Microstructure, phase transformation and mechanical property of Nb-doped Ni–Mn–Ga alloys

B. Tian a, b, *, R. Ji a, b, Y.X. Tong a, b, L. Li a, b, Y.F. Zheng a, b, c

Abstract

This study investigated the microstructure, phase transformation and mechanical property of (Ni98.8Mn24.4Ga57.7)100−xNb x (x = 1, 3, 6, 9) alloys. The Nb1 alloy exhibited a single austenite phase at room temperature. With increasing Nb content for Nb3, Nb6 and Nb9, the alloy changed to a dual phase consisting of austenitic matrix and Nb-rich second phase with a hexagonal structure, and the amount of the second phase increased with the increase of Nb content. The martensitic transformation temperature and Curie temperature were changed and the transformation enthalpy was gradually reduced with increasing Nb content. The change of martensitic transformation temperature and Curie temperature was related to the introduction of Nb in the Ni–Mn–Ga structure that decreased valence electron concentration (e/a), increased unit cell volume and reduced magnetic exchange of the alloys. The concentration (e/a), increased unit cell volume and reduced magnetic exchange of the alloys. The transformation hysteresis and improving the mechanical behavior of the alloys.

Keywords:
A. Shape-memory alloys
B. Brittleness and ductility
B. Martensitic transformation
B. Mechanical properties
D. Microstructure

1. Introduction

Ni–Mn–Ga ferromagnetic shape memory alloys (FSMAs) exhibiting both high response frequency and large magnetic field induced strain (MFIS) [1,2] have been extensively investigated and recognized to be a promising smart material. However, the intrinsic brittleness of these alloys has been a main obstacle to hinder their further practical applications. In order to overcome this problem, doping a fourth element into the alloy has been found to be an effective way in ameliorating the workability and ductility of the alloys. Recently, Fe [3,4], Co [5], Cu [6,7], Ti [8] or rare earth [9,10] has been doped in the Ni–Mn–Ga alloys and the mechanical ductility and strength were enhanced due to the introduction of ductile second phase that strengthened the grain boundaries of matrix and hindered cracks propagation during deformation.

Nb has been usually added in the Ti–Ni based SMAs to adjust the martensitic transformation temperature and increase the transformation hysteresis by forming β-Nb phase and Nb-rich nanoprecipitates [11,12]. In addition, Nb has also been doped in the Ti–Ni–Hf alloy to improve the workability of this alloy by introducing the ductile β-Nb phase [13]. Furthermore, for the Ti–Ni–Nb alloy, after a severe plastic deformation (forging and wire-drawing), the sphere-shape β-Nb phase was converted to nanowires, which greatly enhanced the mechanical strength and ductility of the Ti–Ni matrix through well matching the elastic deformation of the Nb nanowires and the poseudoelasticity of the Ti–Ni matrix [14]. Therefore, doping Nb in the Ti–Ni based SMAs is effective in tailoring the phase transformation temperature, hysteresis and improving the mechanical behavior of the alloys. Recently, Nb has also been added in the Mn–Ni–Sn and Ni–Co–Mn–Sn FSMAs to adjust the martensitic transformation temperature and magnetocaloric effect [15,16]. However, up to now, little information is available in the literature on doping Nb in the Ni–Mn–Ga alloys and the effect of Nb on the phase transformation and mechanical property of Ni–Mn–Ga alloy still remains unknown. Therefore, in this article, Nb is added in the
Ni–Mn–Ga alloys and the microstructure, phase transformation and mechanical property of the alloys are systematically investigated as a function of Nb content.

