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Processing and properties of Ni–Mn–Ga magnetic shape memory alloy based hybrid materials

S.-P. Hannula [a], I. Aaltio [a,*], Y. Ge [a], M. Lahelin [b], O. Söderberg [a]

[a] Department of Materials Science and Engineering, Aalto University School of Chemical Technology, P.O. Box 16200, 00076 Aalto, Finland

[b] Department of Biotechnology and Chemical Technology, Aalto University School of Chemical Technology, P.O. Box 16100, 00076 Aalto, Finland

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ABSTRACT

Magnetic shape memory (MSM) materials based on non-stoichiometric Ni–Mn–Ga (NMG) alloys have attracted extensive interest over the last decade because of their actuating, sensing, and damping properties. In addition to MSM phenomenon, NMG alloys have shown conventional shape memory effect, traditional and magnetic-field-assisted superelasticity, magnetocaloric, and special transport properties. The multifunctionality of MSM alloys may be utilized for actuators, sensors, dampers, and perhaps also for energy harvesting. The dominant mechanism behind the MSM phenomenon is the twin boundary movement in the martensitic phase, and in order to take the full advantage of above mentioned properties single crystals are usually desired. However, growth of Ni–Mn–Ga single crystals is quite tedious and high quality crystals are only limitedly available at a considerably high prize. Therefore, alternative material solutions based on hybrid concepts have attained increasing interest. NMG-polymer hybrids can be tailored for a particular application by a proper combination of NMG alloy and polymer and prepared in various forms including embedded NMG particles, ribbons, or sheets. These materials are especially interesting for applications in vibration damping, actuation, and sensing. Polymer selection is critical for the functionality of NMG-polymer hybrids, and the applied polymer should be selected based on the martensite type of the NMG alloy. E.g., the transition temperatures of both components should be adjusted carefully considering the application. The contact between NMG and polymer and the stiffness of the polymer are important. Excellent damping performance is obtained in the NMG-soft epoxy matrix below the martensite–austenite transition temperature region when compared to that of the pure polymer. The relative damping capacity is found to be better than that of any other known material.

1. Introduction

Ever since the martensitic transformation was discovered in stoichiometric Ni_2MnGa, different martensitic structures observed in various Ni–Mn–Ga (NMG) alloys have attracted considerable interest because of their exceptional functional properties [1,2]. Over the last decade the main focus has been directed to magnetic shape memory effect (MSME) of non-stoichiometric NMG alloys, which exhibit crystal structure-dependent magnetic-field-induced strain at maximum of 6% in the nearly tetragonal five-layered martensite (10M) and 11% in the orthorhombic seven-layered martensite (14M) at a rather moderate magnetic field (below 1 T) [3]. In addition to the magnetic shape memory (MSM) phenomenon, Ni–Mn–Ga alloys have shown conventional shape memory effect [4], traditional and magnetic-field-assisted superelasticity [5], magnetocaloric [6], and special transport properties [7], although, the existence of all these properties in the same alloy is not very likely. The multifunctionality of MSM alloys may be utilized for actuators, sensors, dampers, and also for energy harvesting [8–10]. The dominant mechanism behind the MSM phenomenon is the twin boundary movement in the martensitic phase.

To take the full advantage of above mentioned phenomena single crystals are usually required. However, growth of NMG single crystals is quite tedious and high quality crystals are only limitedly available at a considerably high prize. Therefore, alternative approaches have attained increasing interest. One example of these is the development of porous MSM materials consisting essentially of structured pores and an MSM skeleton prepared by special casting techniques [11]. These materials can potentially be used

* Corresponding author. Tel.: +358 9 47022684; fax: +358 9 47022677.
E-mail address: ilkka.aaltio@aalto.fi (I. Aaltio).

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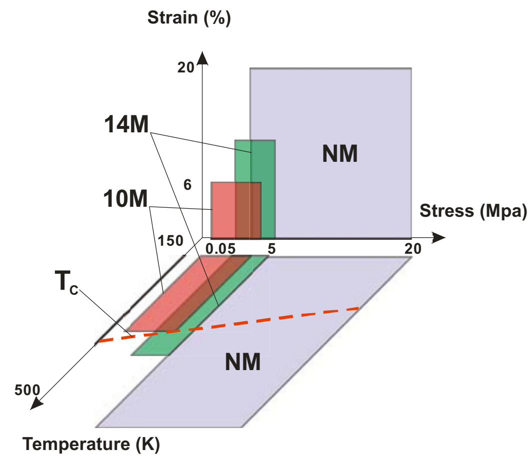

Fig. 1. Stress, strain and temperature windows of the NM, 10M and 14M NMG martensites. The evolution of the Curie temperature (T_C) is shown schematically by the dashed line.

similarly to single crystal alloys although with somewhat reduced elongation, sensing, and load carrying capabilities.

