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Review

Phase transformation and magnetic properties of Ni–Mn–Ga–Ti ferromagnetic shape memory alloys

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ABSTRACT

The influence of partial substitution of Ti for Ga on martensitic transformation temperatures, Curie temperature and magnetization saturation of $Ni_{53}Mn_{23.5}Ga_{23.5}$ ferromagnetic shape memory alloys were investigated in detail. The results show that solubility limits of Ti in the matrix is found to be about 8 at.%. The martensitic transformation temperatures were increased markedly in samples with 0.5–8 at.% titanium, and decreased with more than 8 at.% titanium addition. While the Curie temperature almost remains unchanged at low-Ti content and subsequently decreases obviously. Magnetization saturation of martensitic phase decrease with the increasing titanium content since it is sensitive to ordered atomic arrangement.

Contents

1. Introduction

Ni_2MnGa alloys have attracted much attention as potential actuator and sensor materials due to their giant magnetic field-induced-strain and high response frequency [1–5]. Unfortunately, the brittleness, low strength and poor processability of Ni–Mn–Ga alloys hinder their applications. It has been [6,7] reported that low doping of Fe in Ni–Mn–Ga alloys improves the plasticity without sacrificing its magnetic properties. Moreover, several rare elements, such as Tb, Sm, Dy and Nd, have been added to ternary Ni–Mn–Ga alloys. Their effects on the phase transformation behavior and magnetic and mechanical properties have been studied [8–11]. It is well known that ageing usually affects the martensitic transformation behavior, microstructure and mechanical properties of shape memory alloys [12–14]. Very recently, we reported that the fine Ni_3Ti precipitates form in the Ti-doped Ni–Mn–Ga alloy after aging, which may increase the strength of the alloys and enhance the plasticity without sacrificing the thermomechanical properties [15–17]. Therefore, it is of much importance for firstly investigation on solution-treated in Ni–Mn–Ga–Ti alloy. Thus, the purpose of this letter is to investigate the effect of solution-treated on the magnetic properties and phase transformation temperatures obtained by partly replacing Ga by Ti in $Ni_{53}Mn_{23.5}Ga_{23.5-x}Ti_x$ alloys were reported.

2. Experimental

The alloy with a nominal composition of $Ni_{53}Mn_{23.5}Ga_{23.5-x}Ti_x$ (x = 0, 0.5, 2, 5, 8, 15 at.%) were prepared from high purity elements in an arc-melting furnace under argon atmosphere. The melted ingots were cast into a chilled copper mold to obtain a master rod with a dimension of 10 mm in diameter and 75 mm in length. The master rod was sealed in the vacuum quartz ampoules. Chemical ordering was induced in ingots through annealing at 1273 K for 24 h, followed by ice-water quenching. Some samples for the magnetic and calorimetrix measurements were

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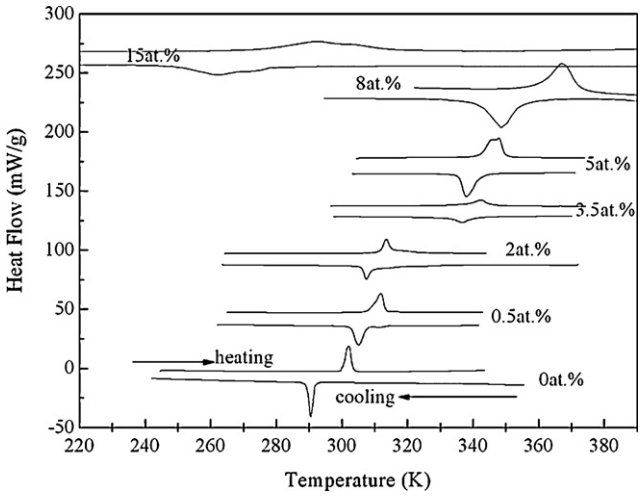

Fig. 1. DSC curves of solution-treated $Ni_{53}Mn_{23.5}Ga_{23.5-x}Ti_x$ (x = 0, 0.5, 2, 3.5, 5, 8, 15) alloys.

cut from the ingots using a wire-cutting machine perpendicular to the longitude axis.

The phase transformation temperatures were determined by PerkinElmer Diamond differential scanning calorimeters (DSC) with typical cooling/heating rate of 5 K/min. The transformation temperatures of the specimens from the different parts of rod have been examined and the difference was less than 2 K. The Curie temperature of the alloys was measured by AC susceptibility. Microstructures of the alloys were studied by MX2600FE scanning electron microscopy equipped with an X-ray energy dispersive spectroscopy (EDS) analysis system. Samples for transmission electron microscopy (TEM) were electrochemically polished in a solution of 10% perchloric acid and 90% ethanol at 253 K and undertaken with a Philips CM-12 electron microscope operated at 120 kV.

