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Effect of Gd addition on microstructure, martensitic transformation and mechanical properties of $Ni_{50}Mn_{36}Sn_{14}$ ferromagnetic shape memory alloy

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ABSTRACT

The effect of Gd addition on microstructure, martensitic transformation and mechanical properties of $Ni_{50}Mn_{36}Sn_{14}$ ferromagnetic shape memory alloy has been investigated. The results show that Gd addition leads to some changes in the microstructure and crystal structure. Martensitic transformation is observed in $Ni_{50}Mn_{36}Sn_{14}$ alloys with adding different amount of Gd. The compressive strength and compressive strain of alloys is notably enhanced with the increase in Gd content. The compressive strength increases from 448 MPa to 707 MPa and the compressive strain increases from 4.5% to 9.0% with increasing Gd content from 0 at.% to 2 at.%. The mechanism of the improved mechanical properties is also revealed.

1. Introduction

Since Sutou [1] et al. report the martensitic transformation (MT) in Ni-Mn-X (X = In, Sn, Sb) Heusler alloys, Ni-Mn-Sn alloys have attracted tremendous attention in the last few years. Off-stoichiometric Ni-Mn-Sn alloys are different from the conventional ferromagnetic shape memory alloy Ni-Mn-Ga, in which a large magnetic-field-induced strain occurs due to a re-arrangement of the martensite variant [2–5]. They undergo a martensitic transformation from the ferromagnetic parent (P) phase to the weak-magnetic martensitic (M) phase with decreasing temperature. Therefore, a huge magnetization change occurs during the martensitic transformation and application of magnetic field decreases the transformation temperature because of the large difference of Zeeman energy between the P phase and the M phase [6]. Based on this new mechanism of martensitic transformation, the martensitic phase transformation of Ni-Mn-Sn alloys can be driven directly by applying a magnetic field. In addition, Ni-Mn-Sn alloys exhibit multifunctional properties and the richness and diversity of the physical phenomena, such as giant magnetocaloric effect, large magnetoresistance effect, metamagnetic shape memory effect and exchange bias [7–11]. These make it a good candidate for application as actuators, sensors, information storage and working substance for magnetic refrigeration.

Unfortunately, Ni-Mn-Sn alloys exhibit extreme brittleness, low strength and poor processability, which severely restricts its application. It was reported that by adding rare earths Y, Tb, Gd or Nd to polycrystalline Ni-Mn-Ga alloy, significant improvements in the compressive strength and ductility were obtained [12–15]. However, research on the effect of Gd addition on the mechanical property and fracture behavior of Ni-Mn-Sn ferromagnetic shape memory alloys (FSMA) is still blank. In order to improve the mechanical properties without sacrificing the magnetic properties, different amount of Gd is added into $Ni_{50}Mn_{36}Sn_{14}$ FSMA. This present paper focuses on the influence of different amount of Gd addition in $Ni_{50}Mn_{36}Sn_{14}$ alloys on the microstructure, mechanical and magnetic properties. The results show that the compressive strength and compressive strain of alloys is notably enhanced with the increase in the amount of Gd addition. In addition, the mechanism of the improved mechanical properties is revealed of adding Gd.

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2. Experimental

The nominal composition of the alloys $Ni_{50}Mn_{36}Sn_{14-x}Gd_x$ ($x = 0$, 0.5, 1, 2 at.%) were prepared with high purity element by melting four times in a non-consumed vacuum arc furnace under argon atmosphere. The samples were annealed in vacuum quartz tubes at 1123 K for 12 h, and quenched in ice water for homogeneity. The microstructure of the alloys was examined using an Olympus metallographic microscope and scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDS). The compression tests were performed at room temperature on an Instron 5569 testing system at a crosshead displacement speed of 0.05 mm/min, and the size of the sample was 3 mm × 3 mm × 5 mm. Fractography was observed by SEM to study the dominant fracture behavior in this alloy system. The crystal structure at room temperature was determined by X-ray diffraction (XRD, Rigaku D/max-Rb with Cu K_α radiation). The phase transformation and magnetic properties were studied with a vibrating sample magnetometer (VSM).

3. Results and discussion

Fig. 1 shows the optical micrographs of solution-treated $Ni_{50}Mn_{36}Sn_{14}$ alloys with different amount of Gd addition at room temperature. It can be seen that the grain size of Ni-Mn-Sn-Gd alloys decreases with increase of Gd content as shown in Fig. 1 (a)–(d). With the rare earth Gd content increases from 0 at.%, 0.5 at.%, 1 at.% to 2 at.%, the average grain size of alloy is 120 μm, 70 μm, 30 μm and 15 μm, respectively. When the content of Gd is 0.5 at.%, the second phase begin to form slightly. The amount of second phase increases with the further increase of Gd content, meanwhile the second phase interconnects gradually and trends to gather at the grain boundaries.

