

Surfactant Modified Nickel-Manganese-Gallium Powder and Silicone Composites

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Abstract. Power supplies are often the limiting factor for operation of many portable electronic devices. Batteries contribute significantly to their weight and impose limitations on operational longevity. Harvesting vibratory energy from the environment for conversion to electrical energy has been proposed as a means to address these problems. Previously, DRDC Atlantic has shown that single crystals of nickel-manganese-gallium (NiMnGa) can produce large reversible stress-induced and magnetic field-induced strains of up to 10%. It has been proposed that NiMnGa magnetic shape memory alloys may be an ideal alloy to harvest mechanical energy. The drawback to monolithic NiMnGa crystals is that they are susceptible to intergranular fracture. To address this issue, a composite of the alloy in a polymer matrix has been examined in the hopes of improving toughness and formability. Good bonding between the polymer and the powder is needed to facilitate optimum transfer of force between the two components. The objective of this study was to understand and optimize the polymer-alloy interactions. The polymer matrix chosen was Dow Corning Sylgard 186. It was determined that the Sylgard 186 prepolymer base interacts with the oxidized surface of the NiMnGa particles. Silane coupling agents were also investigated to examine their effect on the interfacial interactions. No change in properties were observed.

Introduction

The operational usage of many portable electronic devices is limited by the weight and size of the batteries powering them. Energy harvesting may be used to produce power that could subsequently be stored in a rechargeable battery or capacitor to address the electrical needs of portable devices.

Due to their ability to produce large reversible stress-induced and magnetic field-induced strains, magnetic shape memory alloys (MSMA) are attractive for a wide range of potential applications. These include novel aerodynamic and hydrodynamic control systems, active shock amelioration systems and energy harvesting. In MSMA, stress applied relative to the crystallographic axes will cause rotation and realignment of the crystallographic structure. As the individual magnetic moments are linked to the crystallographic structure, this reorientation causes the bulk magnetic moment of the MSMA to change. According to Faraday's law of induction, an electric field can be induced by an alternating magnetic flux. Thus repeated rotation of the bulk magnetic moment can produce an overall oscillating magnetic field that may produce current in an external induction loop and ultimately trickle charge a battery or capacitor [1].

Nickel-manganese-gallium (NiMnGa) based MSMA have been shown to attain stress induced strains of up to 10% [2,3]. This is much larger than the strains observed in magnetostrictive materials ($\leq 0.2\%$), making them ideal for MSMA-based energy harvesting devices. Although several compositional ranges of NiMnGa MSMA have been found to be magnetically active at room temperature, 49 at% Ni, 20 at% Mn and 21 at% Ga represents a typical target composition.

Use of monolithic crystal NiMnGa can be problematic due to its susceptibility to intergranular fracture and grain separation [4]. Suspending NiMnGa powder/particles in a polymer matrix may mitigate these limitations by improving toughness, and formability for machining complex geometries [5]. In addition, although the magnetic shape memory effect is reversible, the alloy will not return to its original shape unless a force (mechanical or magnetic) is applied. The mechanical

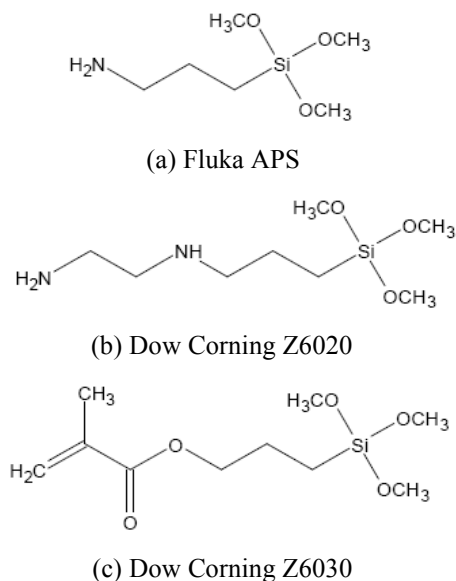


Figure 1: Chemical structures of coupling agents

properties of a polymer matrix can be engineered to allow the polymer to act as a resetting stress. In the composite, after the mechanical stimulus has been removed, the polymer can then apply the resetting load [6].

