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Martensite transformation and superelasticity in polycrystalline Ni–Mn–Ga–Fe microwires prepared by melt-extraction technique

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ABSTRACT

The effects of Fe doping on the microstructure, martensite transformation and superelasticity in melt-extracted $Ni_{50}Mn_{25}Ga_{25-x}Fe_x$ ($x=1$–6) microwires were investigated. The unique solidification process during melt-extraction creates the micron-sized diameter wires with small grains and semicircular cross-section. At ambient temperature $Ni_{50}Mn_{25}Ga_{25-x}Fe_x$ ($x<4$) microwires are austenite phases with a cubic $L2_1$ structure, while microwires with $x>5$ are martensitic phases with seven-layered modulated (7M) structure. The results point out that martensite transformation temperatures are strongly related to Fe content due to the change of valence electron concentration (e/a). Reversible superelastic strains of 0.92% and 0.75% are obtained in $Ni_{50}Mn_{25}Ga_{21}Fe_4$ and $Ni_{50}Mn_{25}Ga_{20}Fe_5$ microwires, respectively. It is demonstrated that the temperature dependence of stress-induced martensite (SIM) stress follows the Clausius–Clapeyron relation. The temperature dependence of SIM stress in Fe-doped Ni–Mn–Ga microwires is 10.5 MPa/K.

1. Introduction

The interest in shape memory alloys (SMAs) has increased in recent decade alternative to conventional actuators such as hydraulic, pneumatic and motor-based systems by taking advantage of their shape memory effect (SME), superelasticity (SE) and damping capacity. SMAs, such as Ni–Ti [1], Cu-based [2–4] and Fe-based [5] alloys, are thermo-responsive materials where deformation can be induced and recovered through temperature change. In contrast, ferromagnetic shape memory alloys (FSMAs) such as Ni–Mn–Ga may respond with a high frequency under an external magnetic field. As a result, FSMAs have attracted many attentions because they exhibited SME and SE as well as high magnetic-field-induced strain (MFIS) and magnetocaloric effect (MCE), which make them potential candidate materials for sensors, actuators or magnetic refrigerant (MR) [6–12]. However, the brittleness of polycrystalline Ni–Mn–Ga ternary alloys is a vital obstacle for their practical applications [13].

Stoichiometric Ni_2MnGa alloy shows high Curie point (~376 K), saturation magnetization (~100 emu/g at 4 K) and magnetic moment per formula (~4.17 μ_B), but low martensite transformation temperature (M_s~202 K) [14]. The M_s and ductility of Ni_2MnGa alloy may be improved by doping a fourth element or grain refinement [15–21]. Among various doping elements, Fe has attracted many attentions because transformation temperatures of Ni–Mn–Ga alloys are sensitive to Fe content [18,19]. The martensite transformation (MT) temperature decreased when Fe substituted Ni in $Ni_{52.5-x}Mn_{23}Ga_{24.5}Fe_x$ alloys, while the temperatures changed little when Fe substituted Mn in $Ni_{51.4}Mn_{25.2-x}Ga_{23.5}Fe_x$ alloys. On the other hand, the MT temperatures increased when Fe substituted Ga in $Ni_{51.4}Mn_{24.5}Ga_{24.1-x}Fe_x$ alloys [18]. It was pointed out that the effect of Fe-doping on MT of Ni–Mn–Ga alloys was related to the valence electron concentration (e/a) [18].

SE in SMAs may be obtained by stress-induced martensite (SIM) transformation when loading and the reverse transformation upon unloading [22]. SE in single crystalline Ni–Mn–Ga alloys has been reported in Refs. [22,23], but few studies have been devoted to the SE in brittle polycrystalline Ni–Mn–Ga alloys [10]. In this paper, polycrystalline $Ni_{50}Mn_{25}Ga_{25-x}Fe_x$ ($x=1$~6 at%) microwires (diameter 30–40 μm, length ~100 mm) were prepared by melt-extraction technique [24]. The relationship between Fe content and MT temperatures was established. Then $Ni_{50}Mn_{25}Ga_{21}Fe_4$ and $Ni_{50}Mn_{25}Ga_{20}Fe_5$ microwires, which experienced MT around room temperature, were selected for SE investigation. The results demonstrated strong dependence of MT

