Journal of Alloys and Compounds 505 (2010) 389–392

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Effect of aging on magnetic properties and phase transition of $Ni_{53}Mn_{23.5}Ga_{23}Ti_{0.5}$ ferromagnetic shape memory alloy

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ARTICLE INFO

Article history:
Received 29 January 2010
Received in revised form 4 June 2010
Accepted 9 June 2010
Available online 18 June 2010

Keywords:
Magnetic shape memory alloy
Phase transformation
Aging
Magnetic properties

ABSTRACT

The effects of aging on magnetic properties and phase transformation were investigated for $Ni_{53}Mn_{23.5}Ga_{23}Ti_{0.5}$ shape memory alloy. The results show that the amount and size of Ni_3Ti particles firstly increase and then amount of second phase decreases with the increasing aging temperature. Moreover, the transformation temperatures gradually decrease; Curie temperatures slightly decrease first and reach their minimum values at 973 K then increase with the increasing aging temperature. The saturation magnetizations firstly remain almost unchanged and then slightly decrease when aging temperature is above 973 K.

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1. Introduction

Since 0.2% magnetic field-induces strain (MFIS) has been firstly found in Ni_2MnGa single crystal in 1996 [1], Ni–Mn–Ga ferromagnetic shape memory alloys (FSMAs) have received more and more attention as potential magnetic actuator and sensor materials due to their large MFIS and high response frequency [2–4]. The MFIS appears as a result of the rearrangement of twinned martensite variants and the motion of twin boundaries when the direction of spontaneous magnetization in magnetic domains in variants changes to the applied magnetic field H [5]. Some of the main influences related to a large MFIS are (1) intrinsic magnetic properties of alloys, which include the high driving magnetocrystalline anisotropy, Zeeman energies [6] and low impeding twin boundary energy [7]; (2) preparation method determining the grain size and the crystallographic texture; (3) measurement process for MFIS being sensitive to the magnitude and direction of H, especially for the oriented samples [8,9].

However, the practical applications of Ni–Mn–Ga alloys have been limited to some extent due to their extreme brittleness and low strength although they exhibit low twinning stress and high magnetic anisotropy. In order to improve the mechanical properties without sacrificing its magnetic and thermoplastic properties, the modification of Ni–Mn–Ga FSMAs by adding the fourth element is becoming a new research field. For this purpose, several rare earth elements have been added into ternary Ni–Mn–Ga alloys, such as Tb, Sm, Dy and Nd, and their effects on the phase transformation behavior, magnetic and mechanical properties have been studied [10–13]. Recently, we have found that by adding Ti in a polycrystalline $Ni_{53}Mn_{23.5}Ga_{23.5}$ alloy, a significant improvement in the compress strength and ductility is achieved by the proper aging treatments [14–16]. However, the effect of aging on magnetic properties has not been reported. In this work, the effect of aging on the martensitic transformation and magnetic properties of polycrystalline $Ni_{53}Mn_{23.5}Ga_{23}Ti_{0.5}$ alloy were studied. The results show that Ti addition can significantly affect the magnetic properties and martensitic transformation temperature of Ni–Mn–Ga alloy by the appropriate aging process.

2. Experimental

The alloy with a nominal composition of $Ni_{53}Mn_{23.5}Ga_{23}Ti_{0.5}$ (at.%) was prepared using high purity elements to melt four times in an arc-melting furnace under an argon atmosphere. The master rod was sealed in a quartz tube under a vacuum, then annealed at 1273 K for 5 h, and quenched into icy water for homogeneity. Aging treatments were performed for 3 h at temperatures of 773–1173 K, respectively, and consequently quenched into water. Moreover, the results show that by adding Ti to $Ni_{53}Mn_{23.5}Ga_{23.5}$ alloy, a significant improvement in the mechanical properties of the alloy is achieved [14]. The phase transformation temperatures are detected by PerkinElmer diamond differential scanning calorimetry (DSC) with the heating and cooling rate of 20 K/min. Microstructures of the alloy were observed by MX2600FE scanning electron microscopy (SEM) equipped with an X-ray energy dispersive spectroscopy (EDS) analysis system. The Curie temperatures of the alloys were measured by AC susceptibility. Saturation magnetization measurements were taken using the physical property measurement system (Quantum Design) in an applied field up to 5 T.