2. Experimental details

The (Ni_{49.8}Mn_{28.5}Ga_{21.7})_{100-x}Nb_x (x = 1, 3, 6, 9) polycrystalline ingots were prepared by arc-melting high purity elements of Ni, Mn, Ga and Nb under an argon atmosphere. The as-cast ingots were sealed in vacuum quartz tubes and annealed at 1173 K for 12 h followed by water-quenching for homogenization. For simplicity, the alloys for x = 1, 3, 6, and 9 were represented by Nb1, Nb3, Nb6 and Nb9, respectively. In addition, the pure Ni_{49.8}Mn_{28.5}Ga_{21.7} alloy without Nb was denoted as Nb0 for comparison. The microstructure was observed using FEI Quanta200 scanning electron microscope (SEM) equipped with energy dispersive spectrometry (EDS) analyzer. X-ray diffraction (XRD) was carried out for phase identification at room temperature using a Panalytical X-pert PRO diffractometer with Cu Kα radiation. Phase transformation behavior of the samples was measured using a Perkin–Elmer Diamond differential scanning calorimeter (DSC) with a heating/cooling rate of 20 °C/min. The compression tests were performed at room temperature using an Instron universal testing machine (Model 3365). The martensitic transformation and Curie transition were also tested by measuring the temperature dependence of low field ac-susceptibility in a frequency of 111.7 Hz and field of ~1 Oe using a susceptibility measurement apparatus manufactured by Institute of Physics, Chinese Academy of Sciences.

3. Results and discussion

Fig. 1(a) shows SEM image of the Nb1 alloy. The alloy exhibits a single phase and large columnar grains with a size of >500 μm. It is noted that some cracks along the grain boundaries can be found, which should result from the sample grinding and polishing processes. This indicates that the Nb1 alloy presents a susceptible intergranular fracture, which is similar to that of the Nb0 alloy [17]. With increasing Nb content, it is seen that the alloy has changed from single phase to a dual phase. For Nb3, the alloy is composed of a dark matrix and a light dot or stick-shape second phase, as shown in Fig. 1(b). For Nb6, the amount of second phase has been increased (Fig. 1(c)) as compared with that of the Nb3 alloy. With continuously increasing Nb content, for Nb9 alloy, the second phase has greatly grown up and formed a large dendritic phase, as seen in Fig. 1(d). The microstructure evolution for the present Nb-doped alloy is similar to that of Cu, Co or Zr-doped Ni–Mn–Ga alloys [5,6,18]. It is noted that there is no apparent cracks associated with the intergranular fractures observed for the dual phase Nb3, Nb6 and Nb9 alloys, as compared with the single phase Nb1 alloy, which implies that the tendency of intergranular fracture has been reduced after the formation of second phase.

Fig. 2(a) shows the EDS result of Nb1 alloy. It is seen that the single phase alloy is composed of Ni, Mn, Ga and Nb elements, meaning that the Nb has mostly entered into the Ni–Mn–Ga structure. Fig. 2(b) and (c) presents the EDS results of matrix and second phase of the Nb3 alloy, respectively. It can be seen that the matrix contains few amount of Nb that seems to be comparable to that in the single phase Nb1 alloy. In contrast, the second phase contains a much higher amount of Nb, indicating that the second phase is a Nb-rich phase. For the Nb6 and Nb9 dual phase alloys, they have the similar EDS results for the matrix and second phase to those of the Nb3 alloy (which are not shown in the figure). This is consistent with the results in Cu, Ti or Zr-doped dual phase alloys, in which the second phase is Cu, Ti or Zr-concentrated [6,8,18], respectively. To further clarify the composition evolution of the Nb-rich phase with increasing Nb content, the compositions of the
matrix and second phase determined from the EDS tests for the dual phase alloys are listed in Table 1. It can be seen that the overall compositions for the matrix are almost similar, indicating the Nb content has saturated in the matrix after formation of the second phase. For the Nb-rich second phases, they also present a close composition for the three dual phase alloys, which means that the Nb-rich second phase keeps an almost similar composition once it was formed, irrespective of changing the Nb content.

