to the primary element) and the other containing a non-reactive element addition were investigated. These prototype alloys must possess two characteristics. First, each system must exhibit a low temperature eutectic phase transformation akin to the previous Al- and Sn-based systems investigated for self-healing. Second, each system exhibited limited solubility of the reactive and non-reactive species, translating to the additive element strongly partitioning to, and thus residing in, the liquid phase during heat treatment.
The selected binary alloys meeting the above criteria were antimony-copper (Sb-Cu) and antimony-zinc (Sb-Zn). For this study, Sb will serve as the base element with Cu the thermodynamically less reactive and Zn the more reactive addition based on free energies of formation as shown on the Ellingham diagram (Figure 7-2). The lower (more negative free energy) the element falls on the diagram, the greater the driving force at a given temperature for the oxide to oxidize any other element of higher energy in its presence.

![Ellingham Diagram](image)

**Figure 7-2**: Ellingham diagram showing relative position of free energy for oxide formation for Cu, Sb, and Zn. Curves plotted with free energy data obtained from (110).

The specific alloy composition utilized for testing was determined by plotting the percent liquid and percent solute in liquid versus temperature (172, 173). For both systems, alloys containing 4 at% solute were chosen to ensure both alloys had a consistent liquid percent and percent solute in liquid during heat treatment. At 4 at% solute, both Sb-Cu and Sb-Zn alloys crossed at 20% (Figure 7-3); this translates to heat
treatment temperatures of 555°C for Sb-Zn and 574°C for Sb-Cu. These temperatures correspond to the solid + liquid phase region (Figure 7-4) for both of the respective binary alloys. An alloy of the eutectic composition, Sb – 37 at% Cu and Sb – 33 at% Zn, was also selected for testing to quantify the fracture toughness of the solidified liquid phase for comparative purposes.


**Sample Fabrication**

The 4 at% solute alloys and eutectic alloys were prepared by placing appropriate amounts of Sb (Sb shot, 99.999%, Alfa Aesar) and Cu (Cu shot, 99.9%, Alfa Aesar) or Zn (Zn shot, 99.99%, Alfa Aesar) in graphite crucibles coated with boron nitride and heating at 750°C in an argon atmosphere until a liquid solution formed. Each alloy was

cast into a coated graphite bar mold and allowed to air cool.

The alloys at the eutectic composition were heat-treated at 400°C in air for 24 hours to homogenize before machining. The Sb-4Zn and Sb-4Cu alloys were heat-treated at 555°C and 574°C, respectively, in air for 24 hours before air-cooling. All specimens were machined to approximately 10mm x 10mm x 14mm and polished to a 320-grit surface finish to reduce the possibility of surface cracks skewing results.

One set of the Sb-4Zn and Sb-4Cu alloys, post initial heat-treatment, were cut in half and polished to a 4000-grit finish on the inner surface. The finely polished surfaces of each half were then held together while the specimen was placed into a steel holder covered with carbon paper to prevent any chemical reaction between the steel and the specimen during heat treatment. This holder was used to clamp to two halves together during heat treatment in an open-air furnace for bonding (Figure 7-5). These specimens underwent a second, healing heat treatment at identical temperatures as previous in
After heat treatment, a chevron notch was machined into all Sb-Zn and Sb-Cu specimens for interfacial fracture toughness testing as per ASTM Standard E-1304 (171). For the healed specimens, the notch was located along the bonded interface.

**Mechanical Testing**

Interfacial fracture toughness testing was conducted on a TerraTek Model 4400A Fractometer. The data collected is summarized in Table 7-1. A t-test using Hsu’s Method (assumes two populations with normal distributions but standard deviations probably unequal) with a 95% confidence interval was run and found there was no statistical significance in the fracture toughness between the monolithic and healed specimens of either Sb-4Cu or Sb-4Zn. The Sb-Cu eutectic alloys were found to possess greater fracture toughness values than eutectic Sb-Zn.

| Table 7-1: Summary of Fracture Toughness Testing of Sb-Cu and Sb-Zn Alloys |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Alloy          | Fracture Toughness (MPa√m) [Avg. ± 1σ] | | |
|                | Monolithic       | Healed          | Eutectic        |
| Sb-Cu          | 2.08 ± 0.22      | 1.59 ± 0.39     | 1.93 ± 0.22     |
| Sb-Zn          | 0.94 ± 0.23      | 1.10 ± 0.12     | 0.50 ± 0.22     |
Representative micrographs of the Sb-4Cu and Sb-4Zn alloys are found in Figure 7-6 at the fracture interface. Both the monolithic and healed alloys exhibit coarse microstructures; on average, the Sb-4Cu grains were approximately 500 μm and Sb-4Zn grains were approximately 700 μm. The morphology of the phases present at the grain boundaries of the Sb-4Cu and Sb-4Zn monolithic and healed specimens was determined to be eutectic in nature. As seen in Figure 7.6, the eutectic phases can be observed along the interface in both the Sb-Cu and Sb-Zn bond specimens. Energy-dispersive spectroscopy (EDS) analysis revealed the presence of ZnO at the bond interface as shown in Figure 7-7. Copper oxide was not found along the Sb-Cu bonded interface; instead a Sb$_2$O$_3$ phase was found on all of the specimen surfaces.

![Figure 7-6: Representative micrographs of a) Sb-4Cu and b) Sb-4Zn (at%) at the interface. Healing was not evident in Sb-4Cu, but was evident in the Sb-4Zn alloy as seen by the crack line following eutectic lines in the bulk alloy and not at the healed interface.](image)

Representative images of the fracture surfaces for both Sb-4Cu and Sb-4Zn healed alloys are shown in Figure 7-8. The dashed lines show the location of the chevron notch, whereas the solid line represents the end of the bonded area over which the fracture occurred. For the Sb-4Cu alloys, the remaining, non-bonded, area is
Figure 7-7: Image along Sb – 4 at% Zn healed interface showing presence of ZnO.

