Tailoring martensitic transformation and martensite structure of NiMnIn alloy by Ga doping In

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**A R T I C L E   I N F O**

Article history:
Received 19 March 2012
Received in revised form 23 April 2012
Accepted 23 April 2012
Available online 5 May 2012

Keywords:
Metals and alloys
Martensitic transformation
Shape memory alloy

**A B S T R A C T**

The martensitic transformation and the martensite crystal structure of alloys Ni\textsubscript{x0}Mn\textsubscript{34}In\textsubscript{16−x}Ga\textsubscript{x} (x = 0, 2, 4, 6, 8, 10, 12, 14, 16) have been investigated in this study. The studied alloys, with cubic L\textsubscript{21} phase (x = 0, 2), seven-layered modulated (14 M) martensite phase (x = 4, 6, 8), and non-modulated (NM) martensite phase (x = 10, 12, 14, 16), exhibit martensitic transformation with critical temperature increasing linearly from 238 K for x = 0 to 486 K for x = 16. The linearity coefficient is estimated to be \sim 15 K per at.\% of Ga. With regards to the lattice parameters, a contracts, whereas b and c contract as the austenite phase transformed to 14 M martensite phase. While it turns to c elongates, a and b contract as austenite transformed to NM martensite phase. It is found that the unit cell volume decreases with increasing Ga content, which contributes to the increase of transformation temperature with Ga content. A maximum strain of 12% is predicted through the lattice distortion in 14 M martensite. Magnetic measurement shows the Curie temperature for martensite increases with Ga content.

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1. Introduction

The Ni–Mn–In alloys and the related doping systems have attracted much attention since the discovery of magnetic field induced reverse martensitic transformation by Kainuma et al. in 2006 [1–3]. The common property of these NiMn-based Heusler alloys is a martensitic transformation from the high-temperature ferromagnetic phase to the low-temperature antiferromagnetic-like phase. The difference in magnetization between the two phases provides the driving force for the structural transformation under the influence of the magnetic field. Thus, the reverse martensitic transformation from the antiferromagnetic-like martensite phase to the ferromagnetic austenite phase can be induced by an external field. With increasing the field strength, the transformation shifts steadily towards lower temperature. In addition to the magneto-actuation, these alloy systems also exhibit a few other interesting properties, such as the giant magnetoresistance effect [2,4] and giant inverse magnetocaloric effect [5,6], indicating them being promising as the multifunctional magnetic materials.

It has been found that the crystal structure of martensite is an important factor affecting the magnetic anisotropy and strain. The value of c/a determines the maximum magnetic-field-induced strain (MFIS). In Ni–Mn–Ga system, large MFIS has been obtained in 10 and 14 M martensite due to the small twinning stress (1–2 MPa) in these structures, while no MFIS has been observed in NM martensite phase due to the large twinning stress (~10 MPa) [7–9]. Therefore it is essential to study the martensite structure in the newly developed NiMnIn and the related doping alloy systems.

The martensite structure is closely related to the martensitic transformation temperature (T\textsubscript{M}) of the alloys [10]. It is widely accepted that T\textsubscript{M} in ferromagnetic shape memory alloy is dependent on the valence electron concentration (e/a) [11]. In Ni–Mn–X (X = Ga, In, Sn and Sb) alloys, T\textsubscript{M} increases linearly with the increase of e/a. However the slopes of the linear dependencies are different for different X species [12], being about 80 K per 0.1 e/a for X as Ga and nearly 116 K per 0.1 e/a for X as In. This gives the opportunity to tune T\textsubscript{M} effectively by substituting X element using a different X species in NiMnX alloys. In this paper, we studied the influence of isoelectron substitution at X site on the properties of martensitic transformation by replacing partial In with Ga in Ni\textsubscript{50}Mn\textsubscript{34}In\textsubscript{16−x}Ga\textsubscript{x}. The martensitic transformation and martensite structure of this alloy system are investigated.

2. Material and methods

The alloy ingots with Ni\textsubscript{50}Mn\textsubscript{34}In\textsubscript{16−x}Ga\textsubscript{x} (x = 0, 2, 4, 6, 8, 10, 12, 14, 16) nominal compositions were prepared by means of arc-melting from high purity component metals under argon atmosphere in water-cooled Cu crucibles. Homogenization was achieved by sealing the ingots under argon atmosphere in quartz ampoules and annealing at 1073 K for 48 h, followed by slow cooling with the furnace.
3. Results and discussion

Fig. 1 shows XRD spectra of the Ni50Mn34In16–Ga_x alloys measured at room temperature. Ga0 and Ga2 samples show pure austenite structures with bcc fundamental lattice reflections of (220), (400) and (422). The superstructure reflections at (111), (311) and (331) are also obvious, implying that the austenite phase is an ordered Heusler structure. By replacing In with Ga, which has a smaller atomic radius, the lattice constants of the austenitic phase become smaller. The unit cell parameters for Ga0 and Ga2 are calculated to be \( a = 0.6008 \text{ nm} \) and \( a = 0.6005 \text{ nm} \), respectively. As Ga content increased to \( x = 4 \), XRD spectrum presents a two-phase structure, showing a cubic austenite and a 14 M monoclinic martensite structure. The lattice parameters for 14 M martensite are \( a = 0.4355, b = 0.5685, \) and \( c = 3.0092 \text{ nm} \) with \( \beta = 92.84^\circ \). This modulated monoclinic structure can be converted to the orthorhombic structure according to the method shown in [13].