The performance of NiMnGa/polymer composites in energy harvesting is dependant on the polymer-NiMnGa interaction at the particle surface. There must be sufficient adhesion to transfer stresses through the polymer, to the MSMA [7]. When dealing with macroscopic alloy samples (*i.e.*, wires *etc.*) surface treatments such as acid etching, sanding, and sandblasting can be used to improve adhesion [7]. These approaches are not suited for use with alloy powders. When optimizing the interaction between a powder and polymer matrix, one approach to strengthening adhesion is to tailor the polymer to the filler. Another approach is the use of coupling agents or surfactants to improve interfacial bonding [7,8]. In a previous study, DRDC Atlantic briefly investigated three Kenrich Kenreact titanate-based surfactants [5]. It was seen that even though the surfactants were not optimized for the silicone being used, an increase in Young's modulus was observed (*e.g.*, from 0.4 MPa to 0.6 MPa). With these results in mind, this study chose silane coupling agents to specifically interact with the desired silicone elastomer. This paper describes progress in the fabrication and characterization of NiMnGa/silicone composites.

Materials

This study utilised NiMnGa-based MSMA in powder form ($d_{\text{avg}} \sim 125 \mu\text{m}$) with an approximate composition of 49 *at%* Ni, 30 *at%* Mn and 21 *at%* Ga. Single crystals of the same composition have been shown to be fully martensitic, ferromagnetic and magnetically active at room temperature. Preparation of the powder is discussed elsewhere [5,6].

Polysiloxanes (silicones) are stable over a wide temperature range, resist oxidation, chemical and biological degradation, possess good dielectric strength and are water repellent. A previous study determined Dow Corning Sylgard 186, a room temperature vulcanizing silicone elastomer to be the best for making the desired composites [5]. It consists of a polysiloxane prepolymer base and a hydrosilane crosslinking agent containing catalyst. Catalyzed by platinum, the hydrosilane adds across vinyl groups in the prepolymer resulting in a crosslinked polymer. The prepolymer base to hydrosilane ratio is 10:1 but varying the amount of hydrosilane crosslinking agent gives a small amount of control over the degree of curing. Prior to cure the polymer has a viscosity of 107,000 cPs and post cure it has a Young's modulus of 1.4 MPa and Shore A hardness of 24.

The bulk of this study examined how the interactions between the silicone and the NiMnGa were affected by the addition of three different coupling agents (Fig. 1). Silane coupling agents were used to alter the surface of the NiMnGa. The silane coupling agents examined were Fluka 3-aminopropyl trimethoxysilane (APS) [8], Dow Corning Z6020[9] and Dow Corning Z6030[10]. All three compounds have trimethoxysilane head groups that can hydrolyze and react with the oxidized alloy surface [11,12]. Fluka APS and Dow Corning Z6020 contain amine tail groups, while Dow Corning Z6030 has an acrylate tail group. The amine tails will interact with the silicone through entanglement, while the acrylate can participate in the hydrosilane curing reaction of the polymer.

Experimental

Coupling Agent Modified Alloy. Both APS and Z6020 modified alloys were prepared using the same procedure. A set of standard coupling agent solutions of 6.0, 8.0, 10.0, 40.0, 75.0 and 100.0 mM were prepared in ethanol. A known mass of NiMnGa powder was submersed in excess

coupling agent solution and agitated for 1 h. The resulting slurry was left for approximately 24 h, after which it was filtered and rinsed 3× with ethanol. The powder was dried under vacuum.

Preparation of Z6030 modified alloys followed the same procedure as that for Z6020, except dry toluene was used as the solvent.

Alloy/Polymer Base Composite Preparation. Samples were made to examine the interaction of the prepolymer base with the alloy (*i.e.*, without coupling agent or curing agent). Prepolymer base was weighed and spun in a FlakTeck Speedmixer™ at 3450 rpm for 15 min to remove entrapped air, after which a known mass of unmodified alloy was added. The two were mixed by hand and then placed in the Speedmixer™ at 1000 rpm for 3 min. *No curing agent was added.* The suspension was allowed to sit for 48 h, although curing was not expected. Then the suspension was diluted with methylene chloride, and centrifuged to separate the alloy. The alloy was washed three times with methylene chloride to remove any excess prepolymer base and dried under vacuum for 24 h at room temperature.

Coupling Agent Modified Alloy/Polymer Composite. Sylgard 186 prepolymer base was weighed into a Speedmixer™ container and spun at 3450 rpm for 15 min to release any dissolved air from the viscous polymer. A known mass of coupling agent modified alloy was added to the base to yield an end concentration of 15 wt%. A sufficient amount of curing agent was added to yield a 10:1 weight ratio of polymer base to curing agent. All components were mixed manually and then placed in the Speedmixer™ for 3 min at 1000 rpm. The resulting suspension was placed in a sonic bath for 15 min to release bubbles that may have formed during the mixing process. The composite was then left to cure at room temperature for 24 h.