Figure 7-8: Fracture surfaces of a) Sb-4Cu and b) Sb-4Zn (at%) healed samples. Notice the greater fracture area for Sb-Zn compared to Sb-4Cu.

coated in a layer of Sb$_2$O$_3$ (as confirmed through EDS analysis) from the oxidation of Sb during heat treatment. It was noted that the Sb-Zn specimens exhibited more bond area than Sb-Cu specimens as evidenced by the fracture surface area (Table 7-2).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Bond Area (%) [Avg. ± 1σ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb-4Cu</td>
<td>39 ± 19</td>
</tr>
<tr>
<td>Sb-4Zn</td>
<td>89 ± 7</td>
</tr>
</tbody>
</table>
Analysis

Thermodynamic Driving Force

During the healing heat treatment for the Sb-4Zn and Sb-4Cu alloys, the eutectic constituents (Sb + β-SbZn or Sb + η-SbCu) liquefied as the temperature was raised above the eutectic temperature. Since Sb is known to oxidize readily at elevated temperatures, especially above 500°C (55), the newly liquefied eutectic phases in the Sb-Cu and Sb-Zn alloys would immediately begin to form Sb$_2$O$_3$ on the exposed surfaces, including the cut and polished interface, in the following manner (110):

\[
\frac{4}{3}\text{Sb} \,(s) + \text{O}_2 \,(g) \rightarrow \frac{2}{3}\text{Sb}_2\text{O}_3 \,(s) \quad [\Delta G^\circ = -332.1 \text{ kJ}] \quad (\text{Eq. 7-1})
\]

Excess Sb$_2$O$_3$ was also discovered in small spheres formed on the outside of each specimen (Figure 7-5). These features were found on all of the bonded specimens after heat treatment. The presence of this surface oxide was noted on every Sb alloy and verified through EDS analysis.

Sb-Zn Specimens

At the heat treatment temperature of 555°C, the reactive alloy heal specimen of Sb-4Zn has 20 at% Zn which has partitioned to the liquid and is available to react with oxygen. The ZnO, possessing a lower Gibbs free energy of formation than Sb$_2$O$_3$, is expected to reduce the Sb$_2$O$_3$ found along the interface (110):

\[
\text{Sb}_2\text{O}_3 \,(s) + 3\text{Zn} \,(s) \rightarrow 3\text{ZnO} \,(s) + 2\text{Sb} \,(s) \quad [\Delta G^\circ = -317.6 \text{ kJ}] \quad (\text{Eq. 7-2})
\]

This formation of ZnO creates a chemical bond welding the two halves of the specimen together during the heat treatment. Although it was anticipated that the Sb-4Zn alloys would display an increase in interfacial fracture toughness over the monolithic value due to its increased propensity of forming a strong bond the interface, it
was noted that the fracture toughness did not deviate significantly after bonding. Close inspection of the crack path in Figure 7-6b shows that the crack progressed through the eutectic in the bulk of the specimen as opposed to the strongly bonded interface. The low fracture toughness of the eutectic facilitated this failure mechanism as it represented the “weakest link.”

**Sb-Cu Specimens**

The Sb-4Cu bond specimens have 20 at% Cu available to oxidize at their elevated bonding temperature of 574°C. However, since Cu₂O possesses a greater Gibbs free energy of formation than Sb₂O₃, it is not thermodynamically favorable for Cu to reduce the Sb₂O₃ formed along the interface during heat treatment, as indicated by the positive free energy of formation shown below (110):

$$\text{Sb}_2\text{O}_3 (s) + 6\text{Cu} (s) \rightarrow 3\text{Cu}_2\text{O} (s) + 2\text{Sb} (s) \quad \Delta G^\circ = 154.9 \text{ kJ} \quad \text{(Eq. 7-3)}$$

There was no evidence of Cu₂O bonding the halves together as there was ZnO in the Sb-4Zn alloys. The Sb₂O₃ in Sb-Cu bonded specimen passivated the crack surface preventing efficient bonding by the liquefied eutectic constituent. This is shown by the reduction of bonded surface area at the interface as shown in Figure 7-8. It is thought the Sb₂O₃ would have started forming at the exterior edges of the interface first and continued inward to the center of the specimen. Therefore, the bonded area of the interface would have only been in the center of each specimen where the Sb₂O₃ was not able to form. As the chevron notch was cut after the heat-treatment was completed, the bonded area was near the tip of the chevron notch, locating the crack front at the center of the specimen. This unexpected processing condition would explain why the
fracture area for the Sb-Cu alloys was only at the interior of each of the chevron notch specimens.

In comparing the healed to monolithic specimens, it was still found that the fracture toughness values in the Sb-4Cu alloys were similar. This is most likely caused by inflation of the fracture toughness values due to the influence of testing geometry. In the chevron-notch test, Newman (170) details how the fracture toughness value for an alloy can be determined when the crack length, a, is between a₀ and a₁ (Figure 7-9). Using finite element analysis, it has been determined the crack length must reach a certain length or the fracture toughness results will be artificially inflated (174). This has been confirmed with experiment (170). Therefore, if the crack, a, did not reach its critical length, aᶜ, because the specimen was not bonded in that area, then a < aᶜ, resulting in an inflated fracture toughness value, Kᵢ > Kᵢᶜ. This artificial inflation is the most likely cause for the similar fracture toughness values for the Sb-Cu bonded and monolithic alloys.