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0925-8388/$ – see front matter. Published by Elsevier B.V.
doi:10.1016/j.jallcom.2010.06.054

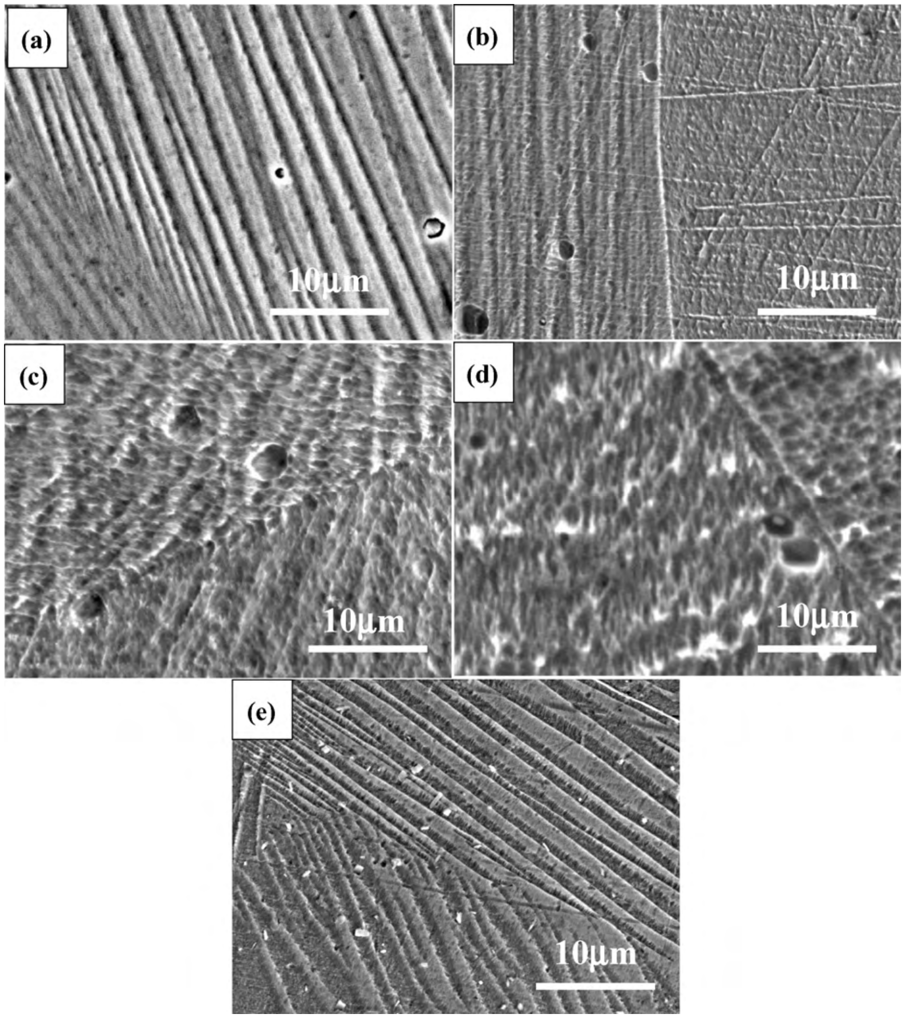

Fig. 1. Effect of aging temperature on microstructure of $Ni_{53}Mn_{23.5}Ga_{23}Ti_{0.5}$ alloy. (a) T = 773 K; (b) T = 873 K; (c) T = 973 K; (d) T = 1073 K; (e) T = 1173 K.

