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Submicron pillars of ferromagnetic shape memory alloys: Thermomechanical behavior

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ABSTRACT

Remarkable shape memory, superelasticity and rubber-like effects on the submicron scale have been disclosed in Ni–Fe(Co)–Ga and Ni–Mn–Ga ferromagnetic shape memory alloys. Arrays of pillars with the different cross-section and length have been prepared onto 001-oriented faces of the alloys single crystals and their thermomechanical behavior across the martensitic transformation was studied in the bending mode inside a scanning electron microscope. Recovered strains of up to 5% and 7% have been obtained as a result of shape memory and superelasticity effects, respectively. These findings are important for the development of novel micro/nanoelectromechanical systems to be controlled, contactless, by a magnetic field.

1. Introduction

Magnetic shape memory alloys (MSMAs) have a great potential as smart materials due to their ability to undergo large strains (>10%) under a moderate external stimulus, such as a temperature change, application of a stress or magnetic field [1]. Their (micro-)nanoscale functionality, as in the case of thin films [2,3] or microstructures [4], is especially interesting considering the excellent work output density of these alloys [5] that enhances their performance in reduced dimensions, both because of the high area/volume ratio of such structures and the rapid actuation under temperature changes because of their low thermal inertia. Therefore, the miniaturization of MSMA structures is a key point to enabling high frequency applications. In addition, the reversible character of the martensitic transformation (MT) ensures the cyclic performance of these alloys making them suitable for micro/nanoelectromechanical systems (MEMS/NEMS) [6,7].

Thermal [8] and magnetic [9] actuation capacities have been widely demonstrated in bulk materials, however, their operation at the nanoscale still entails numerous technical challenges in terms of the preparation of the sample, manipulation and characterization of its performance. The demonstration of their main effects, like shape memory effect, superelasticity and magnetic field induced strain (MFIS) at the nanoscale is therefore essential for further development of MEMS based on these materials.

Alongside the application aspects, understanding of the size-dependent effects down to the nanoscale in shape memory alloys has motivated recent basic investigations. Micro- or nanoscale mechanical testing of materials has been performed by means of a variety of experimental techniques including compression of pillars [10], nanoindentation [11] or tensile testing [12].

It has been observed that the thermomechanical response of SMA changes significantly when the characteristic size of the sample is reduced below one micrometer. For instance, the critical stress to induce the martensitic transformation in Cu–Al–Ni sub-micrometer structures increases up to twice its value in the bulk material [13]. This effect has been explained in terms of the fully homogeneous nucleation of the martensitic variants, due to the reduced amount of martensite specific nucleation sites. The same work demonstrates that the increase of the driving force needed to induce the martensitic transformation at the nanometer scale is also extensible to the thermally induced transformation,

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as it happens at lower temperatures in the macroscopic samples.

It has been also found that the response of different SMAs to the mechanical load is not always superelastic in the sub-micrometer scale. For example, Ni–Ti pillars with diameters below 400 nm do not present a complete recovery after being strained [14]. An explanation of this fact was given in terms of the suppression of martensitic transformation in this alloy below a grain size threshold (≈50 nm) [15]. The ion beam damage of the crystal structure, produced during focused ion beam (FIB) shaping of the pillars, is also considered as a possible reason of this behavior. However, Cu–Al–Ni submicrometer pillars displayed superelastic and shape memory effect for every diameter after being subjected to hundreds of load – unload loops with a maximum strain of 5% [16]. In this case, the smaller twin variant structure of around 20 nm enables the phase transformation and therefore the existence of the functional effects. In the range of tens of microns, Ni–Mn–Ga MSMA micropillars have already demonstrated the ability to undergo compressive strains over 3% with a relatively small residual strain after stress removal [17]. In such experiments, an *ac*-type twinning was identified generating variants with a width of about 1 μm.

In the present study, we have selected single crystals of the classical Ni–Mn–Ga and Ni–Fe(Co)–Ga magnetic shape memory alloys, prepared arrays of pillars with a submicron size cross-section and tested their shape memory and superelastic performance. Such submicrometer sized MSMA objects and their stress/temperature induced transformation behavior were not explored in the past. Pillars have been deformed in a bending mode. Despite its limitations, this mode of deformation brings two benefits: on the one hand, it allows a clear visual appreciation of the shape memory effect and superelasticity, while on the other hand it involves simultaneous tensile and compressive strain so that both of them are probed in a single step upon loading and recovery. Quantitative values of the strain can be obtained by analyzing the micrographs. As a result of the experiments, superelasticity, shape memory effect and rubber-like behavior involving high values of reversible strains have been verified. Being ferromagnetically ordered, the studied materials should allow also the thermomechanical nanoactuation controlled by a magnetic field, whereby suggesting a considerable advance when being implemented in the novel magnetic MEMS/NEMS.