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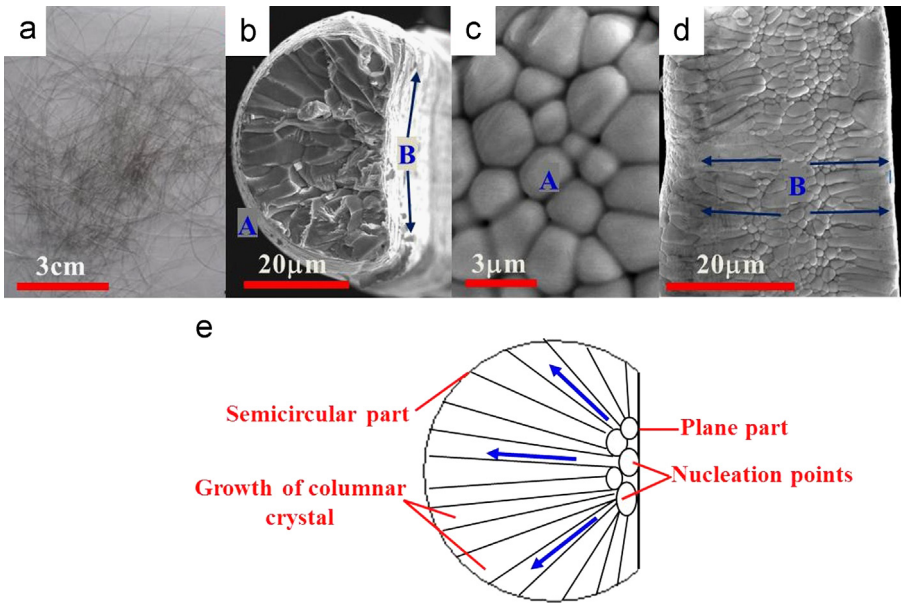

Fig. 1. SEM images of the as-extracted polycrystalline $Ni_{50}Mn_{25}Ga_{20}Fe_5$ microwire. (a) Low magnification image, (b) cross-section, (c), cellular grains, (d) columnar grains in the planar part, and (e) schematic diagram of the crystal growth.

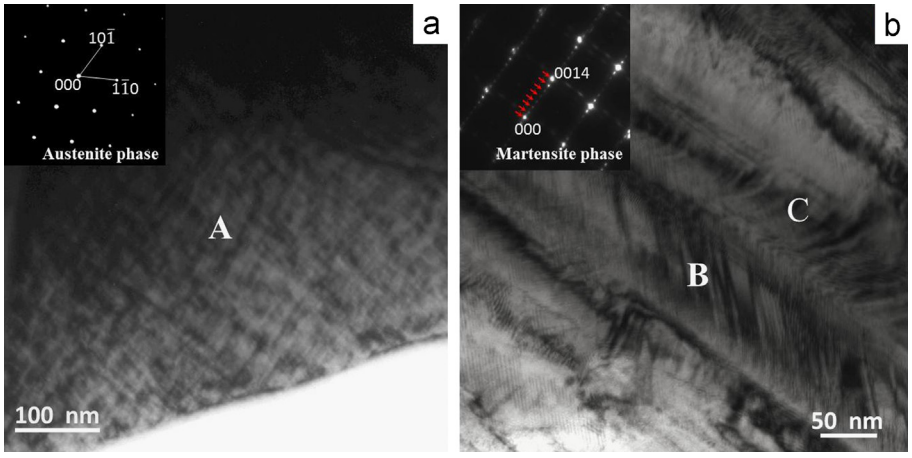

Fig. 2. TEM micrographs showing austenite and martensite structure of the Ni–Mn–Ga–Fe microwires. (a) Austenite phase in $Ni_{50}Mn_{25}Ga_{21}Fe_4$ microwires observed at room temperature. The inset shows diffraction pattern of the austenite phase, (b) martensite structure in $Ni_{50}Mn_{25}Ga_{20}Fe_5$ microwires. The inset shows diffraction pattern of 7M martensite phase.

temperature on Fe content and the characteristic of SE in polycrystalline Ni–Mn–Ga-Fe alloys.

2. Experimental details

Ni–Mn–Ga–Fe ingots were prepared by arc melting of pure elemental materials Ni (99.99%), Mn (99.99%), Ga (99.99%), and Fe (99.99%) in argon atmosphere. The microwires with a nominal composition of $Ni_{50}Mn_{25}Ga_{25-x}Fe_x$ ($x=1$–6 at%) were prepared using a melt-extracted facility. Details of the processing have been reported in Ref. [24] and are briefly described here. The ingot was melted by an induction coil to form a melting pool. A rolling copper wheel (diameter 320 mm, knife edge 60°) was used to extract the melt out of the pool. As a result, the microwires with diameters of 30–40 μm were obtained by rapid solidification during extracted melt. The linear velocities of the wheel flange and feed rate of the ingot were 30 and 3×10^{-5} m/s, respectively.

The morphology of the microwires was investigated in a field-emission scanning electron microscopy (SEM-Helios Nanolab600i) at 20 kV. Thin-foil specimens for transmission electron microscope (TEM) observations were prepared using a precision ion-polishing system. TEM observations were performed in Tecnai G2 F30.

The crystal structure of the as-extracted microwires was determined using X-ray diffraction (D/max-rb with Cu Kα radiation) at ambient temperature. Transformation temperatures of the wires were examined through a differential scanning calorimeter (TA DSC Q200), with heating and cooling rates of 5 K/min. The SE test temperatures of a single microwire were determined by temperature *vs.* internal friction curves obtained on a dynamic mechanical analyzer (DMA Q800), with oscillation frequency of 1 Hz, strain amplitude of 5×10^{-4} and heating/cooling rates of 5 K/min. For superelastic tests, the microwire was heated to 350 K (higher than A_f) and held at this temperature for 12 min, then it was cooled to a test temperature (higher than M_s) and subjected to a tensile loading–unloading cycle at a rate of 0.04 N/min. After a tensile cycle, the microwire was heated to 350 K for 12 min, and then