The increase in bond area for the Sb-Zn alloys over the Sb-Cu alloys is also attributed to an increase in wettability. The addition of a reactive element to an alloy has been shown to increase liquid metal wettability on metal oxide surfaces in other studies of metal-ceramic interfaces (175-178). This increase in wettability and bonding was similar to results found by several groups working on lead-free solders (163, 164, 166, 167). These groups have shown small additions of rare-earth elements when added to lead-free solders, in addition to increasing wettability, also enables bonding to several classes of materials including steels, oxides and carbides.

**Reactive Elements in Sn-Bi Matrix**

To advance this research to self-healing MMCs using the Sn-Bi prototype, a joint investigation with a senior research student, W. Patterson Tuttle was initiated (115). Previous attempts to heal the Sn-Bi alloys in air resulted in an oxide surface at the crack interface, which prevented healing from occurring. It is thought a reactive element addition will reduce this oxide surface and enable healing in open air.

Potential candidates for the reactive element addition in a Sn-Bi composite must have two characteristics. First, the free energy of oxide formation for the addition must be lower than both SnO$_2$ and Bi$_2$O$_3$, ensuring the ability to reduce down the surface oxide at the crack interface. Next, the element must not possess any solubility with Sn in order to ensure it would partition towards the eutectic phase which liquefies during a
healing cycle. Of the 20 elements which matched these criteria, two were selected for further study. Ce was selected because it possesses the lowest melting point of the rare-earth elements and Li because its melting point is below that of both Sn and Bi.

From the work completed by Ramirez and colleagues (164, 166), it was found that less than 2 wt% of rare earth elements were added to lead free solders to increase bonding to various materials. They also found these small alloying additions did not significantly alter the melting point of the solder alloy. Therefore, a composition of Sn – 13.0 at% Bi – 0.2 at% Ce or Li would be investigated for healing potential.

Master alloys of Sn-4 at% Ce and Sn-20 at% Li alloys were prepared by placing appropriate amounts of Sn (Sn shot, 99.8%, Alfa Aesar) and Ce (Ce chips, 99.9%, Alfa Aesar) or Li (Li granuales, 99%, Alfa Aesar) in graphite crucibles coated with boron nitride. The alloys were heated at 600°C for Sn-Ce or 400°C for Sn-Li in an argon atmosphere until a liquid solution formed. Each alloy was cast into a coated graphite bar mold and allowed to air cool. After checking composition via ICP analysis, appropriate amounts of the master alloys were added to Sn and Bi (Bi needles, 99.99%, Alfa Aesar) to create the Sn-Bi-0.2 at% Ce or Li alloys. Each alloy was heated at 350°C in an argon atmosphere, cast into a coated graphite bar mold, and allowed to air-cool. Each bar was then vacuum-encapsulated in Pyrex glass tubes and heat treated for 24 hours at 169°C.

Following air cooling, each bar was machined to approximately 2mm thick wafers. Each wafer was polished to a 320-grit surface finish before being loaded into the steel holder utilized for the Sb alloy healing (Figure 7-5). The Sn-Bi-Ce or Li specimens underwent a second heat treatment at 169°C for 24 hours in an open-air furnace to investigate healing. Following air-cooling, the wafers were mounted and
polished to a 0.03 finish to look at the microstructure at the interface (Figure 7-10). In the image, healing was not evident in the Sn-Bi-Li sample as shown by the gap at the interface between the two wafers. However, the Sn-Bi-Ce showed signs of healing via grain growth across the interface line. Therefore, Sn-Bi-Ce was selected to move forward and to determine its failure stress akin to the experiments conducted on Sn-Bi alloys in Chapter 3.

More Sn – 13.0 at% Bi – 0.2 at% Ce bars were cast as previous. After an initial heat-treatment of 169°C for 24 hours, pieces were machined into rectangular bars and polished to a 320-grit surface finish. A slice was cut through the center of each bar and these interfaces were polished to a 4000-grit surface to ensure smooth contact. The pieces were then loaded into the Kovar diffusion couple jig and had a stress of 30 MPa applied via torque wrench. The sample and jig were then vacuum encapsulated and heat-treated for 24 hours at 169°C to heal the sample. Upon removal, the samples were attempted to load onto the Instron 5582 to be pulled in tension, but broke in handling, signaling lack of healing. Larger bars were attempted to increase the cross-sectional

![Figure 7-10: Representative micrographs of a) Sn-Bi-0.2Li and b) Sn-Bi-0.2Ce (at%) at the interface. Healing was not evident in Sn-Bi-Li, but was in the Sn-Bi-Ce specimen as seen by the grain growth across the interface.](image)
area for healing, but this had little effect. Two higher composition Ce additions, 0.5 and 1.0 at\%, were also attempted but lead to similar results. The samples all had a similar oxide surface similar to that found on the un-successful Sn-Bi composites attempted to be healed in air.

Looking back at Figure 7-10b, the small black circles were investigated and determined to be Ce$_2$O$_3$ via EDS analysis. It is believed that the Ce in the melt is so reactive it is creating Ce$_2$O$_3$ during initial casting even though melting was completed in an argon atmosphere. Therefore, because Ce$_2$O$_3$ formed in the melt, there is not any free Ce metal available during healing to reduce SnO$_2$ and healing is hindered. Future development of the addition of reactive elements to self-healing MMCs will need to account for this processing issue.