3. Results and discussion

The transformation behavior for the $Ni_{53}Mn_{23.5}Ga_{23.5-x}Ti_x$ (x = 0, 0.5, 2, 3.5, 5, 8, 15) alloys are shown in Fig. 1. The DSC curves were characterized by one endothermic and exothermic peak during the heating and cooling process, respectively, corresponding to one-step martensitic transformation. This means that the addition of Ti does not change the transformation path.

Table 1
The EDS results of aged $Ni_{53}Mn_{23.5}Ga_{8.5}Ti_{15}$ alloy.

	Ti (at.%)	Ni (at.%)	Mn (at.%)	Ga (at.%)
Matrix	9.4	53.1	28.6	8.9
Second phase	16.6	71.9	7.0	4.5

Fig. 2 illustrates the secondary electron image of solution-treated $Ni_{53}Mn_{23.5}Ga_{23.5-x}Ti_x$ (x = 0, 0.5, 2, 3.5, 5, 8, 15) alloys. As shown in Fig. 2(a)–(c), straight plate twinned martensite variants are clearly observed at room temperature, whereas the $Ni_{53}Mn_{23.5}Ga_{8.5}Ti_{15}$ specimens contain second phase, as shown in Fig. 2(d), respectively. Fig. 2(e) shows the TEM image of $Ni_{53}Mn_{23.5}Ga_{8.5}Ti_{15}$ alloy. It can be seen that the second particles are distributed in the matrix. According to the EDS results, the Ti/Ni atomic ratio of the Ti-rich phase is approximately 3, yet there are a small number of dissolved Mn and Ga atoms. Moreover, the precipitates are identified as Ni_3Ti type by previous results [18] (Table 1).

Fig. 3 exhibits the effect of Ti content on the martensitic transformation temperature, the transformation hysteresis, Curie temperature and the electronic concentration in $Ni_{53}Mn_{23.5}Ga_{23.5-x}Ti_x$ alloys. It is seen that martensitic transformation temperatures increased with increasing the amount of Ti (x) up to 8 at.%, and then decreased with the further addition. Moreover, it is obvious that the increase of martensitic transformation temperature is accompanied by the increase of e/a while the content of Ti is blow 8 at.%. This is in accordance with the previous results in Ref. [19–21]. The anomaly decrease of the martensitic transformation temperatures in present alloys with 15 at.% Ti may be rationalized as follows. Based on SEM observations (as shown in Fig. 2), when the content of Ti is higher than 8 at.%, the excess Ti element reacted with Ni and formed the Ni-rich Ni_3Ti phase dispersed in the matrix. The depletion of Ni is believed to be responsible for the decrease of martensitic transformation in $Ni_{53}Mn_{23.5}Ga_{8.5}Ti_{15}$ alloy. It is generally accepted that the electronic concentration (e/a) and the atom size factor are dominant factors influencing the martensitic transformation temperatures of Heusler-type Ni–Mn–Ga ferromagnetic shape memory alloy [19–21]. The number of valence electrons is 10 for Ni, 7 for Mn, 3 for Ga and 4 for Ti, respectively. The valence electron concentrations of $Ni_{53}Mn_{23.5}Ga_{23.5-x}Ti_x$ (x = 0, 0.5, 2, 3.5, 5, 8, 15) alloy increases from 7.35 to 7.8 with the increase of Ti