3. Results and discussion

Fig. 1 illustrates the secondary electron images of different aging-treated $Ni_{53}Mn_{23.5}Ga_{23}Ti_{0.5}$ samples. As shown in Fig. 1(a), the typical unitary martensitic phase morphology was observed at room temperature in the $Ni_{53}Mn_{23.5}Ga_{23}Ti_{0.5}$ alloy aged at 773 K. Straight plate twinned martensitic variants are clearly observed at room temperature, whereas other contains a mount of Ni_3Ti precipitate particles, which is in accordance with the results of our previous study [14]. Some water vapor like bubbles can also be observed, resulting from annealing or mechanical polishing process. With increasing aging temperature, the microstructure changes from martensite to a mixture of martensite and Ni_3Ti precipitates, as shown in Fig. 1(b)–(e). It is found that the amount and size of the second phase increase firstly and then amount of the Ni_3Ti precipitate particles decreases with the increasing aging temperature.

Fig. 2 summarizes the effect of aging temperature on transformation temperatures in the aged $Ni_{53}Mn_{23.5}Ga_{23}Ti_{0.5}$ alloy. It can be seen that the martensite transformation temperatures gradually decrease first and then increase with the increasing aging temperature, reaching their minimum values at the aging temperature of 973 K. The typical DSC curve of aged alloy at 873 K for 3 h exhibits an exothermic peak on cooling and an endothermic peak during heating, corresponding to the martensitic and reverse transformations, respectively, as shown in the inset of Fig. 2. The reason for the change of transformation temperatures can be attributed to the introduction of Ni_3Ti precipitate during aging process. In addition, the change of internal stress and atomic rearrangements also affect the transformation temperature

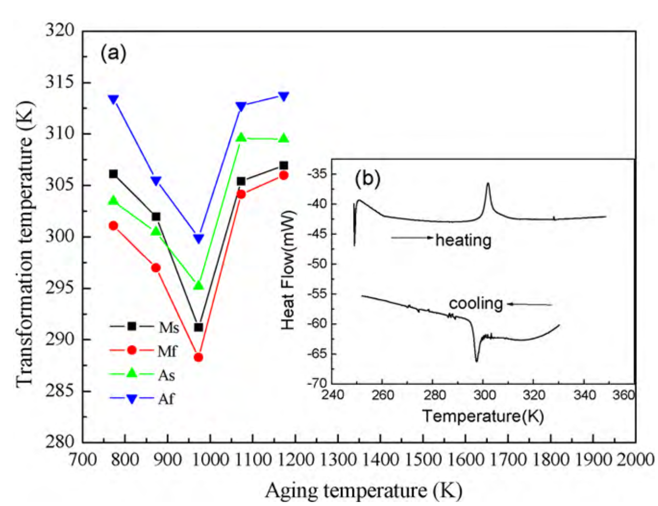

Fig. 2. Effect of aging temperature on transformation temperatures of $Ni_{53}Mn_{23.5}Ga_{23}Ti_{0.5}$ alloy.