Material solutions based on hybrid concept incorporating Ni–Mn–Ga with polymers present another approach for materials with new functionalities [12]. One of the useful properties of MSM-polymer hybrids is high vibration damping capability [13]. The high vibration damping is caused by the hysteretic back and forth motion of the twin boundaries in the MSM material, which occurs at the certain stress–strain-temperature window defined by the MSM material [14]. Compared to the pure polymer sample, DMA measurements show excellent damping performance below the martensite–austenite transition temperature region in the Ni–Mn–Ga – soft epoxy matrix [15].

For the functionality of Ni–Mn–Ga/polymer hybrids matching of polymer to the martensite type of the NMG component is critical affecting the composite properties significantly. The transition temperatures of both components should be adjusted carefully considering the application. E.g, in the NMG MSM alloys, the reverse phase transformation decreases the damping property, while in polymers the glass transition decreases the modulus and drastically changes the mechanical properties. Furthermore, the contact between Ni–Mn–Ga and polymer and the stiffness of the polymer matrix are significant. Selection of the polymer matrix material is based on the requirements of the targeted application and on the chemical, thermal and mechanical compatibility with the MSM material. As shown in Fig. 1, different NMG martensites are basically suitable for different operating temperatures and the stress–strain-regimes in the vibration damping use. The properties vary significantly with composition and structure.

The bonding properties of polymers with the NMG-based MSM materials differ remarkably. According to [12,15] epoxy bonds well with the NMG surface. In this work we therefore mainly concentrate on the NMG-epoxy hybrids. MSM-polymer hybrids can be processed e.g., by mold casting, mixing and extrusion or by lamination of layers. For lamination a precursor structure can be made by first placing suitable spacers between the pre-cut MSM plates and casting the polymer in a mold to fill the empty space.

Change of properties due to aging is common in many commercial soft epoxies. Aging can be problematic in the hybrid MSM composites, since the increasing stiffness of the polymer changes the load distribution in the composite, reducing the stress applied to the MSM components. This usually causes deterioration of the composite properties such as decrease of the vibration damping. It is thus important to pay attention to the aging properties of the components, especially the polymer component. Baking of the composite above the phase transformation temperature of the MSM material transforms the martensite structure and resets the possible pre-orientation. In this paper, we present some ways of processing MSM-polymer hybrid materials and study the influence of using different polymer matrix materials and their aging properties on the MSM-polymer hybrid structure. In addition, we present results of applying external magnetic field to MSM-polymer hybrids processing and properties.

2. Experimental

Cast composite materials were prepared by two different methods. In the first one the readily heat treated NMG columnar crystal and single crystal samples were cut with electron discharge machining (EDM) to pieces of less than 10 mm dimensions, then mechanically milled by ring mill to powder, and then the powder was sieved to 150–300 μm diameter. The powder was heat treated in 800 °C for 2 h in evacuated quartz ampoules for releasing the residual stresses. It was then inserted to a steel ring-mold in a rubber enclosure and compressed by using a piston up to a stress of 3 MPa in order to produce an oriented martensite twin structure to the particles.

The oriented particles were then mixed with the fluid epoxy resin and hardener (Loctite Hysol), and cast to a machined PTFE mold with lid. The mold fixture was closed with screws (all non-magnetic) and immediately set to slowly alternating magnetic field of an electromagnet. The applied magnetic field H_{appl} maximum was ±0.7 T, directed along the long stick-sample axis with 180° gradually ($f \approx 0.1$ Hz) reversing direction. The magnetic field was applied to the sample during the curing until the NMG particles were not expected to move any more in the epoxy matrix. Finishing of the stick samples was made with low-speed diamond saw cutting and wet grinding (samples B in Table 1).

The other hybrid processing route consisted of EDM machining of plates from the single crystal NMG ingot, mechanical wet grinding (400 grit SiC paper) of the surfaces and assembling a precursor layer structure to a plastic foam mold consisting of the

Table 1
Hybrid composite sample materials.

Sample	Ni–Mn–Ga	Polymer	Curing/Heat treatment (T, t)	Vol. ratio (matrix: filler)	Bonding strength (MPa) [15]	RT mart. structure
A, thick plate laminate	$Ni_{52.3}Mn_{27.4}Ga_{20.3}$ single crystal	Hysol 9455	RT, 65 h		3.4	NM
B1, powder composite	$Ni_{48.3}Mn_{30.7}Ga_{21.0}$ $d = 150–300$ μm powder		RT, magn. field/373 K, 0.5 h	1:1		10M
B2, powder composite		Hysol 9484	RT, magn. field/323 K, 24 h	40:60	n.a.	
C1, thin plate (ribbon) laminate	$Ni_{50}Mn_{29}Ga_{21}$ melt spun ribbon	Hysol 9455	RT		3.4	
C2, ribbon laminate		Hysol 9492			2.0	