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Structural, physical and damping properties of melt-spun Ni–Mn–Ga wire-epoxy composites

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ABSTRACT

Ni–Mn–Ga is a ferromagnetic shape memory alloy that exhibits large, magnetic-field- and stress-induced strains via energy dissipating twinning when processed into single crystals. Grain boundaries suppress twinning and render polycrystalline Ni–Mn–Ga brittle. Ni–Mn–Ga/polymer composites overcome the drawbacks of polycrystals and could thus provide a less expensive and easier to handle alternative to Ni–Mn–Ga single crystals for damping applications. Ni–Mn–Ga wires were produced by melt-spinning and were polycrystalline in the as-spun state. Annealed wires were ferromagnetic at room temperature with non-modulated martensite and a bamboo microstructure. The annealed wires displayed a hysteretic stress–strain behavior typical for twinning. Ni–Mn–Ga wire-epoxy matrix composites were fabricated with as-spun and annealed wires. The damping behavior of annealed Ni–Mn–Ga wire-epoxy matrix composites was higher than that of as-spun Ni–Mn–Ga wire-epoxy matrix composites and of pure epoxy.

1. Introduction

Ni–Mn–Ga is a ferromagnetic shape memory alloy (FSMA). Its magnetic-field-induced strain (MFIS), caused by twin boundary motion, was first reported by Ullakko et al. [1] in 1996. Currently, Ni–Mn–Ga is of great interest due to its large MFIS of up to 10% [2] at an actuation frequency of up to 2 kHz [3]. Beside magnetic-field-induced twinning, twin boundary motion can be induced by mechanical stresses. The maximum strain ε achieved by applying a mechanical stress to a Ni–Mn–Ga single crystal depends on the lattice parameters a and c as $\varepsilon = 1 - c/a$. Thus, 10 M pseudo-tetragonal, 14 M pseudo-orthorhombic and NM tetragonal martensite exhibit a maximum twinning strain of 6%, 10% and 20%, respectively [4].

Polycrystalline Ni–Mn–Ga is brittle. Furthermore, grain boundaries hinder twinning, increase the twinning stress and suppress MFIS. Single crystals of Ni–Mn–Ga, however, are expensive to produce. Here, we propose to overcome limitations of polycrystals with composites of Ni–Mn–Ga wires in a polymer matrix. In wires and foams with grains as large as the element diameter (bamboo structure), twin boundaries span across entire grains and are mobile, resulting in large MFIS [5–7]. Such elements can then be embedded in a polymer matrix to form a solid structure. Ni–Mn–Ga powder composites with single-crystalline FSMA particles and broken up fibers were reported recently [8–12], but very little is known for composites with wires having a length to diameter ratio greater than 100.

For application requiring isothermal high strain and high frequency actuation, the twinning stress has to be less than the magneto stress (which is about 3 MPa [13] for Ni–Mn–Ga) to ensure magnetic-field-induced twin boundary motion [14]. For applications requiring damping however, the twinning stress needs to be high to guarantee that the dissipative twin boundary motion induced by applying a mechanical stress results in a high dissipation rate. Due to the low twinning stresses of 10 M and 14 M martensite (as low as 0.1 MPa [14,15]) these martensites can be used as actuator. In NM martensite, twinning occurs typically at much higher stresses of 10–20 MPa [4]. This prevents NM martensite from being used as actuator but it is promising for damping applications.

In this work, as-spun and annealed melt-spun Ni–Mn–Ga wires were thus characterized for their transformation temperature and crystal structure as well as for their mechanical and magnetic behavior. Furthermore, the thermal characteristics of the epoxy used as matrix material were analyzed. Finally, composites with Ni–Mn–Ga wires and epoxy matrix were processed, and their thermal and damping behavior was studied with differential scanning

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calorimetry and dynamic mechanical analysis experiments, respectively.

2. Experimental

The Ni–Mn–Ga wires were prepared from a $Ni_{50.3\pm0.2}Mn_{28.8\pm0.7}Ga_{20.9\pm0.5}$ ingot by melt-spinning, as described in Ref. [16]. The wires had a diameter of 30–90 μm and a length of up to 4 cm. About half of the more than one hundred wires were annealed at 1000 °C for 3 h in a sealed, evacuated and argon backfilled quartz tube, containing Ti and Mn, to stimulate grain growth. Ti served as oxygen getter. Mn was added to the quartz tube to create a Mn atmosphere and prevent loss of Mn via evaporation. Microstructure and composition of the wires were characterized with a FEI XLF30-FEG scanning electron microscope equipped with an energy dispersive X-ray spectroscopy probe (EDS). The transformation temperatures were detected by performing differential scanning calorimetry tests using a DSC Q100 from TA Instruments with a heating/cooling rate of 5 °C/min. To determine the Curie temperature, the magnetization was measured as a function of temperature in a magnetic field of 25 mT using a MicroSense Model 10 Vibrating Sample Magnetometer (VSM) with a heating rate of 6 °C/min and a cooling rate of 4 °C/min. The crystal structure was determined with X-ray diffraction experiments using a Bruker D8 Discover diffractometer with Cu Kα radiation.