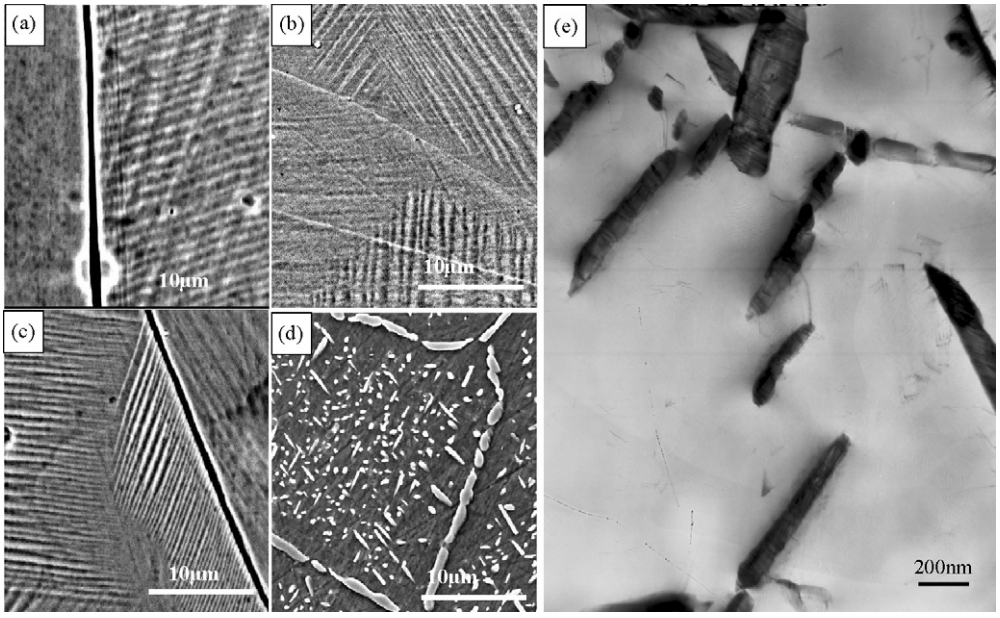

Fig. 2. Microstructures of the solution-treated $Ni_{53}Mn_{23.5}Ga_{23.5-x}Ti_x$ alloys. (a) x = 0; (b) x = 5; (c) x = 8; (d) x = 15; (e) bright field image of solution-treated $Ni_{53}Mn_{23.5}Ga_{8.5}Ti1_5$.

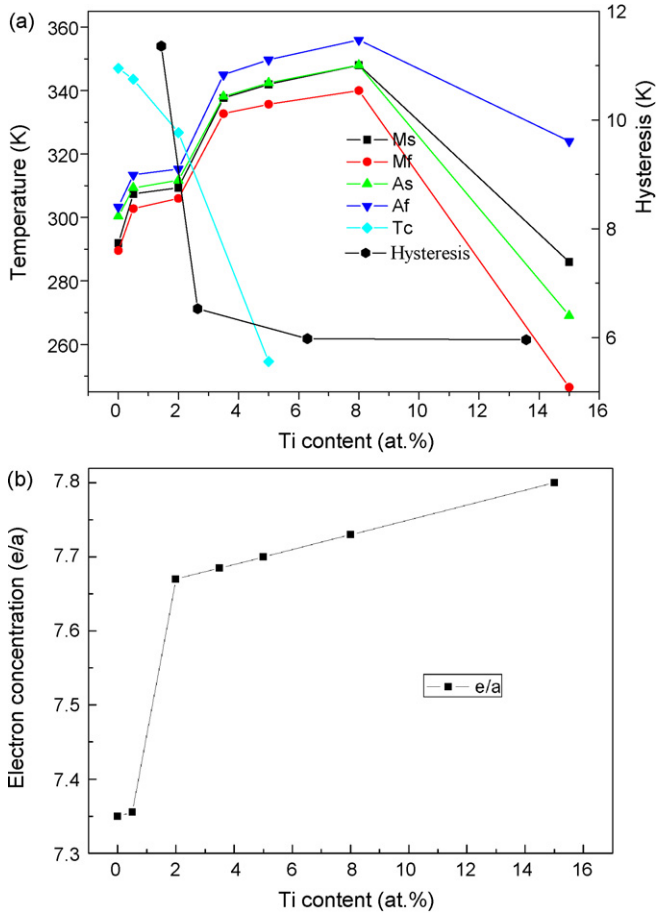

Fig. 3. (a) Ti content dependence of the transformation hysteresis, the transformation temperatures, M_s, M_f, A_s and A_f, and the Curie temperature, T_c of the $Ni_{53}Mn_{23.5}Ga_{23.5-x}Ti_x$ alloys. (b) Effect of Ti content on electron concentration (e/a) of $Ni_{53}Mn_{23.5}Ga_{23.5-x}Ti_x$ alloys.

content. Fig. 3(b) illustrated the relationship between the Ti content and e/a ratio for $Ni_{53}Mn_{23.5}Ga_{23.5-x}Ti_x$ alloys. It is seen that valence electron concentrations increased with increasing the content of Ti. It is seen that the thermal hysteresis decreased with increasing the content of Ti in Fig. 3(a). Wang et al. [22] reported that the thermal hysteresis in the Ni–Mn–Ga ternary shape memory alloys originates from the friction of phase boundary motion. Thus, it is speculated that the Ti-doping decrease the friction losses of phase boundary motion in the $Ni_{53}Mn_{23.5}Ga_{23.5-x}Ti_x$ alloys and improve the mobility of the boundary, which is helpful to obtain the magnetic field-induced-strain under the low magnetic field.