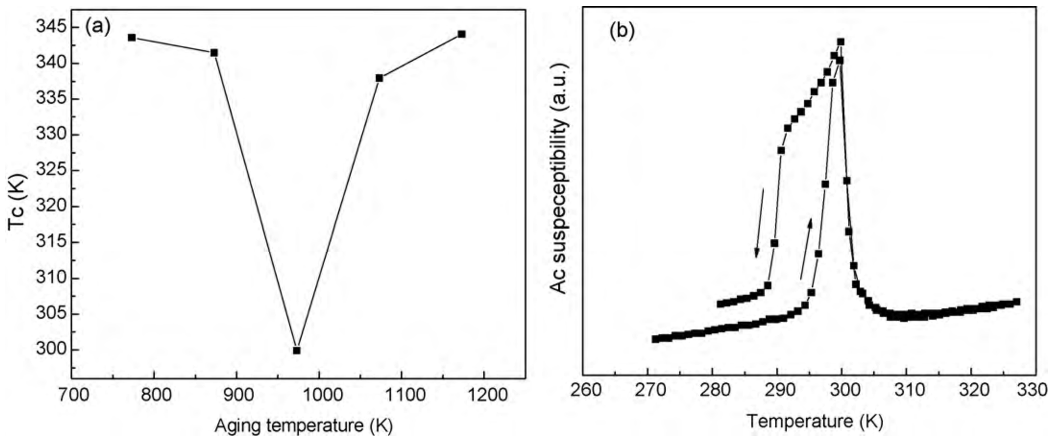

Fig. 3. (a) Effect of aging temperature on the T_c of the $Ni_{53}Mn_{23.5}Ga_{23}Ti_{0.5}$ alloy; (b) aging temperature dependence of ac susceptibility of $Ni_{53}Mn_{23.5}Ga_{23}Ti_{0.5}$ alloy with T = 973 K during the cooling and heating process.

[17]. It is well known that the martensitic transformation temperatures of Ni–Mn–Ga alloys are sensitive to the composition. The decrease in Ni content causes the decrease in the martensitic transformation temperatures [18]. The decrease in the transformation temperatures can be attributed to the precipitation of Ni-rich Ni_3Ti precipitates which reduced the Ni content of the matrix, as shown in Fig. 2. However, the re-dissolving of Ni_3Ti precipitates leads to the increase of the Ni content in the matrix when the aging temperature is above 973 K. So, the martensite transformation temperatures of $Ni_{53}Mn_{23.5}Ga_{23}Ti_{0.5}$ alloy gradually increase with the increasing aging temperature above 973 K. Therefore, in the present case, the change of transformation temperatures is attributed to the element diffusion of Ni between the matrix and the Ni_3Ti phase.

The Curie temperatures firstly decrease slightly and then rapidly, and finally increase with the increase of aging temperature, reaching the minimum value at 973 K, as shown in Fig. 3(a). It can be seen from Fig. 3(a) that increasing aging temperature has an affect on Curie temperature. In addition, a sharp peak appears in the curves of AC susceptibility during the heating and cooling process, showing that the magnetic transition is near the reverse martensitic transformation finish temperature when aging temperature is 973 K, as shown in Fig. 3(b). This phenomenon is similar to the coupling of structural and magnetic transitions in ternary Ni–Mn–Ga alloys [19,20]. Recently, a larger magnetic entropy change (20 J kg^{-1} K^{-1}) has been observed in $Ni_{2.18}Mn_{0.82}Ga$ alloy with the concurrence of magnetic and structural phase transitions under a magnetic field of 1.8 T [21]. Therefore, coupling of the martensitic and magnetic transitions in aged $Ni_{53}Mn_{23.5}Ga_{23}Ti_{0.5}$ alloy can be expected to cause large magnetocaloric effect (MCE). Thus it is reasonable to believe that the content of Ni in the matrix is changed by the existence of the Ni-rich second phase when the alloys are subjected to aging treatment, and results in the variation of the composition of the matrix. As is well known, the chemical composition of material significantly affects the Curie temperatures of Heusler-type Ni–Mn–Ga ferromagnetic shape memory alloy. However, our experimental data is not sufficient to make an unambiguous conclusion about the mechanism responsible for the change of T_c by aging treatment, and further investigation is still needed. Aging at 973 K gives maximal change in martensite transformation points and Curie temperature compeers with quenched from 1273 K sample. The composition of matrix and the precipitate phase corresponds to the maximal volume fraction of Ni_3Ti particles, as shown in Table 1.

Fig. 4 shows the saturation magnetization curves of the $Ni_{53}Mn_{23.5}Ga_{23}Ti_{0.5}$ alloy measured at various aging temperature for 3 h in the magnetic field up to 5 T. It is clear that, all alloys reached saturation magnetization in fields up to 5 T. The saturation magnetization firstly remains unchanged and then slightly decreases when aging temperature is above 973 K.