**Summary**

The healing heat-treatment applied to Sb-4Zn alloys resulted in retention of fracture toughness when compared to a monolithic sample. This is attributed to the reduction of Sb$_2$O$_3$ by Zn to form ZnO bonds along the healed interface. Sb-4Cu was also found to retain fracture toughness, but this is thought to be an artifact of the testing procedure. Addition of reactive element to a Sn-Bi matrix was attempted in order to improve healing of a Sn-Bi composite in air. Of the designed candidates, Ce was found to have the greatest potential. Unfortunately, difficulty in casting resulted in the oxidation of Ce before a healing cycle, and thus full healing was not realized. Future matrix designs with reactive element additions must take this into consideration during casting. However, it is not believed that additional reactive element addition to the matrix alloys needs to only be limited to rare-earth elements; alkaline earth metals also have potential to be used.
CHAPTER 8
CONCLUSIONS

Self-healing materials have shown potential to shift from a Damage Prevention paradigm of traditional materials to one of Damage Management, where the material itself is able to heal structural defects. Applications of this technology would enable improved properties in aeronautical, space, and underwater applications. Self-healing in metallic systems is based on either solid-state or liquid-assisted healing. Solid-state healing is found in fatigue crack and creep mitigation in aluminum and ferrous-based alloys and protective coatings. Liquid-assisted healing is found in electrical applications and metal-matrix composites.

A thermodynamic design-based systems approach will enable faster development of metallic systems for use as structural materials. This methodology uses a systems design chart to act as a roadmap to elucidate relationships across the processing-structure-properties-performance paradigm. This systems design method was used to develop a prototype Sn-Bi matrix reinforced with commercially available NiTi SMA wires. Healing was performed by heat-treating the composite at a temperature which would cause 20% of the matrix alloy to form into a liquid, acting as the healing material while the NiTi wires clamped the crack faces together. For the Sn-Bi system, average healing of 80% retained strength post-healing cycle with over 94% possible. The pressure required to enable the highest healing was found to be 30 MPa at the crack interface.

As the Sn-Bi composites were heavy and lacked strength requirements, higher strength matrix alloy design lead to Al-based binary alloys for use in the composite. Al-Sn was investigated because it exhibited the lowest eutectic temperature. Al-Cu was
investigated because it would show high strength increases per solute addition and decrease the eutectic temperature. Al-Mg was investigated because it showed potential for the highest total solid-solution strengthening of binary Al alloys. Al-Si was investigated because it would decrease the eutectic temperature and increase strength moderately, but would exhibit high castability. Composite samples were fabricated with NiTi SMA wire reinforcements, mechanical testing was completed in tension, and microstructures were examined via optical microscopy. Healing was performed on the cracked tensile samples.

The Al-Si was the only alloy system which exhibited appreciable healing. The Al-Cu and Al-Mg systems were too brittle to allow for transformation in the SMA wires, thus the required clamping force across the interface was not present. Al-Sn samples were found to be too ductile, allowing for necking and permanent strains to deform the NiTi wires. In Al-Si, the moderate ductility without much necking allowed for pre-straining of the SMA wires prior to healing, thus creating the clamping force at the interface to enable healing. Average healing was found to be over 91% retained strength post-healing cycle.

However, the Al-Si system possessed high healing temperatures and low yield strengths. Therefore, a higher strength ternary alloy, Al-Cu-Si, was designed. Samples were fabricated and the strength and thermodynamic models utilized to design the alloy were validated. Healing, however, was found to be relatively lacking due to the brittle nature of the matrix alloy. Therefore, novel processing techniques were investigated, including wire pre-straining prior to casting and hot-pressing. Hot-pressing was found to enable bonding across an interface, and enable multiple wires to be incorporated into
the composite, which greatly increased the failure strain in the Al-Cu-Si composite. Further refinement of this technique is desired to achieve higher healing outputs.

The healing of the Sn- and Al-based composites were all conducted under vacuum, a limitation to the application of liquid-assisted self-healing MMCs. Addition of reactive elements to lead-free solders has shown increase in bonding to oxide-containing surfaces. Therefore, a study was conducted to investigate a prototype Sb-based system with reactive and non-reactive additions. The fracture toughness of the reactive element addition specimen which was healed was found to match the monolithic specimen fracture toughness. Next, the addition of a reactive element to a Sn-Bi-X composite was investigated. However, oxidation of the reactive element during fabrication resulted in poor healing. Further refinement of the casting technique is required to enable incorporation of a reactive element to the Al-based composites.
CHAPTER 9
FUTURE WORK

To advance the research of self-healing MMCs, there are several areas of research with potential to delve into further investigations including 1) new matrix alloys, 2) new SMA reinforcements, 3) incorporation of reactive elements, and 4) optimization of healing cycles.

**Matrix Alloy Development**

While the initial work into different Al-based binary alloys and one ternary alloy has shown promise, further development of Al-based matrix alloys is needed. Increased yield strengths are needed to develop self-healing composites which will be able to replace current traditional materials. Because of the methodology used in developing the self-healing composites, it is thought the thermodynamic design can be used to advance other matrix alloys. One, Al-Mg-Li, shows potential for the highest specific strength via solid-solution strengthening and low density. Another, Al-Mg-Cu, emulates 6000-series Al alloys with the ability for high strength increases through precipitation of secondary phases. Initial research into Al-Mg-Li and Al-Mg-Cu can be found in Appendix A.

Other ternary alloy matrices with self-healing potential include Al-Mg-Cu, Al-Mg-Zn, and Al-Cu-Li. These alloys exhibit a ternary eutectic point on the Al-rich side near a region of Al solid solution.

**Shape Memory Alloy Development**

Currently, the SMA wires incorporated into the self-healing composites are purchased commercially. These wires are not designed to be heated to the high temperatures involved with the healing process in Al-based systems and their strengths
show large decreases after a healing cycle from the as-received values. Therefore, future designs must incorporate SMA wires able to withstand greater temperatures while maintaining their strength. This would enable higher yield strengths from the Al-based composites and thus more application areas for liquid-assisted self-healing MMCs. Work by another member of the Manuel group, Derek Hsu, is currently pursuing high temperature SMA with his doctoral research (179).

