Microstructure and phase transformation of Ni\(_{46}\)Mn\(_{33}\)Ga\(_{17}\)Cu\(_{4-x}\)Zr\(_x\) alloys

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**Abstract**

This study investigated microstructure and phase transformation of Ni\(_{46}\)Mn\(_{33}\)Ga\(_{17}\)Cu\(_{4-x}\)Zr\(_x\) (\(x=0, 2,\) and \(4\)) alloys. The substitution of Cu by Zr changed the alloy from a single martensite to a dual phase consisting of martensitic matrix and Zr-rich second \(γ\) phase at room temperature. The volume fraction of \(γ\) phase increased with the increase of Zr content, which resulted in the change of martensitic transformation temperature and transformation enthalpy of the alloys. After aging the dual phase alloys at 400 \(^\circ\)C and 600 \(^\circ\)C for 10 h, the martensitic transformation temperature was increased and transformation enthalpy was decreased.

1. Introduction

Ni–Mn–Ga alloys have been widely investigated due to their high response frequency and large magnetic field-induced strain (MFIS) [1]. However, the brittle nature of these alloys has influenced further practical applications. In order to overcome the brittleness and meanwhile maintain the large MFIS, an approach of doping the fourth element (Fe, Ti, and Co) into the alloy has been developed. Recently, doping Cu in Ni–Mn–Ga alloy (such as Ni\(_{46}\)Mn\(_{33}\)Ga\(_{17}\)Cu\(_x\)) has been found to be effective in improving the mechanical property of the alloy. Moreover, the Cu-doped Ni–Mn–Ga alloy is also able to exhibit magnetic-field induced reverse martensitic transformation (MFIRM) after careful composition design and optimization [9,10] (the optimized composition is Ni\(_{46}\)Mn\(_{33}\)Ga\(_{17}\)Cu\(_{2}\)). However, it has been found that in our preliminary experimental study, the polycrystalline Ni\(_{46}\)Mn\(_{33}\)Ga\(_{17}\)Cu\(_{2}\) alloy is still very brittle, which could be related to the large grain size and the absence of ductile \(γ\) phase [6,7].

An addition of Zr into Cu–Al–Ni [11,12] and Cu–Zn–Al [13] shape memory alloys has been reported, which can improve the ductility by refining grain size. However, up to now, no information is available to add Zr in Ni–Mn–Ga based alloys. Therefore, in this article, Zr was used to substitute the Cu in Ni\(_{46}\)Mn\(_{33}\)Ga\(_{17}\)Cu\(_{4}\) alloy.

The microstructure and phase transformation of Ni\(_{46}\)Mn\(_{33}\)Ga\(_{17}\)Cu\(_{4-x}\)Zr\(_x\) (\(x=0, 2,\) and \(4\)) alloys were investigated and discussed.

2. Experimental details

The ingots of Ni\(_{46}\)Mn\(_{33}\)Ga\(_{17}\)Cu\(_{4-x}\)Zr\(_x\) (\(x=0, 2,\) and \(4\)) alloys were prepared by arc-melting under an argon atmosphere using high purity elements of Ni, Mn, Ga, Cu and Zr. The ingots were annealed at 1173 K for 12 h in vacuum quartz tubes for homogeneity, and then quenched into water. For simplicity, the alloys for \(x=0, 2,\) and \(4\) are denoted as Cu4, Cu2Zr2 and Zr4, respectively. Cu2Zr2 and Zr4 alloys were aged at 400 \(^\circ\)C and 600 \(^\circ\)C for 10 h in vacuum and then quenched into water. X-ray diffraction (XRD) was carried out at room temperature using a Panalytical X-pert PRO diffractometer with Cu Ka radiation. Microstructure observation was performed using an Olympus-311U optical microscope and a FEI Quanta200 scanning electron microscope (SEM) equipped with an energy dispersive spectrometry (EDS) analyzer. Phase transformation behavior was characterized using a Perkin-Elmer Diamond differential scanning calorimeter (DSC) with a heating/cooling rate of 20 \(^\circ\)C/min.

