Effect of Annealing Temperature on the Shape Memory Properties of Cold-Rolled Dual-Phase Ni–Mn–Ga–Gd Alloy

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Abstract The influence of annealing temperature on the shape memory effect (SME) and recovery ratio of cold-rolled dual-phase Ni₅₈Mn₂₅Ga_{16.9}Gd_{0.1} high-temperature shape memory alloy were investigated. The results showed that the SME can be improved by appropriate annealing. SME of 6.0% and recovery ratio of 98% were observed in the rolled alloy at 550 °C annealing, which were larger than that of the samples annealed at other temperatures. The annealing temperature was in between the recrystallization temperatures of the martensite and γ phase, which leads to the work-hardening state of γ phase kept unchanged during annealing process, and therefore, the critical slip stress of γ phase increased. Thus, the plastic deformation of γ phase reduced during the compression process, and the SME increased.

KEY WORDS: Shape memory alloys; Recrystallization; Cold rolling; Ni–Mn–Ga

1 Introduction

Recently, the research for high-temperature shape memory alloys (HTSMAs) has attracted more and more attentions [1, 2]. Several HTSMA systems such as Cu-based alloys, Ni–Al-based alloys, Ta–Ru and Nb–Ru alloys, Ti–Ni–Pd alloy, Ti–Ta-based alloys [3–12] have been widely investigated. However, some problems are unsolved in these alloys. The transformation temperatures of Cu-based alloys and Ni–

Al-based alloys are unstable due to the precipitation of equilibrium phase [3–5]. The poor thermal stability and high cost of Ta–Ru, Nb–Ru and Ni–Ti–Pd alloy limit their application [6–10]. The martensitic transformation temperature of Ti–Ta-based alloy is unstable due to ω phase precipitation during thermal cycles and aging at high temperature [11]. It can be seen that the poor thermal stability is a common problem of these alloys.

In the past few decades, Ni–Mn–Ga alloys have been extensively explored as ferromagnetic shape memory alloy [13–15]. Meanwhile, Ni–Mn–Ga alloy also becomes a great HTSMAs candidate due to its excellent thermal stability. Although the mechanics properties and shape memory effect (SME) of Ni–Mn–Ga HTSMAs have been systematically studied in the past 10 years [16–23], the effect of thermo-mechanical treatment (cold work, annealing or a combination of both) on shape memory properties has not yet been reported due to its severe brittleness. In our previous publication, a dual-phase Ni₅₈Mn₂₅Ga_{16.9}Gd_{0.1} polycrystalline HTSMA with compressive fracture strain of 51.7% has been obtained [24], and the excellent ductility makes it work well. Here, the SME of cold-rolled dual-phase Ni₅₈Mn₂₅Ga_{16.9}Gd_{0.1} alloy under different annealing temperatures is investigated.

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2 Experimental

The nominal composition of the studied alloy was $\text{Ni}_{58}\text{Mn}_{25}\text{Ga}_{16.9}\text{Gd}_{0.1}$ (at.%). High-purity nickel (99.99%), manganese (99.7%), gallium (99.99%) and gadolinium (99.99%) were melted in a non-consumed vacuum arc furnace under argon atmosphere. The ingot was remelted six times to ensure homogeneity. The ingot was annealed in a vacuum quartz tubes at 800 °C for 24 h and then quenched into ice water. The transformation temperatures are $M_s = 466$ °C, $M_f = 447$ °C, $A_s = 521$ °C and $A_f = 546$ °C, respectively.

The solution-treated ingot was cut into strips of 5 mm thickness. The strips were given reductions in thickness of 20% by cold rolling. Compression deformation was performed at room temperature on Instron 5569 testing system at a crosshead displacement speed of 0.2 mm/min. The compression deformation specimens with the size of $\varnothing 3$ mm $\times$ 5 mm were cut from rolled strips, annealed at different temperatures (450, 550 and 600 °C) for 2 h and then quenched into ice water. X-ray diffraction measurements were taken by a Rigaku D/max-rB with CuK_α radiation. The microstructure was carried out by FEI Tecnai G² 20 Stwin 200 kV TEM equipped with a double-tilt cooling stage. Thin-foil specimens for TEM observation were mechanically polished to about 50 μm , and then, twinjet electropolished with an electrolyte of nitric acid and methanol (3:7 in volume) at -20 °C.

3 Results and Discussion

Figure 1 displays the strain recovery characteristic curves of the cold-rolled $\text{Ni}_{58}\text{Mn}_{25}\text{Ga}_{16.9}\text{Gd}_{0.1}$ samples under different annealing temperatures, and the shape memory behavior in different state is listed in Table 1. It is well known that the properties of the shape memory alloys (SMAs) such as Ti–Ni can be manipulated through

thermomechanical treatment. Cold work alone increases the strength of SMAs but causes lower recoverable strains due to the introduction of random dislocations [25–27]. Annealing at a temperature above recrystallization temperature restores SME by rearranging the dislocations but leads to the decrease in the strength. As shown in Fig. 1a, the strength of 450 °C-annealed alloy is higher than that of solution-treated alloy [24], indicating that the recrystallization temperature of $\text{Ni}_{58}\text{Mn}_{25}\text{Ga}_{16.9}\text{Gd}_{0.1}$ alloy is higher than that at 450 °C. The SME of 450 °C-annealed alloy is only 3% due to the work hardening. When the annealing temperature is 600 °C, the sample turns its original state due to recrystallization, causing the increase in SME and recovery ratio (Table 1). It is noted that the SME of 6.0% at 550 °C-annealed alloy is larger than that of solution-treated alloy, proving that the proper thermomechanical treatment can improve the SME of $\text{Ni}_{58}\text{Mn}_{25}\text{Ga}_{16.9}\text{Gd}_{0.1}$ alloy. This SME value is larger than that of reported dual-phase Ni–Mn–Ga alloy [20].

