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Original Research

Martensite transformation, mechanical properties and shape memory effects of Ni-Mn-In-Mg shape memory alloys☆

Zhenni Zhou[a], Liang Yang[a], Rongchen Li[a], Jun Li[a,b,*], Qiaodan Hu[a,*], Jianguo Li[a]

[a] School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China
[b] Collaborative Innovation Center for Advanced Ship and Deep-Sea Exploration, Shanghai Jiao Tong University, Shanghai 200240, China

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ABSTRACT

The martensite transformation (MT), mechanical properties and shape memory effect (SME) of $(Ni_{50}Mn_{35}In_{15})_{(1-x)}Mg_x$ (x = 0%, 0.08%, 0.3%, 0.6% at%) alloys were comprehensively investigated. The results showed that due to Mg doping the MT temperature shifted to higher temperatures and a worm-like second-phase precipitated at grain boundaries and inside the grains. With increasing Mg content, the amount of precipitates gradually increased, the thermal hysteresis was almost invariant, and the SME was not obviously affected at 3% pre-strain, even when the volume of the second phase reached up to 28.75%. Compressive stress and strain experiments showed that both the strain and strength of the Ni-Mn-In-Mg alloys were improved substantially (by 46.9% and 53.4%, respectively, at x = 0.6%) compared with those of the pure $Ni_{50}Mn_{35}In_{15}$ alloy; this effect is nearly the same as that achieved by the directional solidification method. Because Mg is nonmagnetic, the magnetization difference of the alloy with Mg doping is much lower than that of the alloy without Mg doping. Overall, the results confirm that adding a small amount of Mg is a potentially viable method for improving the mechanical properties of Ni-Mn-In alloys without adversely damaging their functional properties.

1. Introduction

Magnetic shape memory alloys (MSMAs) that exhibit both a magnetic transition and a martensitic transformation are responsive not only to temperature and stress, similarly to traditional memory alloys [1], but also to magnetic fields [2]. Their response rate is higher than that of traditional memory alloys, and their strain is larger than those of giant magnetostrictive materials and piezoelectric materials. Compared with other traditional MSMAs, Ni-Mn-In alloys are special because a magnetic field can induce the phase transformation from martensite to austenite [3]; these alloys are thus metamagnetic shape memory alloys. The alloys exhibit various phenomenological properties, including a huge inverse magnetocaloric effect [4,5], giant magneto-thermal conductivity, giant magnetoresistance [6] and a giant output stress of approximately 100 MPa [2], which are all derived from this unique magnetic field-induced martensitic transformation; hence, these materials are good candidates for application as actuators and sensors. However, the inherent brittleness of these intermetallic compounds, which are fabricated via the conventional melting technique, severely limits their practical application.

At present, the main ways to improve the intrinsic brittleness of Ni-Mn-based alloys are sintering [7], rapid solidification [8] and, the most widely studied approach, doping with a fourth element. Examples include the addition of Ti [9], Fe [10] or Co [11] as a dopant in Ni-Mn-In alloys and the addition of Fe [12], Co [13], Cu [14], Y [15], Gd [16] or Nd [17] as a dopant in Ni-Mn-Ga alloys. The improvement in plasticity is derived from the precipitation of a second plastic phase or from grain refinement. The most obvious improvement in plasticity reported to date was achieved by adding 8% Fe to Ni-Mn-In alloy, where a strain of 49.4% was obtained [8]. The aforementioned studies also show that the second ductile phase formed via doping with a fourth element has two opposing effects: improving ductility and degrading the shape memory effect (SME) [18,19]. Therefore, while researching an effective way to improve the brittleness of the alloy, detecting whether the functionality is damaged is also important. To date, the effects of doping with Mg, which is in the same period as Al [20] and Si [21], on the properties of Ni-Mn-Ga/In/Sn/Sb alloys have not been reported. However, Yin et al. [22] and Guo et al. [23,24] have confirmed that the addition of 0.002% Mg to FeAl and Fe_3Al intermetallic alloys can substantially improve their room-temperature ductility and result in good machinability. The

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* Corresponding authors.
E-mail addresses: li.jun@sjtu.edu.cn (J. Li), qdhu@sjtu.edu.cn (Q. Hu).