Dynamic Mechanical Analysis. The storage modulus of each sample was determined with a TA Instruments Dynamic Mechanical Analyser (DMA Q800), using a tension clamp. The multiple fixed frequency-strain mode was used with a preloading strain of 0.01 N and an amplitude of 25.0 μm. The storage modulus was measured at 100, 50, 20, 10, 5, 2, 1, 0.5, 0.2 and 0.1 Hz at 20°C.

Compositional Analysis. Images were obtained using a Leo 1455VP scanning electron microscope (SEM) equipped with a tungsten filament gun. NiMnGa powders (unaltered and prepolymer base treated) were affixed to an aluminium stub with colloidal graphite and examined uncoated. Energy dispersive x-ray (EDX) spectra were collected using a Princeton Gamma Tech IMIX system equipped with a Prism2000 Si(Li) detector. Nominal accelerating voltages of 5, 10, and 20 keV were utilized to collect the various spectra.

Quantitative compositional analysis of the unaltered and treated NiMnGa powders was accomplished by digestion of portions in ultrapure nitric acid and subsequent inductively coupled plasma–mass spectrometry (ICP-MS) using an Agilent 7500ce instrument. All samples, standards and blanks were diluted gravimetrically with 2% nitric acid to minimize signal fluctuations due to varying solution ionic strength. ⁸⁹Y, at a concentration of 1 ppb, was used as an internal standard in all analyses. The major isotope was used for quantitation of each element, except iron. ⁵⁷Fe was used to eliminate interference from ⁴⁰Ar¹⁶O.

Evaluation of the Alloy-Polymer Bond.

As discussed in the introduction, the alloy is the active component and requires transmission of stress from the surroundings, through the polymer, to the alloy. To this end, an investigation of the alloy and polymer interaction was undertaken.

The Sylgard 186 prepolymer base contains a vinyl-terminated polysiloxane as well as octamethoxysilane. The hydrosilation reaction between the vinyl-terminated polysiloxane and

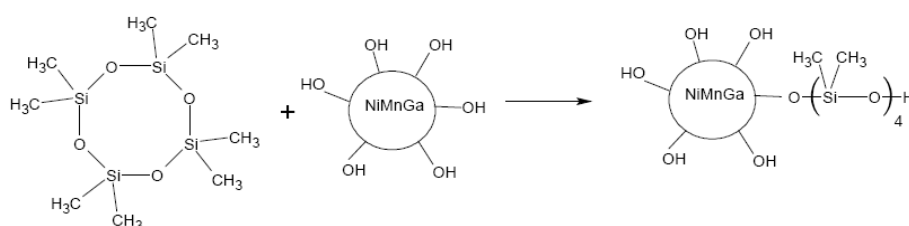


Figure 2: Proposed ring opening of Sylgard 186 prepolymer base catalysed by NiMnGa.

hydrosilane is the primary chemical reaction for curing, but the octamethoxysilane will ring-open in the presence of a Lewis acid to produce long,

linear chains. The long chains act as chain extenders, and contribute to the softness of the polymer. It is believed that the oxidized surface of the NiMnGa powder, acting as a Lewis acid could react with the octamethoxysilane, catalysing the ring opening reaction as seen in Fig. 2. This reaction occurs prior to the addition of curing agent.

As described in the experimental section, samples of NiMnGa coated with prepolymer base were prepared and rinsed to remove any excess silicone that had not reacted with the alloy surface. The resulting particles, coated with a thin layer of polysiloxane were analysed for silicon content using ICP-MS. The unaltered alloy gave a baseline reading of 130 ppm silicon, while the base prepolymer coated samples ranged from 420 – 500 ppm with an average of 440 ppm (sd = 30 ppm). It can easily be seen that there is silicon remaining on the alloy.