**Reactive Element Incorporation**

Oxidation at the fracture surface has been found to prevent healing in Sn- and Al-based matrix alloys with self-healing potential. Therefore, incorporation of reactive element additions similar to those designed in Chapter 7 has the potential to enable healing in an oxygen-containing environment. This would be critical to improving self-healing MMCs for use in terrestrial applications.

With the success of the Sb-based prototype alloys, the design of reactive elements to the Al-based matrices must be pursued. Due to the reactivity of Al, potential additions are mostly limited to rare-earth metals (e.g. Ce, Gd, Y) and alkaline earth metals (e.g. Ca, Y). The reactive element addition must oxidize preferentially over all other elements in the matrix alloy to ensure it will reduce any formation of surface oxides at the crack interface. The addition must also partition to the eutectic phase, to ensure it will be melted during the healing cycle, thus enabling faster reduction kinetics of surface oxides.

**Healing Cycle Optimization**

After more advanced composites are developed, optimization of the healing cycle is required. Currently, healing is conducted over a 24 hour period. However, a reduction of this time would enable incorporation of self-healing MMCs into more applications.
Optimization would not only include the time, but also the temperature required for healing, which directly affects the percent liquid. Previous work had shown 15-20% was optimal for Sn-Bi alloys (78), but it is not known whether or not this translates directly to the Al-based alloys instead. While Chapter 5 detailed how 20% liquid worked in an Al-Si composite, a reduction of this percent would also decrease the healing temperature. However, optimization must be evaluated against the ability to heal.
APPENDIX A
MECHANICAL AND THERMAL TESTING DATA

For the matrix alloys, NiTi reinforcements, and composite specimens investigated for self-healing capabilities, mechanical and thermal data was collected. Below are the tensile curves for all specimens included in this dissertation and thermal testing data for the NiTi wires and Al-Cu-Si matrix.

Sn-Bi

For the Sn-Bi system, tensile curves for the matrix alloy specimens can be found in Figure A-1. For each virgin composite specimen, tensile results can be found in Figure A-2. Images of Sn-Bi composite specimen A and C in the virgin and healed condition can be found in Figure A-3 and Figure A-4, respectively.

Figure A-1: Mechanical testing results of Sn-21wt%Bi matrix alloys after heat-treatment for 24 hours at 169°C.
Figure A-2: Mechanical testing results of Sn-21wt%Bi composites ($V_f = 0.3-0.4\%$) after heat-treatment for 24 hours at $169^\circ C$.

Figure A-3: Mechanical testing comparison of Sn-21wt%Bi Composite ‘A’ ($V_f = 0.31\%$) in the virgin and healed composite condition.
Figure A-4: Mechanical testing comparison of Sn-21wt%Bi Composite 'C' (Vf = 0.40%) in the virgin and healed composite condition.

The NiTi reinforcements used were also investigated for tensile data. Figure A-5 shows tensile curves for the as-received NiTi BH-0075 wires (Ni – 50.6 at% Ti, Ø = 0.18 mm, cold drawn, Memry Corporation). Figure A-6 shows tensile data after heat-treatment of 500°C for 3 hours, whereas Figure A-7 shows the wires after a heat-treatment of 500°C for 3 hours then 169°C for 24 hours. Wires removed from a Sn-Bi composite sample which had been heat-treated for 500°C for 3 hours, cast into the composite, then heat-treated again for 169°C for 24 hours (2x) and removed from the matrix alloy by using acid (solution of 2:1:1 H₂O, HNO₃, and HCl) to dissolve the matrix are shown in Figure A-8.
Figure A-5: Tensile testing results of as-received NiTi BH-0075 wires.

Figure A-6: Tensile testing results of NiTi BH-0075 wires heat-treated for 3 hours at 500°C.
Figure A-7: Tensile testing results of NiTi BH-0075 wires heat-treated for 3 hours at 500°C and then again at 169°C for 24 hours.

Figure A-8: Tensile testing results of NiTi BH-0075 wires removed from a Sn-Bi composite sample which had been heat-treated for 3 hours at 500°C and 169°C for 24 hours (2x).
The NiTi BH wires were also investigated for their thermal properties via DSC. Several wires were heat-treated for 3 hours at 500°C and tested from -50°C to 200°C at a rate of 10°C. A representative DSC curve after the 3 hour heat-treatment is shown in Figure A-9. Additional BH wires were heat-treated for 3 hours at 500°C then for 24 hours at 169°C and tested in a similar fashion. A representative DSC curve for these NiTi BH wires is shown in Figure A-10. The average values for the wires tested under both heat-treatment conditions is shown in Table 3-4.

Figure A-9: Thermal transition temperatures for a BH-0075 NiTi wire heat-treated for 3 hours at 500°C.
Figure A-10: Thermal transition temperatures for BB-00755 NiTi wire heat-treated for 3 hours at 500°C and then 24 hours at 169°C.

**Al-Based Binary Systems**

For the Al-Sn composite system, tensile curves for the composite specimens can be found in Figure A-11. Similar tensile tests for the Al-Cu and Al-Mg composites can be found in Figure A-12 and Figure A-13, respectively.

Figure A-11: Mechanical testing results of Al – 19.5 at% Sn (51.6 wt% Sn) composites ($V_f = 1.5$-1.8%) after heat-treatment for 4 hours at 250°C.
Figure A-12: Mechanical testing results of Al – 4.5 at% Cu (10 wt% Cu) composites (\(V_f = 2.2-2.4\%\)) after heat-treatment at 566°C for 24 hours.