In order to explain the mechanism of shape memory property improvement, XRD analysis and TEM observation are carried out. Figure 2 shows XRD patterns of $\text{Ni}_{58}\text{Mn}_{25}\text{Ga}_{16.9}\text{Gd}_{0.1}$ alloys at the solution-treated state and thermomechanical treatment at 550 °C. As can be seen in the figure, solution-treated $\text{Ni}_{58}\text{Mn}_{25}\text{Ga}_{16.9}\text{Gd}_{0.1}$ alloy possesses the dual-phase structure of martensite and second phase. Six reflection peaks can be indexed by the complex tetragonal-structured martensite (denoted as M), and two reflection peaks represent face-centered cubic-structured second phase (denoted as γ) [16]. The inserted TEM image was from the solution-treated $\text{Ni}_{58}\text{Mn}_{25}\text{Ga}_{16.9}\text{Gd}_{0.1}$ alloy. There are not a number of dislocations in both the martensite and the γ phase. After thermomechanical treatment, the position and intensity of reflection peaks keep unchanged. From a number of experiments, we have found that the SME along the rolling direction is almost the same as that perpendicular to the rolling direction. Thus, it can be inferred that the improvement in SME might not be caused by the texture formation.

Fig. 1 Strain recovery characteristic curves of $\text{Ni}_{58}\text{Mn}_{25}\text{Ga}_{16.9}\text{Gd}_{0.1}$ alloy annealed at 450 °C **a** and 550 °C **b** under the pre-strain of 10%. The dotted line represents the recovery strain after heated to 600 °C for 1 min

Table 1 Shape memory behavior (%) of $\text{Ni}_{58}\text{Mn}_{25}\text{Ga}_{16.9}\text{Gd}_{0.1}$ alloy under different states at pre-strain of 10%

Sample	Solution treated [24]	Thermomechanical treatments		
		450 °C	550 °C	600 °C
Strain after unloading	6.5	5.5	6.2	6.4
Strain after heating	1.4	2.5	0.2	1.5
SME	5.1	3.0	6.0	4.9
Recovery ratio	86	75	98	85

Fig. 2 XRD patterns of $\text{Ni}_{58}\text{Mn}_{25}\text{Ga}_{16.9}\text{Gd}_{0.1}$ alloy at solution-treated state and after thermomechanical treatments. The inset is the TEM image of solution-treated sample

Figure 3 shows TEM images of $\text{Ni}_{58}\text{Mn}_{25}\text{Ga}_{16.9}\text{Gd}_{0.1}$ alloy annealed at 450 °C. The martensite and γ phase have the same morphology as that of the cold-rolled alloy (TEM images are not provided here). The boundaries of martensitic variant are curved and irregular (Fig. 3a). A large number of random dislocations formed in variants and γ phase (Fig. 3b, c), showing that $\text{Ni}_{58}\text{Mn}_{25}\text{Ga}_{16.9}\text{Gd}_{0.1}$ alloy is in work-hardening state.

Fig. 3 TEM images of rolled $\text{Ni}_{58}\text{Mn}_{25}\text{Ga}_{16.9}\text{Gd}_{0.1}$ alloy after 450 °C annealing: **a** bright field image; **b**, **c** magnification images of area A and B in **a**

When the cold-rolled alloy is annealed at 550 °C, the number of dislocations in martensitic variants decreases significantly as shown in Fig. 4. However, the dislocation density of γ phase is still high. Therefore, the γ phase is in the state of work hardening. From the results mentioned above, it can be concluded that the annealing temperature is higher than recrystallization temperature of martensitic matrix, but lower than that of γ phase.

The published literature shows that γ phase is a soft phase, which is beneficial to improve the ductility [16, 24], but the SME will be damaged due to plastic deformation of γ phase during deformation process, so when the solution-treated alloy deformed is heated to 600 °C, irreversible strain of 1.4% is observed (Table 1), while the negative influence of γ phase is eliminated to a certain extent by proper thermomechanical treatment. When the rolled alloy is annealed at 550 °C, the martensite turns its original state due to the recrystallization, but the γ phase is still a hard phase which is in work-hardening state. The increase in the critical slip stress of γ phase leads to the decrease in

Fig. 4 TEM images of rolled $\text{Ni}_{58}\text{Mn}_{25}\text{Ga}_{16.9}\text{Gd}_{0.1}$ alloy after 550 °C annealing: **a** bright field image; **b** magnification image of area A in **a**

irreversible strain of γ phase during the deformation process. Thus, the SME and recovery ratio of $\text{Ni}_{58}\text{Mn}_{25}\text{Ga}_{16.9}\text{Gd}_{0.1}$ alloy increase. This mechanism of the shape memory property improvement is different from any of previous reports [16, 19, 24].

4 Conclusion

The shape memory properties of dual-phase $\text{Ni}_{58}\text{Mn}_{25}\text{Ga}_{16.9}\text{Gd}_{0.1}$ alloy can be improved by cold rolling and appropriate annealing. Thermomechanical treatment increases the critical slip stress of γ phase and decreases the

plastic deformation of γ phase during deformation process. Thus, a larger SME of 6% is obtained.

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