The Curie temperature decreased almost linearly as the Ti content increased. It is seen that martensitic transformation temperatures gradually increase while the Curie temperature decreases linearly with increasing the Ti content up to 8 at.%. These results lead to the coupling of magnetic and structural transitions in the composition for Ti = 2.5 at.%. It is interesting to note that the curves can be distinguished into three regions with increasing Ti content up to 8 at.%. When the content of Ti less than 2.5 at.%, structural transition temperatures are lower than the magnetic transition temperatures and the alloys show the same transition sequence. During cooling, the alloys first transit from paramagnetic austenite to ferromagnetic austenite at Curie temperature, and then to ferromagnetic martensite at martensitic transformation temperature. The second region is characterized by a coupled magnetostructural transition when the content of Ti is about 2.5 at.%. It implies the paramagnetic austenite phase transforms directly into the ferromagnetic martensitic. Finally, the third region (2.5 at.% < x < 8 at.%) is characterized by a high martensitic transformation temperature and a low curie temperature. In this region, the martensitic transformation takes place prior to the magnetic transition, and during cooling, the transition takes the following sequence: paramagnetic parent phase → paramagnetic martensite → ferromagnetic martensite.

The magnetic behavior in M–H curves of $Ni_{53}Mn_{23.5}Ga_{23.5-x}Ti_x$ alloys was measured to evaluate the saturation magnetization, since its large values is recognized as favorable features to the MFIS [23]. The magnetization curves of solution-treated $Ni_{53}Mn_{23.5}Ga_{23.5-x}Ti_x$ (x = 0, 0.5, 2, 3.5, 5 at.%) alloys measured at 270 K are shown in Fig. 4(a). For the two alloys with x = 0 and 0.5 at.%, the magnetization curves quickly increased until saturation (about 65 emu/g) for an applied magnetic field close to 7 KOe, exhibiting the typical characteristics of ferromagnetic materials. However, for the alloys with x > 3.5 at.%, the martensite phase does not saturate totally even at a magnetic field of 50 KOe. In these cases, the "law of approximation to saturation" was used to estimate the magnetization saturation. Fig. 4(b) shows the effect of Ti content on the magnetization saturation of the alloys. It is seen that in the range of x < 0.5 at.%, the saturation magnetization did not show obviously change. In the range of x = 0.5–5 at.%, the saturated magnetization decreased abruptly from 65 to 4.78 emu/g, which might be related with a different occupancy of Ti atoms. In the present work, the

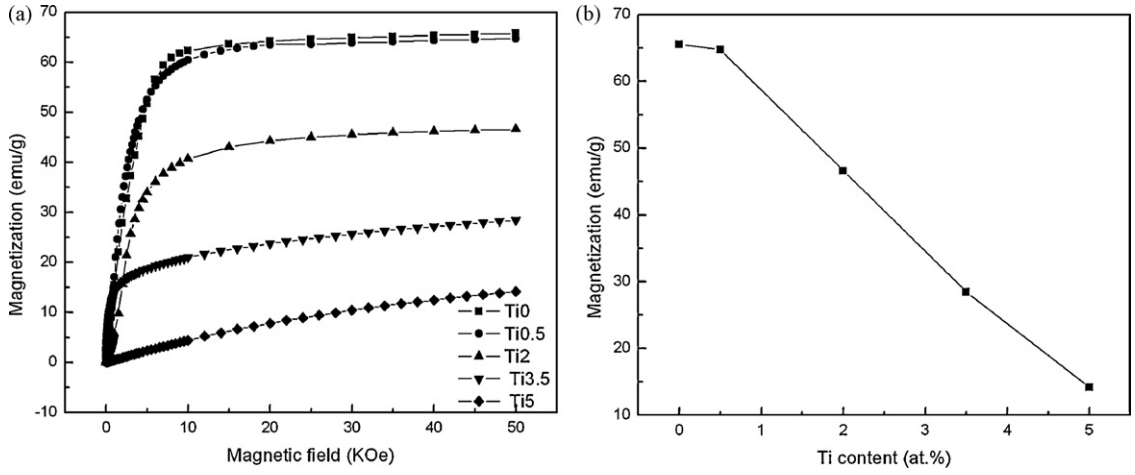

Fig. 4. (a) M–H curves of $Ni_{53}Mn_{23.5}Ga_{23.5-x}Ti_x$ (x = 0, 0.5, 2, 5) alloys at 270 K and (b) dependence of saturation magnetization on Ti content of $Ni_{53}Mn_{23.5}Ga_{23.5-x}Ti_x$ alloys at 270 K.

Ga was chemically substituted by Ti. The atomic sites and possible alteration of the ferromagnetic coupling are still unknown, which requires further study.

4. Conclusions

The effects of Ti addition on martensitic and magnetic transitions of polycrystalline $Ni_{53}Mn_{23.5}Ga_{23.5-x}Ti_x$ ferromagnetic shape memory alloys were investigated. The solubility limit of Ti in the matrix is found to be about 8 at.%. The martensitic transformation temperatures increased with increasing the amount of Ti (x) up to 8 at.%, and then decreased with the further addition. While the Curie temperature almost remains unchanged at low-Ti content and subsequently decreases obviously. Magnetization saturation of martensitic phase decreases with increasing Ti content.

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