Fig. 3(a) shows DSC curves of the alloys. It is seen that all the alloys exhibit a single-step martensitic transformation, similar to that of the Nb0 alloy [19]. M_p and A_p stand for the martensitic transformation peak temperature and austenitic transformation peak temperature, respectively, as marked on the curve of Nb1 alloy. The transformation enthalpy (\(\Delta H\)) is determined by the area of the transformation peak, which is also indicated on the curve. The transformation temperatures (M_p and A_p), transformation hysteresis (A_p–M_p) and transformation enthalpies \(\Delta H_{A-M}\) of austenite → martensite and \(\Delta H_{M-A}\) of martensite → austenite for the alloys are derived from the DSC curves and listed in Table 2. For comparison, these values associated with martensitic transformation for the Nb0 alloy [19] are also added in the table. It is found that the M_p was continuously decreased with increasing Nb from Nb0 to Nb3 and then slightly increased with increasing Nb to Nb6 and Nb9. The A_p presents a similar changing trend to the M_p. For the transformation hysteresis, the Nb1, Nb3 and Nb6 exhibit a similar value of 13–14 °C, which is higher than that of the Nb0 alloy (~8 °C). However, with further increasing Nb to Nb9, the hysteresis is reduced to be at ~7 °C. Both \(\Delta H_{A-M}\) and \(\Delta H_{M-A}\) are gradually reduced with increasing the Nb content. The martensitic transformation temperatures and hysteresis closely depend on the alloy composition and the transformation enthalpy should be related to the transformation volume of the alloy. The increase of valence electron concentration (e/a) associated with composition often increases the martensitic transformation temperatures of Ni–Mn–Ga alloys [20]. The number of valence electrons for Ni, Mn, Ga and Nb is 10, 7, 3 and 5, respectively. According to the composition of Nb0, Nb1 and the matrix of dual phase Nb3, Nb6 and Nb9 alloys, it can be calculated that the e/a of Nb0, Nb1, the matrix of Nb3, Nb6 and Nb9 is 7.63, 7.59, 7.47, 7.46 and 7.43, respectively.

### Table 1
Composition of matrix and second phase determined from EDS for the dual phase alloys.

<table>
<thead>
<tr>
<th>Dual phase alloys</th>
<th>Matrix</th>
<th>Second phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Mn</td>
</tr>
<tr>
<td>(Ni49.8Mn28.5Ga21.7)97Nb3</td>
<td>47.5</td>
<td>28.0</td>
</tr>
<tr>
<td>(Ni49.8Mn28.5Ga21.7)94Nb6</td>
<td>47.2</td>
<td>28.1</td>
</tr>
<tr>
<td>(Ni49.8Mn28.5Ga21.7)91Nb9</td>
<td>47.0</td>
<td>27.8</td>
</tr>
</tbody>
</table>

Fig. 2. EDS results of (a) Nb1, (b) austenitic matrix and (c) second phase of Nb3 alloys.
presenting a gradual decrease trend. Therefore, the decrease of martensitic transformation temperatures should be related to the decrease of e/a of the alloys. In addition, size factor is another parameter in influencing the martensitic transformation temperature, that is, the increase of unit cell volume decreases martensitic transformation temperature [20]. The atomic radius for Ni, Mn, Ga, and Nb is 0.135, 0.140, 0.130, and 0.145 nm, respectively. It is apparent that the introduction of Nb in the Ni–Mn–Ga structure increases the unit cell volume and thus decreases the martensitic transformation temperature. Therefore, the overall decrease trend of martensitic transformation temperatures with increasing Nb content should be attributed to the combined effect of the decrease of e/a and the increase of unit cell volume. The reduction of transformation enthalpy is mainly attributed to the formation and increase of the Nb-rich second phase with increasing Nb content that decreased the matrix volume taking part in the martensitic transformation. This is similar to the effect of Zr-rich second phase on the phase transformation behavior of the Zr-doped Ni–Mn–Ga alloys [18].

The martensitic transformation and Curie transition of the alloys are also characterized by susceptibility measurements, as shown in Fig. 3(b). It is found that all the alloys demonstrate a similar transformation character to that of the Nb0 alloy [17].

