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Scripta Materialia 68 (2013) 679–682
Scripta MATERIALIA
www.elsevier.com/locate/scriptamat

Two-way shape memory effect of polycrystalline Ni–Mn–Ga–Gd high-temperature shape memory alloys

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Received 30 December 2012; revised 14 January 2013; accepted 14 January 2013
Available online 26 January 2013

The two-way shape memory effect (TWSME) of polycrystalline $Ni_{54}Mn_{25}Ga_{21-x}Gd_x$ alloys is investigated. The largest TWSME value (2.9%) without training is observed in $Ni_{54}Mn_{25}Ga_{20.7}Gd_{0.3}$ alloy due to a small amount of $Gd(Ni,Mn)_4Ga$ phase formation, and this value increases to 3.5% after thermomechanical training. The TWSME rapidly decreases over the first few thermal cycles, and then slowly reaches a stable value as the number of cycles increases further. Finally, a 2.5% TWSME of as-trained $Ni_{54}Mn_{25}Ga_{20.7}Gd_{0.3}$ alloy is obtained after 50 thermal cycles.

Keywords: Ni–Mn–Ga–Gd alloys; High-temperature shape memory alloys; Two-way shape memory effect; Thermomechanical training

In recent years, shape memory alloys (SMAs) have been successfully used in a variety of applications due to their unique abilities such as shape memory effect (SME), superelasticity, etc. Among the various properties of SMAs, the two-way shape memory effect (TWSME) is the most relevant to application in actuators since no resetting force needs to be considered in the design. Ti–Ni alloy has been widely researched in SMA actuators, and its outstanding TWSME gives it excellent performance in practical applications [1,2]. However, the lower transformation temperature of Ti–Ni alloy limits the scope of its application. Thus, the development of high-temperature shape memory alloy (HTSMA) actuators seems likely to become a focus of future research. Compared with other HTSMAs, Ni–Mn–Ga alloys have attracted increasing interest for their high transformation temperature, large SME and high stability [3–9]. Their outstanding performance in high-temperature environments also makes Ni–Mn–Ga alloys potential excellent candidates for high-temperature actuators. The TWSME has been observed in Ni–Mn–Ga polycrystalline thin films and bulk single crystals [10–12]. Callaway et al. [13] obtained a significant value of TWSME strain of 3.8% in $Ni_{53}Mn_{25}Ga_{22}$ single crystal with non-modulated martensitic structure after thermal cycling under high compressive stress. Chernenko et al. [14] found a giant TWSME of 9% in high-temperature $Ni_{57.5}Mn_{22.5}Ga_{20.0}$ single crystal. In practical applications, polycrystalline alloys have an advantage over single crystals because of their easy preparation, though there has been no reported study of the TWSME of polycrystalline Ni–Mn–Ga HTSMA due to its intrinsic brittleness. It has been proven that rare earth Gd addition can toughen Ni–Mn–Ga SMAs by grain refinement [15]. In this paper, the TWSME of polycrystalline $Ni_{54}Mn_{25}Ga_{21-x}Gd_x$ HTSMA is investigated, and the related mechanism is also discussed.

The nominal compositions of the alloys studied were $Ni_{54}Mn_{25}Ga_{21-x}Gd_x$ (x = 0, 0.1, 0.3 and 0.5). High-purity nickel, manganese, gallium and gadolinium, with purity levels of 99.99%, 99.7%, 99.99% and 99.99%, respectively, were melted in a non-consuming vacuum arc furnace under an argon atmosphere to prepare $Ni_{54}Mn_{25}Ga_{21-x}Gd_x$ alloys. The ingots were remelted six times to ensure homogeneity. The samples were annealed in vacuum quartz tubes at 1073 K for 24 h and then quenched into ice water. The microstructure of alloys was surveyed by optical microscopy and scanning electron microscopy (SEM, MX2600FE). The reverse martensitic transformation finishing temperatures of $Ni_{54}Mn_{25}Ga_{21-x}Gd_x$ alloys ranged from 217 to 231 °C [16], which were determined by differential scanning calorimetry (DSC) with a heating/cooling rate of 20 K min^{-1}. The SME and TWSME were studied by compressive tests in a universal mechanical testing machine. The samples

