Martensitic Transformation and Its Thermal Cycling Stability in $\text{Ni}_{56}\text{Mn}_{21}\text{Cu}_4\text{Ga}_{19}$ High-Temperature Shape Memory Ribbon

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Abstract The microstructure, martensitic transformation, and thermal cycling stability of $\text{Ni}_{56}\text{Mn}_{21}\text{Cu}_4\text{Ga}_{19}$ high-temperature shape memory ribbons subjected to different annealing conditions were investigated and compared with that of the bulk master alloy. It was shown that γ phases precipitated in the bulk and the ribbons annealed for 5 h at 800 and 900 °C, which lead to the same poor thermal cycling stability. However, the formation of γ phase was inhibited in the ribbons annealed at 700 °C for 30 min and 5 h, which remarkably improved the thermal cycling stability and also shifted the martensitic transformation to a lower temperature with a drop of about 60 °C than other three samples.

KEY WORDS: Ni–Mn–Cu–Ga; Annealing; Melt spinning; Martensitic transformation; Shape memory alloy

1 Introduction

Over the last few decades, Ni–Mn–Ga ferromagnetic shape memory alloys (FSMAs) have attained high interest due to their excellent magnetic field-induced shape deformation up to 10% [1–3]. Recently, people also found the potential of Ni–Mn–Ga alloys as a high-temperature shape memory alloy which can operate at a temperature higher than 120 °C [4]. By adjusting the composition (usually increasing the content of Ni) [5–7] or alloying with other elements such as Cu [8, 9], Fe [10], and Co [11], the reverse transformation start temperature (A_s) was shifted to a very high level. Chernenko

et al. [5] first reported a Ni–Mn–Ga alloy whose A_s was higher than 350 °C. Xu et al. [10] found that A_s further shifted to about 427 °C by substituting Ga with Ni. For $\text{Ni}_{56}\text{Mn}_{25-x}\text{Cu}_x\text{Ga}_{19}$ ($x = 2, 4$, and 8) alloys, A_s was as high as 520 °C [9]. As we know, the brittleness was a shortcoming for Ni–Mn–Ga alloys all the time. Thus, the addition of Cu was of special interest for the reason that it not only raised A_s but also remarkably improved the ductility of Ni–Mn–Ga alloys [9, 12]. $\text{Ni}_{56}\text{Mn}_{17}\text{Cu}_8\text{Ga}_{19}$ polycrystalline alloy prepared by conventional arc melting can be hot rolled to a 0.5-mm-thick plate and exhibited the maximum tensile strain of 3.75% [9]. It was confirmed that the significant increase of the ductility in Cu-doped Ni–Mn–Ga alloys was due to the formation of γ phase. However, $\text{Ni}_{56}\text{Mn}_{21-x}\text{Cu}_x\text{Ga}_{19}$ alloys with γ phase and plus γ' would result in a poor thermal cycling stability, which is disadvantageous for practical applications [13].

The melt spinning technique is an effective method to reduce or even inhibit the formation of second phases in Ni–Fe–Ga and Ni–Co–Mn–Sn alloys, due to the rapid solidification speed [14–16]. For example, large amounts of γ phases occurred in $\text{Ni}_{38}\text{Co}_{12}\text{Mn}_{41}\text{Sn}_9$ master alloy, whereas no traces of γ phases were detected in the as-fabricated ribbon [16]. A question now arises whether the thermal cycling

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stability of Ni–Mn–Cu–Ga alloys can be improved by preparing γ phase-free samples with the melt spinning. The main purpose of this study is to clarify this question. We fabricated a $\text{Ni}_{56}\text{Mn}_{21}\text{Cu}_4\text{Ga}_{19}$ ribbon, whose bulk counterpart was reported to form γ phases and was highly unstable during thermal cycling (the martensitic transformation peak disappeared just after the first thermal cycle) [13]. We investigated its microstructure, martensitic transformation, and thermal cycling stability subjected to different annealings.