Table 2
Transformation peak temperatures, hysteresis, enthalpy and Curie temperatures for different samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>( T_m ) (°C)</th>
<th>( A_p ) (°C)</th>
<th>Hysteresis (°C) ((A_p - M_p))</th>
<th>( \Delta H_{M,A} ) (J/g)</th>
<th>( \Delta H_{M,A} ) (J/g)</th>
<th>( T_c ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((N_{49.8}M_{28.5}G_{21.7})<em>{100}N</em>{0})</td>
<td>25.56</td>
<td>33.96</td>
<td>8.40</td>
<td>-4.98</td>
<td>4.92</td>
<td>90.0</td>
</tr>
<tr>
<td>((N_{49.8}M_{28.5}G_{21.7})<em>{99}N</em>{1})</td>
<td>-34.60</td>
<td>-21.43</td>
<td>13.17</td>
<td>-2.86</td>
<td>3.17</td>
<td>80.0</td>
</tr>
<tr>
<td>((N_{49.8}M_{28.5}G_{21.7})<em>{97}N</em>{3})</td>
<td>-57.79</td>
<td>-43.35</td>
<td>14.44</td>
<td>-2.45</td>
<td>2.26</td>
<td>67.9</td>
</tr>
<tr>
<td>((N_{49.8}M_{28.5}G_{21.7})<em>{94}N</em>{6})</td>
<td>-55.81</td>
<td>-42.32</td>
<td>13.49</td>
<td>-2.10</td>
<td>2.03</td>
<td>67.9</td>
</tr>
<tr>
<td>((N_{49.8}M_{28.5}G_{21.7})<em>{91}N</em>{9})</td>
<td>-43.25</td>
<td>-36.36</td>
<td>6.89</td>
<td>-1.75</td>
<td>1.78</td>
<td>67.1</td>
</tr>
</tbody>
</table>

Fig. 4. XRD patterns of Nb1, Nb3, Nb6 and Nb9 alloys.

Fig. 5. Compressive stress–strain curves of Nb0, Nb1, Nb3, Nb6 and Nb9 alloys.
susceptibility changes with a wide hysteresis at the temperature of $<0\,\text{°C}$ corresponds to the martensite $\leftrightarrow$ austenite transformation. The abrupt susceptibility change with a negligible hysteresis at the temperature of $>60\,\text{°C}$ stands for the austenitic Curie transition.

The Curie transition of second phase observed in the Zr-doped Ni–Mn–Ga alloys [21] is not detected in the present Nb-doped Ni–Mn–Ga alloys. The martensitic transformation temperature ($T_M$) and austenitic transformation temperature ($T_A$) are indicated in Fig. 6.

Fig. 6. Fracture surfaces of (a) and (b) Nb1, (c) and (d) Nb3, (e) and (f) Nb6 and (g) and (h) Nb9 alloys.
on the curve of Nb1 alloy, which are determined at the middle point of the transformation curve that corresponds to the transformation peak temperatures \( M_p \) and \( A_p \) in DSC curves, respectively. The austenitic Curie transition temperature (TC) for the Nb1 alloy is also indicated on the curve. It is seen that \( T_{A1} \) and \( T_{A2} \) present a similar changing trend to the results obtained in the DSC measurements in Fig. 3(a), that is, firstly continuously decreased with increasing Nb from Nb0 to Nb3 and then slightly increased from Nb3 to Nb6 and Nb9. The transformation hysteresis (\( T_{A1} - T_{A2} \)) for the Nb9 is apparently narrower than that for the Nb1, Nb3 and Nb6 alloys, which is also consistent with the DSC results. The TC of all samples is determined from the susceptibility measurement curves and listed in Table 2. For comparison, the TC of Nb0 alloy [17] is also included in the table. It is noted that the TC is continuously decreased from Nb0 to Nb3 and then keeps almost constant with increasing Nb content to Nb6 and Nb9. The decrease of TC means the reduction of magnetic exchange. For Ni–Mn–Ga alloy, the magnetic moment mainly originates from Mn–Mn interactions [17]. The introduction of Nb with a large atomic size would partially change the distance between the Mn atoms and thus reduce the Mn–Mn interaction and magnetic exchange. For the dual phase Nb3, Nb6 and Nb9 alloys, it is noted that the Nb content in the matrix is very close, therefore these dual phase alloys exhibit a similar Curie temperature.

Fig. 4 shows the XRD patterns of the alloys. The Nb1 alloy is mainly indexed to be a cubic austenite phase. With increasing Nb content, except for the diffraction peaks of austenite, some other diffraction peaks appears, which should belong to the Nb-rich second phase according to the microstructure observation results. The second phase can be indexed to be a hexagonal structure with lattice constants of \( a = 0.4898 \) nm and \( c = 0.7915 \) nm. The relative intensity of diffraction peaks for the second phase increased with increasing Nb content due to the volume increase of the second phase. It should be noted that the present Nb-rich second phase exhibits a hexagonal structure that is different from the fcc structure for the Fe, Cu or Zr-rich second phase [3,6,18].