Fig. 3 shows typical spectra observed from SEM/EDX analysis on the unaltered NiMnGa powder (Fig. 3(a)) and NiMnGa powder after the addition of prepolymer base (Fig. 3(b)). In both figures, peaks expected for nickel, manganese and gallium are present. Each subfigure is an overlay of spectra obtained at 5, 10 and 20 keV acceleration voltages. Different accelerating voltages were used to explore the surface composition of the particles. The higher the voltage, the more energetic are the electrons and the deeper they penetrate into the sample. Lower energy electrons probe the surface more accurately. The spectra for the unaltered NiMnGa show very little change with decreasing acceleration voltages. The oxygen peak is largest (relative to Ni) at 5 keV and decreases at higher voltages. This indicates that the alloy surface is oxidized. Aluminium is also present and is highest at 20 keV. This is likely due to the higher energy electrons penetrating deeper and sampling the aluminium stub. The spectra for the alloy and prepolymer base show a presence of Si. The amount of Si relative to the Ni peak changes with the accelerating voltage used. Again, the lower energy voltages mean that the electron beam does not penetrate as deeply into the particle, thus more accurately sampling the surface layer. The increase in the Si and O signals with decreasing accelerating voltage indicate that the Si quantified in the ICP-MS is localized to the surface of the particles.

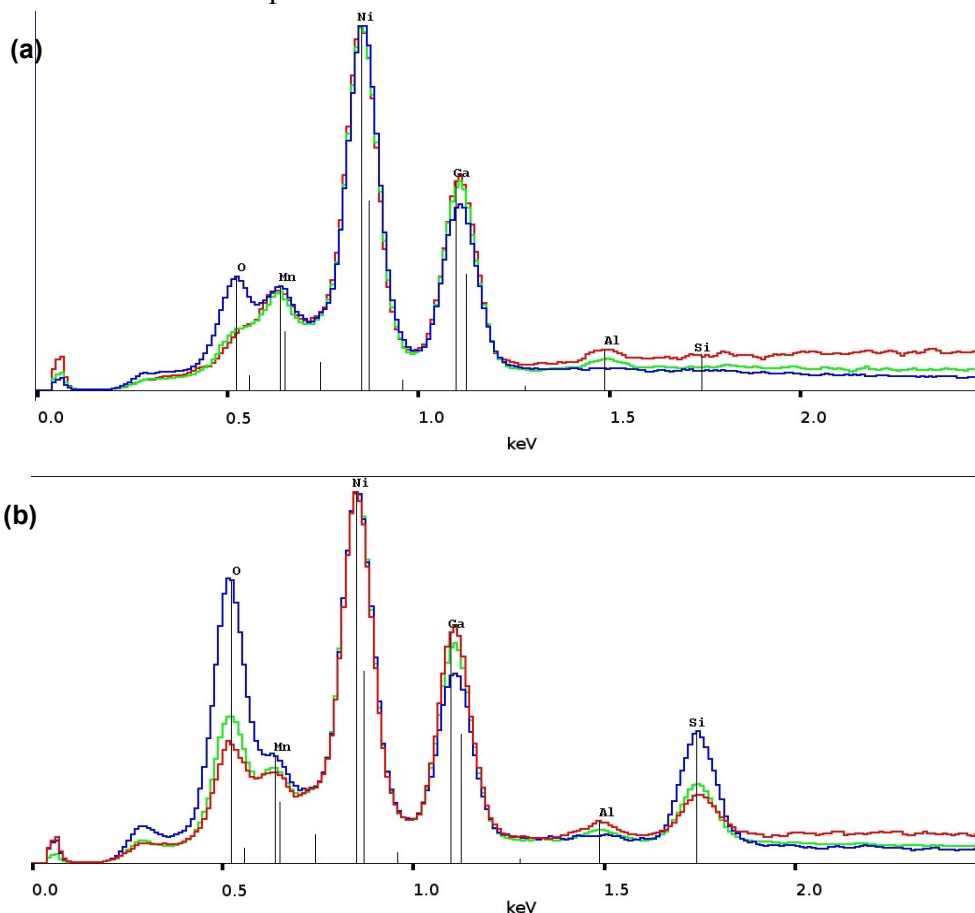


Figure 3: SEM/EDX spectra obtained at accelerating voltages of 5 (blue), 10 (green), 20 (red) keV for (a) unaltered NiMnGa powder, (b) NiMnGa powder reacted with prepolymer base.

Fig. 4 shows SEM micrographs of the samples analysed using SEM/EDX. The unaltered alloy (Fig. 4(a)) is more granular than the amorphous prepolymer base coated alloy (Fig. 4(b)). This significant difference in appearance, along with the EDX and ICP-MS data indicates a change in the surface composition of the sample.