Figure A-13: Mechanical testing results of Al – 16.6 at% Mg (15.2 wt% Mg) composites (\(V_f = 1.9-4.0\%\)) after heat-treatment at 460°C for 24 hours.

For the Al-Si system, tensile testing was completed for the matrix alloys specimens (Table A-1). The representative stress-strain curves for the matrix alloy can be found in Figure A-14. Al-Si composite specimen tensile data can be found in Figure
A-15. Similar tensile tests for Al-Si composites containing increased NiTi reinforcements can be found in Figure A-16. Images of Al-Si composite specimen ‘B’ and ‘C’ in the virgin and healed condition can be found in Figure A-17 and Figure A-18, respectively.

Table A-1: Tensile testing results of Al – 3.0 at% Si (3.1 wt% Si) matrix alloys after heat-treatment at 592°C for 24 hours

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Modulus (GPa)</th>
<th>0.2% Yield Stress (MPa)</th>
<th>Ultimate Stress (MPa)</th>
<th>Failure Strain (%)</th>
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<tr>
<td>1</td>
<td>63.3</td>
<td>42.3</td>
<td>76.1</td>
<td>2.02</td>
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<tr>
<td>2</td>
<td>58.4</td>
<td>47.8</td>
<td>75.6</td>
<td>2.18</td>
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<tr>
<td>3</td>
<td>67.6</td>
<td>44.9</td>
<td>84.4</td>
<td>2.27</td>
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<tr>
<td>4</td>
<td>77.9</td>
<td>42.8</td>
<td>72.3</td>
<td>1.77</td>
</tr>
<tr>
<td>Average</td>
<td>66.8</td>
<td>44.5</td>
<td>77.1</td>
<td>2.06</td>
</tr>
<tr>
<td>± 1σ</td>
<td>8.3</td>
<td>2.5</td>
<td>5.2</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Figure A-14: Mechanical testing results of Al – 3.0 at% Si (3.1 wt% Si) matrix alloys after heat-treatment at 592°C for 24 hours.
Figure A-15: Mechanical testing results of Al – 3.0 at% Si (3.1 wt% Si) composites ($V_f = 2.0-2.4\%$) after heat-treatment at 592°C for 24 hours.

Figure A-16: Mechanical testing results of Al – 3.0 at% Si (3.1 wt% Si) composites ($V_f = 3.7-4.4\%$) after heat-treatment at 592°C for 24 hours.
Figure A-17: Mechanical testing comparison of Al – 3.0 at% Si composite ‘B’ ($V_f = 2.0\%$) in the virgin and healed composite condition.

Figure A-18: Mechanical testing comparison of Al – 3.0 at% Si composite ‘C’ ($V_f = 2.4\%$) in the virgin and healed composite condition.
Al-Based Ternary System

For the Al-Cu-Si system, the tensile stress-strain diagrams for the matrix alloy can be found in Figure A-19. The tensile data for the composite specimens is found in Figure A-20.

Figure A-19: Mechanical testing results of Al – 4.1 at% Cu – 2.0 at% Si (9.0 wt% Cu – 1.9 at% Si) matrix alloys after heat-treatment at 530°C for 24 hours.

Figure A-20: Mechanical testing results of Al – 4.1 at% Cu – 2.0 at% Si (9.0 wt% Cu – 1.9 at% Si) composites (Vf = 2.3-2.9%) after heat-treatment at 530°C for 24 hours.
NiTi Wires

Mechanical Properties

For the Al-Si and Al-Cu-Si composites, type BB-35 NiTi wires (Ni – 49.3 at% Ti, Ø = 0.87 mm) were used as continuous reinforcements. Tensile properties of the NiTi wires in the as-received condition are shown in Figure A-21. BB wires which were heat-treated for 24 hours at 592°C and pulled in tension are shown in Figure A-22. Tensile results of BB wires heat-treated for 24 hours at 530°C once, twice, or three times to simulate casting and healing processes in Al-Cu-Si composite manufacturing are shown in Figure A-23.

Figure A-21: Tensile testing results of as-received NiTi BB-35 wires.
Figure A-22: Representative tensile results of NiTi BB-35 wires heat-treated for 24 hours at 592°C for either one cycle or two cycles.

Figure A-23: Tensile testing results of NiTi BB-35 wires heat-treated for 24 hours at 530°C for one, two, or three cycles to simulate the entire healing process for Al-Cu-Si–based composites.
Thermal Properties

The NiTi BB wires were also investigated for their thermal properties via DSC. A sample DSC curve of the as-received BB wires is shown in Figure A-24. Wires which were heat-treated for 24 hours at 530°C for one cycle are shown in Figure A-25 and two cycles in A-26. A representative DSC curve for BB wires heat-treated at 592°C for 24 hours is shown in Figure A-27 with all data included in Table A-2. BB wires put through two cycles of 592°C for 24 hours are shown in Figure A-28 with all wire data included in Table A-3.

Figure A-24: Representative thermal transition temperatures for as-received BB-35 NiTi wire.
Figure A-25: Thermal transition temperatures for BB-35 NiTi wire heat-treated for 24 hours at 530°C.

Figure A-26: Thermal transition temperatures for BB-35 NiTi wire heat-treated for 24 hours at 530°C two times.
Figure A-27: Representative thermal transition temperatures for BB-35 NiTi wire heat-treated for 24 hours at 592°C.