2 Experimental

A polycrystalline bulk sample with a nominal composition $\text{Ni}_{56}\text{Mn}_{21}\text{Cu}_4\text{Ga}_{19}$ was arc melted using high-purity elements. The alloy was then induction melted in a quartz tube and ejected onto a rotating copper wheel with a surface velocity of 10 m/s. One ribbon was annealed at 700 °C for 30 min to remove crystal defects and residual stresses

introduced by the melt spinning and was still free of second phases. The other three ribbons were annealed for 5 h at 700, 800, and 900 °C, respectively. During the heat treatment, all these ribbons were sealed in a vacuum quartz tube and quenched in water after annealing. The microstructure and compositions were examined by scanning electron microscopy (SEM, Quanta 200) equipped with an energy dispersive X-ray spectroscopy (EDS). X-ray diffraction (XRD) was performed on a PANalytical Xpert'pro diffractometer using CuK_α radiation. The phase transformation was studied using a Perkin Elmer Diamond differential scanning calorimeter (DSC). The heating and cooling rate was 20 °C/min.

3 Results and Discussion

Figure 1a shows the microstructure of the bulk sample. A number of irregular second phases with the dark contrast are clearly observed in the gray matrix. Figure 1b displays

Fig. 1 **a** SEM image, **b** line-scanning image of Ni, Cu, Mn, and Ga elements, **c** XRD pattern of the bulk sample

the line-scanning results of Ni, Mn, Cu, and Ga elements. As compared to the matrix, the black second phase keeps the similar content in Mn and is a little higher in the contents of Ni and Cu, while somewhat lower in Ga, which are consistent with the feature of previously reported γ phase [13]. XRD pattern in Fig. 1c further confirms that it was a γ phase with a face-centered cubic structure. The size of γ phase ranges from about 2 to 40 μm . It is interesting that several light particles occur inside several big γ phases. The reason is not yet clear. Line-scanning results indicate that these light particles have a similar composition to the matrix.

Figure 2 shows the microstructures of the ribbons annealed at various temperatures. Different from the bulk sample, the ribbon annealed at 700 $^{\circ}\text{C}$ for 30 min (Fig. 2a) exhibits only a single martensite phase composed of thin twins, which can be clearly observed from the amplified image in the inset. When the holding time at 700 $^{\circ}\text{C}$ is increased to 5 h, several fine particles (denoted by arrows) occur at the grain boundaries, as shown in Fig. 2b. EDS

and back-scattered electrons image (presented in the inset of Fig. 2b) indicate that these particles have the same composition as the matrix. It means that second phases do not form when annealing at 700 $^{\circ}\text{C}$ regardless of the holding time. For the ribbons annealed at 800 and 900 $^{\circ}\text{C}$ for 5 h, many large black particles (marked by the arrows) precipitate along the grain boundaries and the grain sizes remarkably increase. These precipitates are determined to be γ phases by the composition analysis and XRD results. The above microstructural evolution after annealing implies that, for the Cu-alloyed Ni–Mn–Ga, γ phase can be completely suppressed by the melt spinning just like in other SMAs [14–16]. These γ phases will not precipitate after annealing at 700 $^{\circ}\text{C}$ for 30 min and 5 h but will form when subjected to annealing at 800 and 900 $^{\circ}\text{C}$ for 5 h. It indicated that the formation of γ phase mainly depends on the annealing temperature.

Figure 3 shows the DSC curves of the bulk sample and differently treated ribbons subjected to thermal cycling. On the curve, A_p and M_p correspond to the reverse and forward

Fig. 2 SEM images of the ribbons: **a** 700 $^{\circ}\text{C}/30$ min, **b** 700 $^{\circ}\text{C}/5$ h, **c** 800 $^{\circ}\text{C}/5$ h, **d** 900 $^{\circ}\text{C}/5$ h

Fig. 3 DSC curves of the bulk sample and differently treated ribbons subjected to thermal cycling: **a** bulk sample, **b** ribbon annealed at 700 °C for 30 min, **c** ribbon annealed at 700 °C for 5 h, **d** ribbon annealed at 800 °C for 5 h, **e** ribbon annealed at 900 °C for 5 h

Table 1 The corresponding composition of the matrix and γ phase, transformation temperatures (A_p and M_p), and thermal hysteresis ($A_p - M_p$). Here, the values of A_p and M_p were determined from the first thermal cycle