In order to further confirm the distribution of rare earth element Gd in alloys, SEM observation and EDS were carried out. Fig. 2 shows the backscattered electron images of $Ni_{50}Mn_{36}Sn_{14}$ alloys with different amount of Gd doping. The grain size is clearly reduced with increasing Gd content, which is consistent with the results of Fig. 1. Additionally, it is evident that the addition of Gd markedly changes the microstructure of ternary $Ni_{50}Mn_{36}Sn_{14}$ alloy. $Ni_{50}Mn_{36}Sn_{14}$ alloy exhibits a single-phase structure, whereas all the Gd containing alloys contain a second phase (white area), as shown in Fig. 2. When $x = 0.5$, small amounts of the second phase disperse in the matrix. The volume fraction of the second phase increases gradually with the further increase of Gd content, and tends to distribute along the grain boundaries. When the content of Gd reaches 2 at.%, the second phases along the grain boundaries grow and fully connect to each other. In this way, a network-like distribution and local enrichment of the second phases are found in this alloy. Combined with the EDS results shown in Table 1, it indicates that the second phase contains about 11.7 at.% Gd, however 0.1 at.% Gd is detected in the matrix. This means that the solubility of Gd in the matrix is very low and insolvable Gd distributes mainly along the grain boundaries to form the Gd-rich phase.

Fig. 3 shows the XRD patterns of $Ni_{50}Mn_{36}Sn_{14}$ alloys with different amount of Gd addition at room temperature, and A(hkl),4O(hkl),10 M(hkl) indicate the miller indices for $L2_1$, 4O, 10 M structure respectively. For ternary $Ni_{50}Mn_{36}Sn_{14}$ alloy, the typical diffraction peaks from austenite can be clearly detected. The patterns can be indexed on the basis of a cubic single-phase austenite phase with the highly ordered $L2_1$-type crystal structure. When the amount of Gd addition is 0.5 at.% and 1 at.%, besides the reflection from austenite, two peaks from four-layered orthorhombic (4O) structure appear, indicating that martensite and austenite coexist in these two alloys at room temperature. As shown in Fig. 3(d), when the amount of Gd addition is 2 at.%, the alloy mainly corresponds to 10 M orthorhombic. The A(220) peak disappears and the alloy shows almost a fully martensitic microstructure at room temperature where the austenitic peaks become very weak. In addition, some extra peaks can be observed in the alloys (marked by red point in Fig. 3). This suggests that the new phase may be the Gd-rich phase, which is rather similar to that of $SmNi_4Ga$ reported by Joshi [16], and the authors think that the XRD pattern of all the

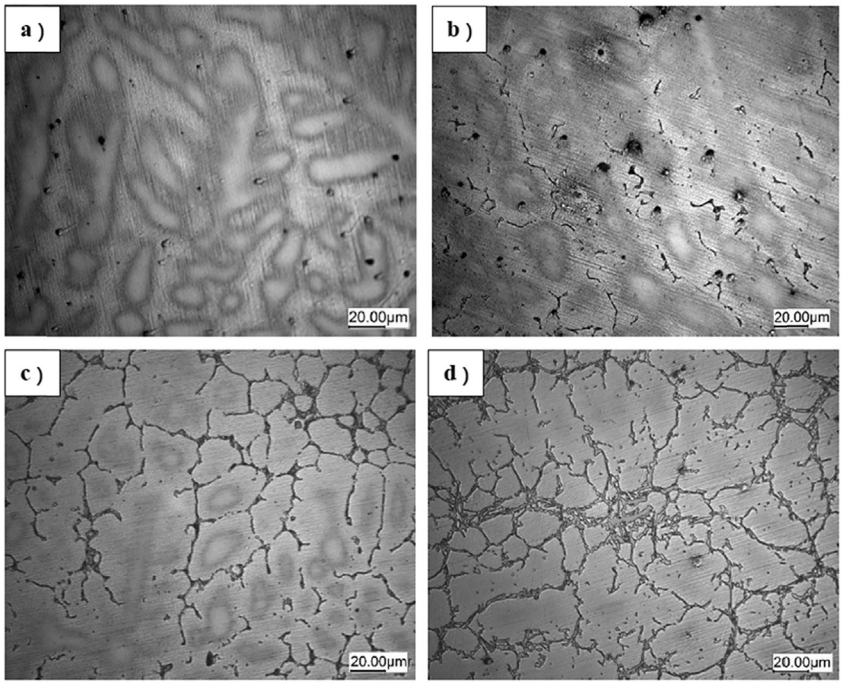

Fig. 1. Optical micrographs of solution treated $Ni_{50}Mn_{36}Sn_{14}$ alloys with adding different amount of Gd, and the amount of Gd addition is (a) 0; (b) 0.5 at.%; (c) 1 at.%; (d) 2 at.%.