Converting this experimental 14 M lattice parameters to the cubic axes, we obtain \( a = 0.6269 \text{ nm}, b = 0.5966 \text{ nm} \) and \( c = 0.5685 \text{ nm} \). For \( x = 6 \) and \( x = 8 \), the XRD patterns are fully indexed to the 14 M martensite with monoclinic martensite, indicating pure martensite at room temperature for both Ga6 and Ga8 samples. Further increasing the Ga to \( x = 10 \), the sample shows martensite phase with a non-modulated tetragonal L10 structure. The lattice parameters of the martensite are determined to be \( a = b = 0.5488 \text{ nm} \) and \( c = 0.6728 \text{ nm} \). As Ga content \( x \) is higher than 10, the samples keep a L10 structure. From the results presented above, it can be seen that the martensite structure changes as the Ga concentration is increased. The crystal structure at room temperature varies from L21 to 14 M, and then to L10, as Ga content \( x \) increases from 0 to 16.

The crystal structure and lattice parameters for different Ga contents are summarized in Table 1. The corresponding \( c/a \) ratios and the unit cell volume are calculated. The unit cell volume is calculated using the cubic, orthorhombic and tetragonal lattice parameters obtained from XRD.

Fig. 2 shows the lattice parameters as a function of Ga content \( x \). It is seen that the transformation from the L21 cubic austenite to the orthorhombic martensite is realized by contractions in the \( b \) and \( c \)-directions, resulting in an expansion in the corresponding \( a \) direction. As the transformation is from L21 \( \rightarrow \) L10 martensite, the lattice constants \( a \) and \( b \) contract and \( c \) elongates. The lattice ratio changes from \( c/a < 1 \) to \( c/a > 1 \) as the martensite structure transforms from 14 M to L10 type. In 14 M martensite, \( c/a \) decreases as Ga content increases from 4 to 8. The theoretical maximum value of strain, \( 1 - c/a \), increases with Ga content. Using the data in Table 1, a maximum strain of 12% is predicted for Ga8 sample, which is larger than the strain achieved in NiMnGa alloy with 14 M martensite structure.[8] A definitive identification of the strain value can only be achieved with further experimental results in single crystal.

The lattice distortion in L10 martensite, \( c/a - 1 < 1 \), is greater than 20% and it increases with increasing Ga content. Although the value of lattice distortion is large, it is hard to achieve large MFIS or strain in NM since the twinning stress in NM is much larger than that in 14 M martensite [9].

Fig. 3 presents DSC curves for the Ni50Mn34In16–Ga_x alloys. All samples exhibited a single reversible austenite \( \leftrightarrow \) martensite transformation. It is seen that the martensitic transformation behaviour evolved progressively with increasing Ga addition.

Valence electron concentration \( e/a \) dependence of \( T_M \) has been studied in the ternary system Ni–Mn–X (X = In, Ga, Al, Sn) [12]. It was shown that in the NiMnX system, \( T_M \) increases linearly with \( e/a \), but the slope is different for different X. At the high temperature end, all the \( e/a - T_M \) dependency lines meet at the composition of Ni50Mn50 with \( e/a = 8.5 \) in the phase diagram.[12] As the slope for NiMnGa is smaller than that for NiMnSn, holding a constant \( e/a \), the NiMnGa has higher \( T_M \) than that of NiMnSn. Therefore, for the isoelectron substitution in our NiMnInGa system, the increase of the \( T_M \) with the increase of Ga substitution for In is due to the different slopes of \( e/a - T_M \) dependence in NiMnGa and NiMnIn alloy systems. The different \( e/a \) dependence on the martensitic transformation may be attributed to the size effect of the unit cells due to the different atomic volumes of Ga and In elements, as discussed below.

Fig. 4 shows the unit cell volumes of the orthorhombic and tetragonal martensite (\( V_M \)) and the cubic austenite (\( V_A \)) phases as functions of the Ga content. Also shown in the graph on y-axis are the martensitic transformation temperatures characterized by the peak temperatures for the forward transformation \( T_M \) obtained from the DSC curves. It is found that \( T_M \) increased nearly linearly with Ga content. The linearity coefficient is estimated to be \( \sim 15 \text{ K per at.% of Ga} \). The unit cell volume for both the austenite
and the martensite phase is found to decrease with increasing Ga addition, obviously related to the smaller size of Ga atoms relative to that of In. Indium has an atomic radius of 0.167 nm and Ga has an atomic radius of 0.140 nm. It is also evident that the decrease in the unit cell volume with increasing Ga content is much steeper for the case of the martensite phase relative to that of the austenite phase. Accompanying with the decrease of the unit cell volume, $T_M$ increased gradually with increasing Ga addition. It was considered the decrease of the unit cell volume is responsible for the increase of $T_M$ [14,15]. Furthermore, the transformation from the austenite to the martensite is accompanied by a volume contraction. Using the limited data to extend the $V_M$ and $V_A$ lines, it may be tentatively suggested that the transformation volume change, $\Delta V$, is expected to increase with increasing Ga content in the alloy.