Sample	Matrix composition	γ phase composition	A_p (°C)	M_p (°C)	$A_p - M_p$ (°C)
Bulk	Ni _{53.0} Mn _{20.9} Cu _{5.3} Ga _{20.8}	Ni _{57.8} Mn _{19.6} Cu _{6.3} Ga _{16.3}	519	463	56
Ribbon-700 °C/30 min	Ni _{54.9} Mn _{19.4} Cu _{5.7} Ga ₂₀	–	460	395	65
Ribbon-700 °C/5 h	Ni _{54.2} Mn _{20.9} Cu _{5.4} Ga _{19.6}	–	450	391	59
Ribbon-800 °C/5 h	Ni _{52.9} Mn _{21.1} Cu _{5.5} Ga _{20.5}	Ni _{60.5} Mn _{18.2} Cu _{7.0} Ga _{14.4}	517	452	65
Ribbon-900 °C/5 h	Ni _{52.9} Mn _{21.1} Cu _{5.2} Ga _{20.8}	Ni _{58.6} Mn _{19.1} Cu _{7.4} Ga _{14.9}	520	459	61

transformation peak temperature, respectively. Each sample is cycled seven times. It should be pointed out that two overlapped peaks occur throughout the forward transformation in the ribbon annealed at 700 and 900 °C, which may be ascribed to the inhomogeneous composition. Because one ribbon is too light to detect a large latent heat in DSC measurement, we had to place a few ribbons each time in the DSC sample holder, which caused the inhomogeneity of composition. To ensure the consistency, the value of the lower-temperature peak is chosen as the M_p . The detailed composition of the matrix and γ phase, transformation temperatures, and thermal hysteresis are listed in Table 1.

By comparing these DSC curves, three points are summarized as follows. First, for all the studied samples, the first reverse transformation temperatures are always higher than those in the second cycle, which is called the martensite stabilization and is a common phenomenon in SMAs [6, 13, 17]. Second, the bulk sample, the ribbons annealed at 800 and 900 °C exhibit a much larger transformation peak upon the first heating and cooling curve than that in the subsequent thermal cycles. With increasing the thermal cycles, the transformation peaks get smaller and smaller and finally disappear after 2–3 cycles. This indicates that the above three samples have poor thermal cycling stability. However, for the ribbon annealed at 700 °C for 30 min and 5 h, even after seven cycles, the transformation peaks almost keep unchanged, suggesting a good thermal cycling stability. At last, the ribbon annealed at 800 and 900 °C exhibits similar transformation temperatures to the bulk sample (A_p and M_p are around 519 and 458 °C), which can be ascribed to the similar two-phase microstructure (as shown in Figs. 1, 2) and similar composition in the matrix (as shown in Table 1). After annealing at 700 °C for 30 min, both the forward and reverse transformation are remarkably shifted to a low temperature ($A_p = 460$ °C, and $M_p = 395$ °C) due to the increase of e/a [13] and greatly decreased the grain size [18]. The same mechanism is also applied to the ribbon annealed at 700 °C for 5 h whose A_p and M_p drop to 450 and 391 °C, respectively.

Figure 4 shows the dependence of transformation temperatures on the thermal cycling. One can see that, even

Fig. 4 Effect of thermal cycling on the A_p and M_p

though A_p and M_p exhibit a slight decrease after several thermal cycles, thermal stability of the ribbons annealed at 700 °C is obviously improved irrespective of the holding time. This is consistent with the result in the Ni–Mn–Ga alloys containing single martensite, which exhibits a highly stable martensitic transformation after 1,000 thermal cycles [19]. The suppression of γ phases plays a key role in obtaining a good thermal cycling stability. Besides, relatively small matrix grains increase the strength, which also makes a contribution [20]. The bulk sample and the ribbons annealed at 800 and 900 °C show a similar instability of thermal cycling resulting in the disappearance of transformation peaks after several cycles, which can be ascribed to the precipitation of γ phases as discussed below. Firstly, in Cu-containing Ni–Mn–Ga alloy, the precipitated γ particle is a hard phase and does not participate in the martensitic transformation [13]. During the transformation, γ phases apply a resistance to the motion of martensite/austenite interface leading to the poor thermal cycling stability [13]. Secondly, the decrease of matrix strength resulting from coarse grains is favor for the production of defects during cycling [20], which also weakens the thermal cycling stability. Finally, for those samples consisting of the martensite and γ phase, the ordered γ' phase is formed during thermal cycling which also contributes to the instability of thermal cycling [13].

4 Conclusions

In summary, thermal cycling stability of $\text{Ni}_{56}\text{Mn}_{21}\text{Cu}_4\text{Ga}_{19}$ alloy was clearly improved by means of the melt spinning followed by such an appropriate post-treatment as annealing at 700 °C due to the suppression of γ phases. After annealing at 700 °C, the transformation temperatures upon the first thermal cycle decreased by about 60 °C as compared to that of the ribbons annealed at 800 and 900 °C for 5 h.

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