3. Results and discussion

The Cu4 alloy exhibits a martensite with a lamellar twinned substructure and a grain size ranging from 300–500 \(\mu\)m, as shown in Fig. 1(a) and (b). It has been reported that the martensite existing in such alloy system is often a 7M modulated phase with...
orthorhombic structure or T non-modulated phase with tetragonal structure [8,14]. Fig. 1(c) shows that the twinned martensite structure cannot be found in this magnification and some white dot-like second phases appeared and homogeneously distributed in the matrix, after substituting 2 at% Cu by Zr. Fig. 1(d) with high magnification shows that the second phases mainly exhibited stick and dot shapes, and some twinned martensite laths can be found in the matrix, as indicated by arrow in the figure (M stands for martensite, the dashed line is parallel to the different oriented martensite lath). With the increase of Zr content, the amount of the second phase increases, as shown in Fig. 1(e) and (f). The matrix microstructure becomes unclear in the Zr4 alloy compared with that in the Cu4 and Cu2Zr2 alloys at the same magnification due to the existence of large amount of second phases that covers the structure of matrix, as seen in Fig. 1(e). Fig. 1(f) shows that the second phases in Fig. 1(d) have grown to form a large piece of second phase with a dendrite shape and the martensite structure (as indicated by arrow) can be found in the matrix.

The EDS results of matrix and second phase of the Cu2Zr2 alloy in Fig. 1(g) and (h), respectively, indicate that the Zr element mainly concentrated in the second phase. The result for the Zr4 alloy is similar to that for the Cu2Zr2 alloy. These results indicate that the second phase is a Zr-rich phase, which is similar to the result in the dual phase Cu and Ti-doped Ni-Mn-Ga alloys in which the second phases are Cu and Ti-concentrated, respectively [5,7].

Fig. 2(a) presents the DSC curves of Cu4, Cu2Zr2 and Zr4 alloys. All the alloys demonstrate a single stage martensitic transformation with different transformation temperatures and latent heats. The martensitic transformation peak temperature \( T_{M-A} \), reverse transformation peak temperature \( T_{A-M} \) and the associated transformation enthalpy \( \Delta H \) (transformation peak area) have been determined from the DSC curves and presented in Table 1. It is seen that both \( T_{M-A} \) and \( T_{A-M} \) for the Cu2Zr2 alloy are reduced slightly compared with those of the Cu4 alloy. Whereas, with the further increase of Zr content, both \( T_{M-A} \) and \( T_{A-M} \) for the Zr4 alloy increased to temperatures that are much higher than those for the Cu4 alloy. The \( \Delta H \) has gradually reduced with the increase of Zr content. According to the EDS result, it is inferred that the change of phase transformation temperature and transformation enthalpy of the alloys should be mainly caused by the formation of Zr-rich second phase which altered composition of the martensitic matrix and decreased phase transformation volume of the matrix. Moreover, the increase of volume fraction of the second phase with

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**Fig. 1.** The optical photos of (a) Cu4, (c) Cu2Zr2 and (e) Zr4 alloys and SEM images of (b) Cu4, (d) Cu2Zr2 and (f) Zr4 alloys. EDS results of (g) matrix and (h) \( \gamma \) phase for the Cu2Zr2 alloy, the EDS tests are performed at the rectangle area indicated in (d).

**Fig. 2.** (a) DSC curves and (b) XRD patterns of the Cu4, Cu2Zr2 and Zr4 alloys.
increasing Zr content will continue shifting the composition of the matrix, resulting in a further changing of phase transformation temperature and transformation enthalpy.