Table A-2: Thermal transition temperatures of BB-35 NiTi wires heat-treated for 24 hours at 592°C.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Number</th>
<th>A&lt;sub&gt;S&lt;/sub&gt;</th>
<th>A&lt;sub&gt;f&lt;/sub&gt;</th>
<th>M&lt;sub&gt;S&lt;/sub&gt;</th>
<th>M&lt;sub&gt;f&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>39.2</td>
<td>49.9</td>
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<td>2</td>
<td>40.4</td>
<td>53.9</td>
<td>15.6</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>40.3</td>
<td>56.4</td>
<td>15.4</td>
<td>1.0</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>40.0</td>
<td>53.4</td>
<td>15.8</td>
<td>3.4</td>
</tr>
<tr>
<td>± 1σ</td>
<td></td>
<td>0.6</td>
<td>3.3</td>
<td>0.6</td>
<td>2.8</td>
</tr>
</tbody>
</table>
Figure A-28: Representative thermal transition temperatures for BB-35 NiTi wire heat-treated for 24 hours at 592°C two times.

Table A-3: Thermal transition temperatures of BB-35 NiTi wires heat-treated for two cycles at 592°C for 24 hours.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Number</th>
<th>A_s</th>
<th>A_f</th>
<th>M_s</th>
<th>M_f</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40.0</td>
<td>53.4</td>
<td>15.6</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>39.8</td>
<td>53.4</td>
<td>15.2</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>40.1</td>
<td>53.7</td>
<td>15.9</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>40.0</td>
<td>53.5</td>
<td>15.5</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>± 1σ</td>
<td>0.2</td>
<td>0.2</td>
<td>0.4</td>
<td>0.4</td>
<td></td>
</tr>
</tbody>
</table>

**Thermal Transitions in Al-Cu-Si**

The percent liquid in the Al-Cu-Si matrix alloy was investigated via DSC. The resultant data for transition temperatures and heat of fusion is shown in Figure A-29.
Figure A-29: Thermal transition temperatures for Al – 4.1 at% Cu – 2.0 at% Si (9.0 wt% Cu – 1.9 at% Si) matrix alloy after heat-treatment at 530°C for 24 hours.
APPENDIX B
ALUMINUM-MAGNESIUM-BASED MATRIX DESIGN

Future iterations of matrixes for self-healing MMC must advance the strength of the composite in order to compete with traditional structural materials. To do this, different alloying additions and heat-treatments must be attempted. This chapter details two such compositions which show promise for future developments – Al-Mg-Li and Al-Mg-Si. Al-Mg-Li alloys are known to possess high specific strength due to the solid-solution strengthening abilities of Mg and Li in Al as well as the low density from these additions. Al-Mg-Si alloys are able to obtain high strength through precipitation of second phases, and thus different heat-treatments must be investigated to achieve the highest strength while maintaining its healing capabilities.

**Al-Mg-Li Matrix**

Looking at the Al-based ternary matrix alloys, an alloy based on the Al-Mg-Li system has the potential reach the highest strength values achievable in solid-solution (Figure 4-4), while also decreasing the eutectic temperature (Figure 4-3) and decreasing composite density. These are all highly desirable properties based on the system design chart for self-healing MMCs (Figure 4-1).

**Matrix Design**

The Al-Mg-Li phase diagram was calculated using Pandat software with their magnesium database, PanMagnesium (107) (Figure B-1); it was found be similar to the phase diagrams found in literature (180). The lowest melting eutectic found on the Al-rich side was calculated to be Al – 36.1 at% Mg – 1.5 at% Li (34.1 wt% Mg – 0.40 wt% Li) at a temperature of 445°C.
Figure B-1: Liquidus projection of the Al-Mg-Li system. The lowest melting eutectic point calculated to be 445°C at a composition of Al – 36.1 Mg – 1.5 Li (at%) as indicated by the arrow. Calculated using Pandat (107).

At the ternary eutectic temperature of 445°C, an isotherm was calculated (Figure B-2 for the Al-rich region). Drawing a line between the eutectic point and the closest solid-solution Al region, a pseudo-isopleth was calculated (Figure B-3). At a healing temperature of 460°C, it was calculated that a composition of Al – 18.7 at% Mg – 1.1 at% Li (17.3 wt% Mg – 0.3 wt% Li) would yield 20% liquid during a healing heat-treatment. A fluctuation of ± 5°C from the healing temperature results in a range of only 17-22.5% liquid in the matrix.
Figure B-2: Isotherm at 445°C in the Al-Mg-Li ternary alloy system. The dashed line represents the connection between the ternary eutectic and nearest Al solid solution phase field. Calculated using Pandat (107).

Figure B-3: Pseudo-isopleth of Al-Mg-Li system along the line from the ternary eutectic point to the closest Al solid-solution phase region. At a healing temperature of 460°C, a composition of Al – 18.7 at% Mg – 1.1 at% Li will yield 20% liquid in the matrix. Calculated using Pandat (107).
Composite Fabrication

Appropriate amounts of Al (Al shot, 99.99%, Alfa Aesar), Mg (Mg pieces, 99.99%, American Elements), and Li (Li granules, 99%, Alfa Aesar) were melted in a furnace at 750°C contained within an argon atmosphere until a liquid solution. NiTi SMA wires, designated BB-35, were laid horizontally in the graphite tensile bar mold heated to 350°C. The Al-Mg-Li melt was poured over the wires in the mold and allowed to air cool. Each tensile bar was then placed horizontally into a furnace for 24 hours at 460°C, monitored by an external thermocouple, then air-cooled to set the eutectic microstructure (Figure B-4).

Figure B-4: Representative microstructure of an Al – 18.7 at% Mg – 1.1 at% Li (17.3 wt% Mg – 0.3 wt% Li) matrix exhibiting a non-continuous eutectic phase surrounding Al solid-solution phase.