To determine the mechanical properties of the melt-spun wires at different gauge lengths varying from 1.5 to 13 mm for the as-spun and from 1.5 to 8 mm for the annealed wires, tensile tests of the single wires were performed at room temperature. Each wire was glued with cyanoacrylate-glue on the clamps of a UTS tensile testing machine equipped with a home-made 5 N load cell. Besides loading the wires until fracture, loading–unloading cycles up to a maximum strain of about 0.7% and 2%, respectively, were performed for the as-spun and annealed wires with a gauge length of 3 mm. In all loading cases, the test speed was set to 0.005 mm/s.

As matrix material, the epoxy system Araldite LY 3297/Aradur 3298 (with a mix ratio of 100:40 by weight) from Huntsman, USA was chosen. This epoxy system is a commercially available, standard epoxy with a Young's modulus (E-modulus) of about 3 GPa at room temperature. Curing schedule was for 9 h at 80 °C. Resulting glass transition temperature was measured with a differential scanning calorimeter (DSC Q100 from TA Instruments) with a heating/cooling rate of 5 °C/min.

Composites were produced with vacuum infusion. The wires were placed and aligned by hand, as illustrated in Fig. 1, in a mold composed of a metallic bottom plate, silicone walls and a movable metallic cover bar that fits in the gap of about 3 mm width of the silicon walls. The resin was mixed, degassed for 30 min and then infused at room temperature to fill the mold with minimal movement of the wires and formation of pores. The wire volume fraction of the composites was determined by the packing of the wires under the pressure of the metallic cover bar induced by the vacuum bag and resulted in about 20 to 25 vol.%. As a reference, pure epoxy was also cast in a silicon mold, cured like the composite specimens at 80 °C for 9 h and ground to obtain about the same height as the composite specimens. The final specimen heights were 0.50 mm for the pure epoxy samples (4 specimens), about 0.45 mm for the as-spun Ni–Mn–Ga wire-epoxy matrix composites (3 specimens) and about 0.40 mm for the annealed Ni–Mn–Ga wire-epoxy matrix composites (4 specimens). To determine the morphology of the wire composites, surface and cross-section were observed under an optical microscope. Damping tests were conducted on a TA Instruments DMA Q800, USA, in a temperature range from 0 to 120 °C with a heating rate of 5 °C/min using the single cantilever mode with a maximum strain amplitude of 0.5% and a frequency of 1 Hz. The gauge length was 17.56 mm for all samples. In order to better interpret the results of the damping

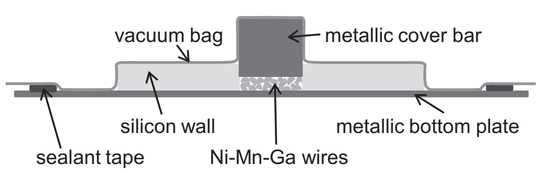

Fig. 1. Vacuum infusion set-up to produce Ni–Mn–Ga-wire epoxy-matrix composite samples for damping tests. The resin is infused perpendicular to the plane shown here.

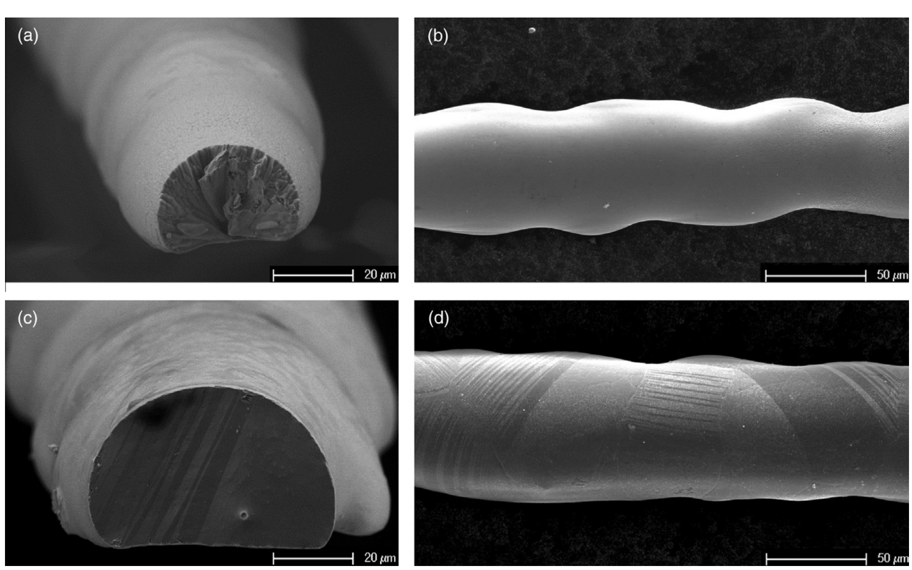

Fig. 2. SEM micrographs of cross section and surface of the as-spun (a, b) and the annealed (c, d) melt-spun Ni–Mn–Ga wires. The wires exhibited a semi-circular cross-section and an irregular diameter. The as-spun wires had dendritic like grains, the annealed wires exhibited a twinned bamboo- or near bamboo-structure.