2. Experimental

Three previously grown and characterized single crystals of Ni–Mn–Ga and Ni–Fe(Co)–Ga Heusler alloys, have been selected to prepare the nanopillars [18–20]. The selected single crystals exhibit tetragonal modulated (10 M) and non-modulated (NM) martensitic structures and forward (T_M) and reverse (T_A) transformation temperatures in the range from −59 °C to +28 °C. Table 1 summarizes the compositions, structures and values of T_M/T_A of all crystals. When in bulk, they show excellent functional characteristics in particular a shape memory effect and superelasticity [18–20].

Plates with a size of around 1 × 1 × 0.5 mm^3 and crystallographic orientation of ⟨100⟩ for the largest face were cut and mechanically polished. The arrays of pillars with different diameters have been milled by the focused ion beam (FIB) technique on the polished surface. We have used Helios 450S DualBeam FIB/SEM electron

Table 1
Composition, structure and martensitic transformation temperatures of the single crystalline alloys used for preparation of pillars.

Alloy	Composition	Martensitic structure	T_M/T_A (°C)	Reference
A1	$Ni_{50.1}Fe_{18.5}Ga_{27.1}Co_{4.3}$	NM	−59/−55	[18]
A2	$Ni_{49.4}Mn_{27.7}Ga_{22.9}$	10 M	+1/+11	[19]
A3	$Ni_{49.3}Mn_{27.9}Ga_{22.8}$	10 M	+21/+28	[20]

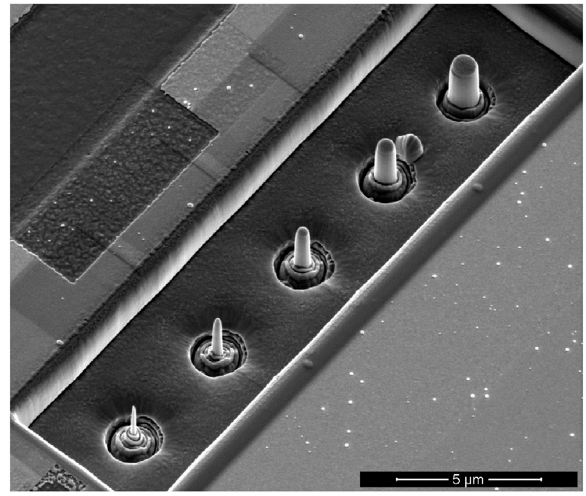

Fig. 1. SEM image of an array of nanopillars with diameters of 1000, 700, 500, 300 and 150 nm milled in a Ni–Mn–Ga single crystal (alloy A3). The image was taken under a tilt of 30°.

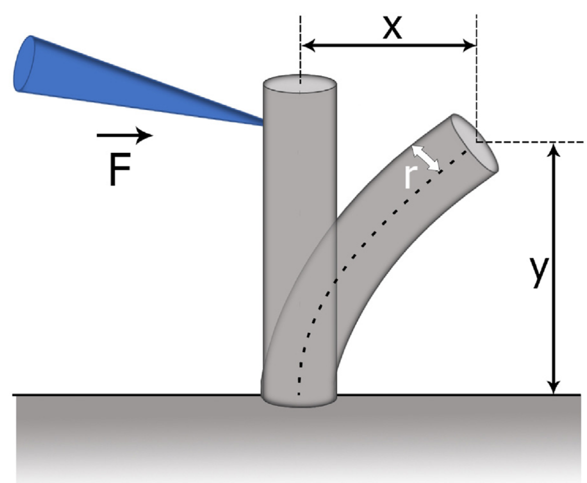

Fig. 2. Schematic of the bending deformation of a pillar with the applied force, F, from the nanomanipulator.

microscope (FEI Co, Netherlands). The pillars have a circular cross-section with diameters ranging between 150 and 1100 nm, while their height has been varied between 1.5 μm and 6.4 μm. The thickness of the damaged layer of the pillars is estimated to be equal to about 25 nm (see Supplement) for the Ga ions energy of 30 kV used in this work. Importantly, the preliminary measurements show a Ga-depleted content of the outer layer. An example of the array of cylindrical nanopillars prepared from A3 crystal is shown in Fig. 1.

The application of mechanical stress (see Fig. 2) has been performed in bending mode using a Kleindiek Nanotechnik nano-manipulator (Kleindiek Nanotechnik GmbH, Germany) inside the scanning electron microscope (Quanta 250F ESEM, FEI Co, Netherlands) chamber. Cone shaped tips have been used to push the upper part of a pillar. Positioning precision of the nano-manipulator is about 0.5 nm, control of displacements has been determined by post processing of the images with sub-pixel accuracy. The temperature of the sample has been controlled and monitored in the range between −150 °C and 50 °C by a cryostage during heating ramps only. An uncertainty of the measurements of absolute and relative values of the sample temperature was accepted as 3 °C and 1 °C, respectively. The strain (ε) of the pillars has been evaluated from the electron microscopy images using ImageJ software. For