Fig. 5 shows the compressive stress–strain curves of the alloys from Nb0 to Nb9. The signal \("\times\"\) on the curves indicates the complete fracture point. It is seen that all the alloys exhibit a similar deformation behavior that the compression curves are not smooth and present several serrations corresponding to stress drops before complete fracturing, which is similar to that of the Zr-doped alloys [18]. All the samples have been fractured to several pieces after complete fracturing, meaning that several cracks in different directions have formed during the compression process before final collapsing. This indicates a low ductility of all the alloys. Each serration on the curve corresponds to occurrence of one crack. The final fracture strength at \("\times\"\) point has been slightly enhanced with increasing Nb content. The strength for the first stress drop associated with the first serration (which stands for the initial failure) has a similar trend to the final fracture strength with increasing Nb content, as indicated by the arrows. Through comparison, it is noted that the fracture strength for the present Nb-doped dual phase alloys (210–390 Mpa) is much lower than that for the Zr-doped dual phase alloys (450–670 Mpa) [18]. The mechanical test results indicate that the Nb-doping is not effective in improving the ductility of Ni–Mn–Ga alloy.

Fig. 6 presents SEM images of the fracture surfaces for the alloys. Fig. 6(a) and (b) are fracture surface of the Nb1 alloy. It is seen that the surface is mainly characterized by a mixture of flat intergranular fracture and rough transgranular fracture characters, being consistent with the microstructure observation result for Nb1 alloy in Fig. 1 (the intergranular fracture was observed after grinding and polishing). The Nb0 alloy has a similar fracture surface character to the Nb1 alloy, as seen in Ref. [22]. With increasing Nb content, the fracture surface becomes rough gradually due to the introduction of second phase in the dual phase Nb3, Nb6 and Nb9 alloys, as shown in Fig. 6(c), (e) and (g), respectively. Meanwhile, it is noted that the matrix primarily exhibits river-like transgranular fracture and the intergranular fracture is absent. The flat intergranular fracture surface in the dual phase alloys is mainly from the second phase, as indicated in Fig. 6(d), (f) and (h) for Nb3, Nb6 and Nb9, respectively, especially for the Nb9, the flat dendritic fracture surface of the second phase can be clearly seen. The evolution of fracturing character for the present Nb-doped alloys is similar to that of the Zr-doped alloys [18], that is, the intergranular fracture dominates in the single phase alloy and the dual phase alloys exhibit a mixture of transgranular fracture of matrix and intergranular fracture of second phase. However, as mentioned in the above compression results, the fracture strength of the Nb-doped dual phase alloys is much lower than that of the Zr-doped dual phase alloys. This could be related to the different structure of the second phase in these two alloys. The Nb-rich second phase has a hexagonal structure and the Zr-rich second phase exhibits a fcc structure. Hexagonal structure phase offers a fewer slip systems than the fcc structure phase and presents a lower ductility, which is not favorable to matching deformation of the matrix and results in a higher cracking extent on the interfaces of the second phase and matrix and thus low mechanical strength and ductility of the alloys.

4. Conclusions

The microstructure, phase transformation and mechanical property of Nb-doped Ni–Mn–Ga alloys were investigated in this article. The alloy changed from a single austenitic phase to a dual phase containing austenitic matrix and Nb-rich second phase with increasing Nb content. The martensitic transformation temperature was continuously decreased with increasing Nb from Nb0 to Nb3 and then slightly increased with increasing Nb from Nb3 to Nb6 and Nb9. The Curie temperature was deceased from Nb0 to Nb3 and then keeps almost constant with increasing Nb content. The transformation enthalpy was progressively reduced with increasing Nb content from Nb0 to Nb9. The change of martensitic transformation temperature and Curie temperature with increasing Nb content was attributed to the decrease of \( e/a \) and increase of the unit cell volume of the alloys. The reduction of transformation enthalpy is mainly caused by the Nb-rich second phase that decreased the volume fraction of the matrix participating in martensitic transformation. All the alloys demonstrated a relatively low mechanical strength and ductility with a progressively fracturing character, which could be related to low ductility of the hexagonal Nb-rich second phase that was not conducive to match the deformation of the austenitic matrix.

Author agreement

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References