Table 1
The EDS results of aged at 973 K $Ni_{53}Mn_{23.5}Ga_{23}Ti_{0.5}$ alloy.

	Ti (at.%)	Ni (at.%)	Mn (at.%)	Ga (at.%)
Matrix	0.4	53.2	25	21.4
Second phase	16.4	71.4	7.6	4.6

In aged Ni–Mn–Ga–Ti alloy, The Ni_3Ti precipitates and the matrix have a certain coherent relationship. With increasing aging temperature, the size of the precipitates increases and such a strict relationship between the precipitate phase and matrix remains unchanged, leading to rotation of local magnetization vector under coherent strain field. At the same time, the precipitation of Ni_3Ti phase leads to a continual decrease in Ni content in the matrix, resulting in partial Mn atoms antiferromagnetically couple with the neighboring Mn atoms. Therefore, the overall Mn–Mn exchange interaction is weakened, which may result in the decrease in the saturation magnetization. In the Ni–Mn–Ga alloy, the magnetic

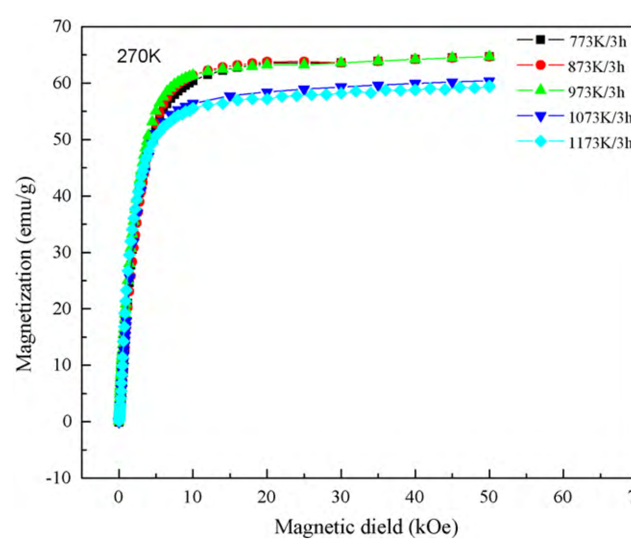

Fig. 4. *M–H* curves of $Ni_{53}Mn_{23.5}Ga_{23}Ti_{0.5}$ alloy aged at different temperatures for 3 h.

coupling of Mn–Mn has been completed through itinerant electron of Ni and Ga. During aging treatment process, the decrease in the Ni content in the matrix causes the decrease of the conduction electron-reduced of pairs of Mn atoms, weakening the exchange effect of Mn–Mn atoms, resulting in the decrease in the saturation magnetization.

When the aging temperature is above 973 K, the re-dissolution of Ni_3Ti precipitates leads to the volume fraction of second phase so that Ni content increases in the matrix. In addition, the increase in the precipitate size hampers the rotation of local magnetization vector, increasing the resistance of rotation of magnetic domain. So that extrapolation that the decrease of saturation magnetization by the two together.

4. Conclusions

Aging temperatures significantly modify the morphology, martensitic transformation temperatures, Curie temperatures and saturation magnetization in the $Ni_{53}Mn_{23.5}Ga_{23}Ti_{0.5}$ alloys. The main conclusions are as follows,

(1) The amount and size of the second phase increase at first and then amount of the Ni_3Ti precipitate particles decreases with increasing aging temperature, reaching the maximum amount at 973 K.
(2) The martensite transformation temperatures gradually decrease at first and then increase with increasing aging temperature, reaching their minimum values when aging temperature is 973 K.
(3) The Curie temperature firstly decreases and then increases with increasing aging temperature, reaching the minimum value at 973 K.
(4) The saturation magnetization almost keeps unchanged firstly and then slightly decreases when aging temperature is above 973 K.

Acknowledgement

This work is supported by the National Natural Science Foundation of China (Grant Nos. 50901026, 50971052).

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