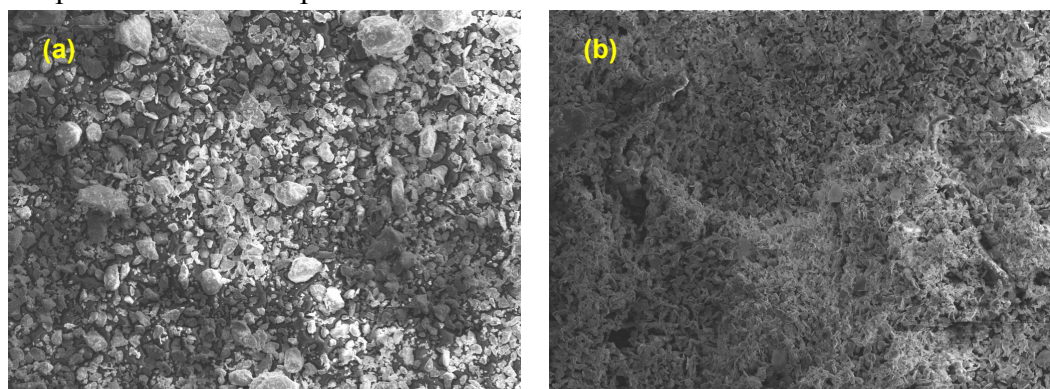


Figure 4: Scanning electron microscopy images. (a) unaltered NiMnGa at 380 \times , (b) prepolymer base coated NiMnGa at 380 \times .

Evaluation of the Coupling Agents. The addition of hard fillers to a polymer tends to have a reinforcing effect, causing an increase in hardness and storage modulus in the resulting composites. If the coupling agents improve the interfacial interactions between the filler and the polymer, a greater reinforcing effect should be observed. This would result in an increase in the storage modulus. Therefore dynamic mechanical analysis can be used as an indirect method for investigating the quality of interfacial interactions when using different coupling agents.

Unfilled Sylgard 186 has a storage modulus of 1.39 MPa. All storage moduli reported here were measured at 1 Hz. In the absence of coupling agent, the modulus of the 15 wt% NiMnGa/silicone composite is 1.45 MPa.

The results for all three coupling agents are shown in Fig. 5(a)–(c). There was no significant change in the storage modulus of the composite when any of the coupling agents were used. The standard deviation measured for each concentration is greater than the difference between storage moduli of the different concentrations.

Discussion

The goals of this project were to understand the interfacial interactions between powder NiMnGa and a silicone polymer, and to examine the effect of coupling agents on these interfacial interactions. Within the composite, stronger interactions would be able to transfer external kinetic forces more easily.

The prepolymer base interacts with the oxidized NiMnGa surface, forming a silicone coating as evidenced by the SEM/EDX results. Around this coating the rest of the silicone matrix can react, forming the composite. The effects of coupling agents on interfacial interactions were examined indirectly using dynamic mechanical analysis. None of the coupling agents studied had any effect on the storage modulus of the composite. This is likely because the prepolymer base can adhere to the alloy surface, and the methoxysilane hydrolysis reaction of the coupling reagents does not improve upon the adhesion. Smith *et al.* showed an improvement when using silane coupling agents with nickel-titanium (NiTi) in polymer matrix materials [7]. The polymer used was poly(methyl methacrylate), which would not react with the NiTi surface without a coupling agent.

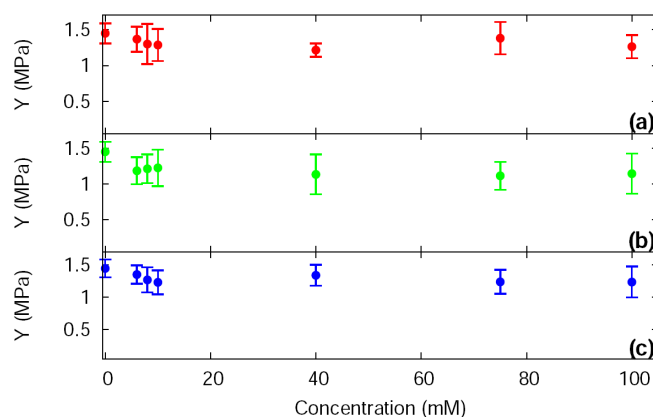


Figure 5: Storage modulus data for coupling agent modified 15 wt% NiMnGa/silicone composites; (a) Fluka APS, (b) Z6020, and (c) Z6030.

With the silicone used here, there is no need for coupling agents because they do not improve the interfacial adhesion. The prepolymer does not require chemical assistance to interact with the NiMnGa powder.

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