Mechanical Testing

After heat-treatment, the Al-Mg-Li composite bars were ground to a 320-grit surface finish before being tested in tension using the Instron at a rate of 1.0%/min. Results of the testing are shown in Table B-1. Because of the brittle nature of the
composites, the 0.2% offset yield strength is not able to be reported. A tensile graph of Composite 2 is shown in Figure B-5.

Table B-1: Mechanical testing results for Al-Mg-Li matrices reinforced with 2-3 vol% SMA wire reinforcements

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Vf Wires (%)</th>
<th>Modulus (GPa)</th>
<th>Ultimate Stress (MPa)</th>
<th>Failure Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.00</td>
<td>48.3</td>
<td>62.3</td>
<td>0.12</td>
</tr>
<tr>
<td>2</td>
<td>3.04</td>
<td>53.7</td>
<td>126.5</td>
<td>0.31</td>
</tr>
<tr>
<td>3</td>
<td>2.29</td>
<td>52.6</td>
<td>41.9</td>
<td>0.11</td>
</tr>
<tr>
<td>Avg.</td>
<td>2.78</td>
<td>51.5</td>
<td>76.9</td>
<td>0.18</td>
</tr>
<tr>
<td>± 1σ</td>
<td>0.42</td>
<td>2.9</td>
<td>44.1</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Figure B-5: Representative tensile results of an Al-Mg-Li matrix reinforced with 3.04 volume percent NiTi SMA wire reinforcements.

After tensile testing, the fractured composite bars were encapsulated under vacuum (in a Pyrex tube laying flat on graphite wrapped in Ta foil) and heat-treated a second time for 24 hours at 460°C in an attempt to heal the crack. Healing was not found due to oxidation at the fracture interface as shown in Figure B-6. Casting defects such as oxide inclusions were also found, which is thought to have been the major
factor in the composite displaying pre-mature failure and lack of ductility. Investigation of into improved fabrication techniques, such as the hot-pressing found in Al-Cu-Si, may enable to use of this matrix as a self-healing MMC.

Figure B-6: Fracture surface of Al-Mg-Li composite showing oxidation on the crack interface after a healing cycle. Note the presence of an oxide inclusion from casting which acted as the initiation point of failure.

**Al-Mg-Si Matrix**

The 6000-series of Al alloys based on the Al-Mg-Si system has potential to increase strength through precipitation of Mg$_2$Si in the matrix. Paired with the pressing technique developed for Al-Cu-Si composites, this system has potential to improve the strength values achieved in self-healing MMCs through extra fabrication steps; i.e. heat-treatment and quenching.

The matrix of Al-Mg-Si was designed in a similar manner to previous alloys through calculations using Pandat software with their magnesium database, PanMagnesium (107). The lowest melting eutectic found on the Al-rich side was calculated to be Al – 5.7 at% Mg – 12.5 at% Si (5.2 wt% Mg – 13.0 wt% Si) at a
temperature of 556°C. At the ternary eutectic temperature of 556°C, an isotherm was calculated to find the nearest solid-solution Al region to the eutectic point. As before, a pseudo-isopleth was calculated between these two points (Figure B-7). At a healing temperature of 565°C, it was calculated that a composition of Al – 1.8 at% Mg – 3.2 at% Si (1.6 wt% Mg – 3.3 wt% Si) would yield 20% liquid during a healing heat-treatment. A fluctuation of ± 5°C from the healing temperature results in a range of only 18.0-21.2% liquid in the matrix.

Figure B-7: Pseudo-isopleth of Al-Mg-Si system along the line from the ternary eutectic point to the closest Al solid-solution phase region. At a healing temperature of 565°C, a composition of Al – 1.8 at% Mg – 3.2 at% Si will yield 20% liquid in the matrix. Calculated using Pandat (107).

Unlike previous alloys, however, the Al-Mg-Si system would benefit the most from developing different thermal treatments to increase strength through precipitation. Thus to maximize the strength, different heat-treatment sequences need to be investigated. Also, the healing cycle would also need to be paired with these different
heat-treatments in order to determine how the strengthening treatments for the matrix would affect eventual healing of the composite.

Summary

As shown above, there are more Al-based matrix compositions which have only just begun to be investigated for self-healing capabilities. Future studies must be completed to optimize healing cycles, matrix compositions, and precipitation heat-treatments in order to obtain MMCs which rival traditional materials.
LIST OF REFERENCES


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BIOGRAPHICAL SKETCH

The author was born in Waterloo, Iowa. Growing up outside Mt. Auburn, Iowa, he attended Vinton-Shellsburg High School and graduated in 2004. Deciding on Iowa State University, he chose to pursue a Bachelor of Science in Materials Engineering. At ISU, he spent one summer in London studying at Brunel University and a semester in Australia studying at the University of Wollongong. He also spent a summer interning for US Steel, a fall interning with Caterpillar, and over 4 years working as a research hourly for Scott Chumbley at Ames Laboratory. He graduated magna cum laude in 2009.

Following, he chose the University of Florida to pursue his graduate education in Materials Science & Engineering. He achieved a Master of Science and was awarded a Science, Mathematics, and Research for Transformation (SMART) Scholarship in 2011. He was also named “Honorable Mention” for the National Science Foundation (NSF) Graduate Research Fellowship and named a winner of the National Defense Science & Engineering Graduate Fellowship. He was awarded the Howard Hughes Medical Institute (HHMI) Science for Life Graduate Award and was a world finalist in the Institute of Materials, Minerals, and Mining (IOM3) Young Person’s World Lecture Competition. He received his Doctor of Philosophy from the University of Florida in the summer of 2013.