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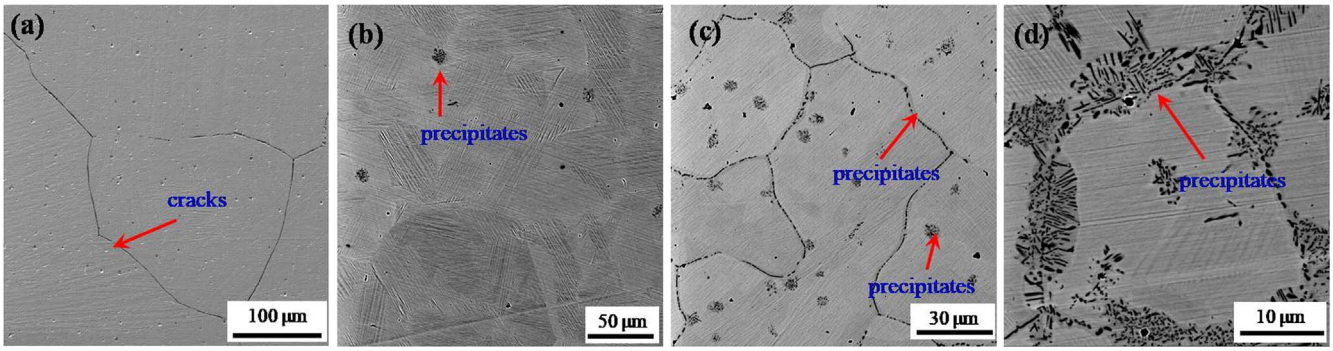

Fig. 1. BSE images of the studied alloys: (a) x = 0; (b) x = 0.08%; (c) x = 0.3%; (d) x = 0.6%.

mechanism involves the accumulation of Mg in grain boundaries; dislocations can continuously slip through the Mg-rich boundaries into the adjacent grains, thus improving the plasticity. However, excessive Mg doping is found to adversely affect the alloys' mechanical properties.

In this study, a minor amount of Mg as an additive rather than as substitutional atoms was added to Ni-Mn-In alloys. Because the atomic radius of Mg is 0.172 nm, which is larger than that of Ni (0.162 nm) and In (0.155 nm) but similar to that of Mn (0.179 nm), Mg atoms are difficult to dissolve into the lattice gaps. Consequently, the solubility of Mg in the matrix is low, leading to the formation of second-phase precipitates or to convergence at the grain boundaries. In fact, by synergic tuning of the microstructure via minor Mg alloying in Ni-Mn-In magnetic shape memory alloys, the strain and strength of the alloy were successfully improved by 46.9% and 53.4%, respectively, greater improvements than those achieved by a dual-phase $Ni_{52}Mn_{32}In_{16}$ alloy prepared by the zone melting liquid metal cooling directional solidification method [25]; however, the manufacturing cost is much lower. Furthermore, small hysteresis and no significant SME damage were also detected in this alloy. This study is instructive for improving the mechanical properties of Ni-Mn-In alloys without adversely damaging their functional properties.

2. Experimental procedure

Polycrystalline $(Ni_{50}Mn_{35}In_{15})_{(1-x)}Mg_x$ (x = 0%, 0.08%, 0.3%, 0.6%. at%) alloys, named A0, A1, A2 and A3, respectively, were prepared via arc melting in a pure argon atmosphere from raw materials including Ni (purity 99.99 wt%), Mn (purity 99.99 wt%), In (purity 99.995 wt%) and Mg (purity 99.99 wt%). The ingots were flipped and re-melted four times to ensure homogeneity after annealing at 1173 K for 24 h, followed by water quenching.