Fig. 5 shows the $M$ vs. $T$ plots at 50 Oe measured upon cooling from 380 to 5 K for different Ga-doped samples. For Ga0 sample, upon cooling, the magnetization of the austenite increased rapidly through its Curie transition of paramagnetic austenite to ferromagnetic austenite at $T_{AC} \approx 311$ K, followed by a decrease in the magnetization believed to be associated with the forward structure transformation from the austenite to martensite at $T_M \approx 240$ K. As the temperature further decreases, the magnetization gradually increased at $T_{CM} \approx 210$ K due to a second magnetic transition, where

![Fig. 2. Effect of Ga addition on the lattice parameters of Ni50Mn34In16–xGa$_x$ alloys.](image)

![Fig. 3. Transformation behaviour of Ni50Mn34In16–xGa$_x$ alloys.](image)

![Fig. 4. Effect of Ga addition on the unit cell volume and transformation temperature of Ni50Mn34In16–xGa$_x$ alloys.](image)

![Fig. 5. Temperature dependences of the field cooling magnetization measured in 50 Oe.](image)
the magnetic state of the martensite becomes ferromagnetic. The magnetic behaviour of alloy Ga2 was similar to alloy Ga0, but having higher $T_{\text{Cur}}$, $T_M$, and lower $T_{\text{Cur}}^N$. For Ga4 sample, the paramagnetic austenite started transforming to ferromagnetic austenite at $\sim 300$ K, followed immediately by the martensitic transformation of the austenite at $T_M$ (291 K). The Curie temperature of the martensite ($T_{\text{Cur}}^N$) is observed at 258 K. With respect to the Ga0 sample, the doping of Ga for partial In increased $T_{\text{Cur}}$, and decreased the temperature interval between the $T_{\text{Cur}}$ and $T_M$. The Curie temperature of martensite is increased, compared with $T_{\text{Cur}}^N$, which shows little change with Ga content. $T_M$ increases relative rapid.

The Curie transition temperature is mainly determined by the ferromagnetism exchange interaction. The increasing $T_{\text{Cur}}^N$ with Ga content illustrates the exchange interaction of martensite is enhanced by Ga doping In. As a Heusler alloy, excess Mn atoms occupy the In sites in the Ni$_{50}$Mn$_{34}$In$_{16}$-Ga$_x$ alloys. In such configurations, the Mn at Mn site and Mn at In site are the second nearest neighbours. For the cubic austenite → orthorhombic martensite distortion, using the limited data to extend the lattice constants $a$, $b$ and $c$ lines in Fig. 2, it may be suggested that the contractions in the $b$ and $c$ directions and the elongation in the $a$ direction increase with the Ga content. The contraction shortened the nearest distance between the Mn–Mn atoms and the distance is $\sim 0.284$ nm ($c/2$) for Ga4 sample, which is larger than the critical distance of 0.28 nm for Mn–Mn turning from ferromagnetic to antiferromagnetic coupling [16]. Thus an improved Mn–Mn exchange interaction is obtained by the decrease of their distance, resulting in an increased $T_{\text{Cur}}^N$ with Ga content.

4. Conclusions

The crystal structure and the martensitic transformation of Ni$_{50}$Mn$_{34}$In$_{16}$-Ga$_x$ polycrystalline alloys have been investigated. Based on the experimental results that have been presented above, the following may be drawn:

1. At room temperature, Ni$_{50}$Mn$_{34}$In$_{16}$-Ga$_x$ ($x = 0, 2, 4, 6, 8, 10, 12, 14, 16$) alloys exhibit cubic L2$_1$ phase ($x = 0, 2$), 14 M martensite phase ($x = 4, 6, 8$) and NM martensite phase ($x = 10, 12, 14, 16$).
2. According to the lattice parameters, the lattice distortion increases with increasing Ga content, and a theoretical value of maximum lattice strain of 12% is obtained in 14 M martensite.
3. The critical temperature of martensitic transformation in Ni$_{50}$Mn$_{34}$In$_{16}$-Ga$_x$ alloys increases with increasing Ga content. This is attributed to substitution of Ga for In in Ni$_{50}$Mn$_{34}$In$_{16}$-Ga$_x$ system causing reduction of unit cell volume.
4. The Curie temperature of the martensite increases with Ga content due to the enhanced ferromagnetic exchange interaction between Mn–Mn atoms.

Acknowledgements

The authors wish to acknowledge the financial supports by the National Natural Science Foundation of China in Grant No. 51000101, the Fundamental Research Funds for the Central Universities (Grant No. FRF-BR-10-008A), and Research Fund for the Doctoral Program of Higher Education of China (Grant No. 20100006120001).

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