Fig. 2(b) shows room temperature XRD patterns of Cu4, Cu2Zr2 and Zr4 alloys. The Cu4 alloy can be indexed to be a martensite phase with an orthorhombic structure [8]. The lattice parameters are determined to be $a=0.6430$ nm, $b=0.5821$ nm, and $c=0.5621$ nm. The Cu2Zr2 and Zr4 alloys can be indexed to be a mixture of martensite and second phase. The martensite is indexed to be a similar structure with Cu4 alloy. The second phase can be indexed to be fcc structure, namely $\gamma$ phase [3]. The lattice parameter of the present $\gamma$ phase is $a=0.6902$ nm. Therefore, the $\gamma$ phase corresponds to the Zr-rich second phase shown in the microstructure observation.

The aging treatment often influences the volume fraction of second phase and thus affects the martensitic transformation behavior of the shape memory alloys [5,15]. Fig. 3(a) and (c) show the DSC results of the Cu2Zr2 and Zr4 alloys after aging treatment at 400 °C and 600 °C, respectively. For comparison, the result of the original alloy is also included in these figures. The $T_{A-M}$, $T_{M-A}$ and $\Delta H$ are derived from the DSC curves and listed in Table 1. It can be seen that, with the increase of aging temperature, the $T_{A-M}$ and $T_{M-A}$ increase a little and the $\Delta H$ decrease remarkably for these two alloys. It has been reported that the aging can induce the further precipitation of the second phase in the dual phase alloys [5]. Therefore, the further increase of the second $\gamma$ phase content after aging may be responsible for the change of transformation temperatures and latent heats.

Fig. 3(b) and (d) show the room temperature XRD patterns for the aged samples of Cu2Zr2 and Zr4, respectively. It can be seen that the position of diffraction peaks for martensite and second $\gamma$ phase after aging has no change in comparison with those of original alloys and there is no other phase formed during aging. Therefore, the increase of transformation temperature and reduction of latent heat with increasing aging temperature should be related to the precipitation of the second $\gamma$ phase in the matrix, which supports the above DSC results.

### 4. Conclusions

The substitution of Cu by Zr in Ni$_{46}$Mn$_{33}$Ga$_{17}$Cu$_x$/Zr$_x$ ($x=0, 2,$ and 4) alloys results in the formation of Zr-rich second $\gamma$ phase. The volume fraction of $\gamma$ phase increases with the increase of Zr content and aging temperature. After aging at 400 °C and 600 °C, the transformation temperatures were increased and associated enthalpies of the dual phase alloys was decreased, respectively, with the increase of aging temperature.

<table>
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<tr>
<th>Samples</th>
<th>$T_{A-M}$ (°C)</th>
<th>$T_{M-A}$ (°C)</th>
<th>$\Delta H_{A-M}$ (J/g)</th>
<th>$\Delta H_{M-A}$ (J/g)</th>
</tr>
</thead>
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<tr>
<td>Ni$<em>{46}$Mn$</em>{33}$Ga$_{17}$Cu$_4$</td>
<td>71.42</td>
<td>85.07</td>
<td>-11.86</td>
<td>11.90</td>
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<tr>
<td>Ni$<em>{46}$Mn$</em>{33}$Ga$_{17}$Cu$_2$Zr$_2$</td>
<td>64.30</td>
<td>77.01</td>
<td>-7.12</td>
<td>7.22</td>
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<td>Aging-400 °C/10 h</td>
<td>71.61</td>
<td>80.38</td>
<td>-7.00</td>
<td>7.20</td>
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<tr>
<td>Aging-600 °C/10 h</td>
<td>72.47</td>
<td>82.14</td>
<td>-4.92</td>
<td>4.52</td>
</tr>
<tr>
<td>Ni$<em>{46}$Mn$</em>{33}$Ga$_{17}$Zr$_4$</td>
<td>129.52</td>
<td>143.85</td>
<td>-6.10</td>
<td>5.40</td>
</tr>
<tr>
<td>Aging-400 °C/10 h</td>
<td>143.61</td>
<td>158.82</td>
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<td>3.00</td>
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<td>Aging-600 °C/10 h</td>
<td>144.88</td>
<td>157.09</td>
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<td>1.70</td>
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Acknowledgments

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References