Samples for optical observation were mechanically polished and chemically etched in a solution of 100 ml water + 5 g ferric chloride. The microstructure was observed via optical microscopy (OM, Axio Imager A1m) and scanning electron microscopy (SEM, Phenom XL). Martensite transformation (MT) temperatures and the entropy change, ΔS, were determined by differential scanning calorimetry (DSC, NETZSCH 204F1) carried out at a heating/cooling rate of 5 K/min. The composition of the samples was analyzed via energy-dispersive X-ray spectroscopy (EDS) in conjunction with SEM. To determine the magnetic properties, magnetization-temperature (*M-T*) curves were recorded with the samples under a magnetic field of 0.01 T (heating/cooling rate of 3 K/min) using a physical property measurement system (Quantum Design PPMS-9T (EC-II)).

Adobe Photoshop was used to determine the percentage of precipitates. All precipitation areas in each SEM image were filled with the same color to determine the percentage of the total area occupied by the filled region. The average area of the precipitates was then determined in all images.

Sample hardness was evaluated using a Vickers hardness (*HV*) testing machine with a loading period of 10 s at 25 g. Seven points were measured in both the area of high precipitate concentration and the matrix area on sample A3; the *HV* values were averaged, with the highest and lowest values excluded.

Compression tests were performed using an AG-100KNA material testing machine at room temperature and at a velocity of 0.03 mm/min. The compressive strength and SME of the samples were measured based on the stress–strain curves. The height of each specimen was measured before loading (h_0), after unloading (h_1) and after heating at 500 K (h_2). The residual strain after unloading (ε_{er}) and the SME (ε_{SME}) were calculated as $\varepsilon_{er} = (h_0 - h_1)/h_0 \times 100\%$ and $\varepsilon_{SME} = (h_2 - h_1)/h_0 \times 100\%$, respectively. The recovery rate was calculated as $R = (\varepsilon_{SME}/\varepsilon_{er}) \times 100\%$.

3. Results and discussion

3.1. Microstructure

Back-scattered electron (BSE) images showing the microstructure of all samples indicate that martensite was present in all alloys, as shown in Fig. 1. In addition, many apparent grain-boundary cracks can be observed in the BSE images of sample A0 (indicated by arrows in Fig. 1a). In sample A1 (x = 0.08%), few cracks are visible and a few precipitates appear both inside the grains and on the grain boundaries; these observations demonstrate that the solubility of Mg in the alloy was lower than 0.08%. When the Mg content increased to 0.3%, almost every grain boundary was "labeled" by the precipitates, as shown in Fig. 1c, causing the grain boundary to become highly visible in the BSE images. Notably, when the Mg content increased from 0.08% to 0.6%, the volume fraction of precipitates increased substantially from 0.45% to 28.75%, as shown in Fig. 2.

Fig. 3 shows the morphology, composition and structure of the

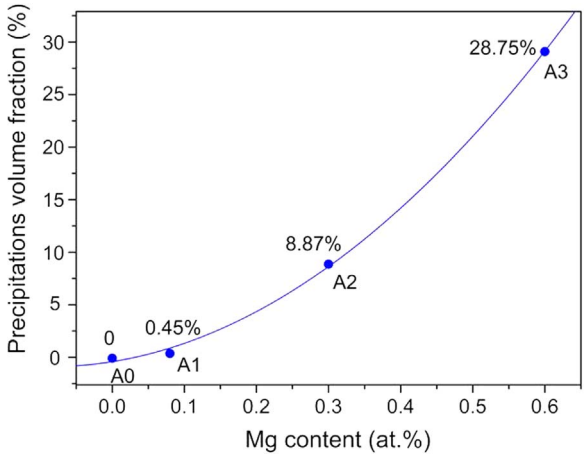

Fig. 2. Effect of Mg content on the volume fraction of the precipitates.