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1359-6462/$ - see front matter
http://dx.doi.org/10.1016/j.scriptamat.2013.01.022

were cut along the direction perpendicular to the columnar grains of ingots. The samples' dimensions were 3 mm diameter × 5 mm and the deformation rate was 0.2 mm min^{-1}, respectively. The heights of the samples were measured before loading (L_0), after loading (L_1), after unloading (L_2), after heating to 500 °C for 2 min (L_3) and after cooling to room temperature (L_4) by a micrometer with an accuracy of 0.01 mm. The pre-strain during compression was defined as $\varepsilon_{pre} = (L_0 - L_1)/L_0 \times 100\%$. The SME and TWSME were obtained as: $(L_3 - L_2)/L_0 \times 100\%$ and $(L_3 - L_4)/L_0 \times 100\%$, respectively. A two-way shape memory training [17] experiment was conducted using thermomechanical cycles. A constant compressive strain was applied to the samples at room temperature (martensitic state). After deformation, the compressive samples were heated to 500 °C for complete shape recovery, and then cooled to room temperature. After repeating the above steps 10 times, the TWSME was revealed.

A study of the SME in polycrystalline $Ni_{54}Mn_{25}Ga_{21-x}Gd_x$ alloys [16] revealed an interesting phenomenon. After shape recovery was completed, the compressive samples shortened again with a reduction in temperature. Obviously, this phenomenon is a TWSME. The TWSME of polycrystalline $Ni_{54}Mn_{25}Ga_{21-x}Gd_x$ alloys with different pre-strains are listed in Table 1. The TWSME increases with the increase in Gd content and reaches a maximum value (~2.9%) in $Ni_{54}Mn_{25}Ga_{20.7}Gd_{0.3}$ alloy; with further increase in Gd content, the TWSME decreases. As shown in Figure 1a and b, the microstructure of $Ni_{54}Mn_{25}Ga_{21}$ alloy and $Ni_{54}Mn_{25}Ga_{20.9}Gd_{0.1}$ alloy are monophase. The larger irreversible deformation occurs in $Ni_{54}Mn_{25}Ga_{21}$ alloy when the pre-strain is 6%, leading to SME and TWSME of only 0.9% [16] and 0.8%, respectively. The better mechanical properties due to grain refinement improves the ability of $Ni_{54}Mn_{25}Ga_{20.9}Gd_{0.1}$ alloy to resist irreversible deformation, and therefore the TWSME is larger than that of $Ni_{54}Mn_{25}Ga_{21}$ alloy. When the Gd content is 0.3 at.%, a small amount of $Gd(Ni,Mn)_4Ga$ phase [16] occurs in the matrix as shown in Figure 1c, causing the formation of an extra stress field, which has a positive influence on TWSME. Thus, the largest value of TWSME is observed in $Ni_{54}Mn_{25}Ga_{20.7}Gd_{0.3}$ alloy. It can be seen from Figure 1d that the volume fraction of $Gd(Ni,Mn)_4Ga$ phase in $Ni_{54}Mn_{25}Ga_{20.5}Gd_{0.5}$ alloy increases with further addition of Gd content, and the further generation of $Gd(Ni,Mn)_4Ga$ phase hinders the movement of interface between martensitic variants and austenite, leading to the suppression of the TWSME.

Table 1. Two-way shape memory effect of $Ni_{54}Mn_{25}Ga_{21-x}Gd_x$ alloys.

Sample	Pre-strain (%)	TWSME (%)
x = 0	6	0.8
x = 0.1	6	1.2
x = 0.3	4	1.4
	6	2.9
	8	2.8
	10	1.6
x = 0.5	6	1.7

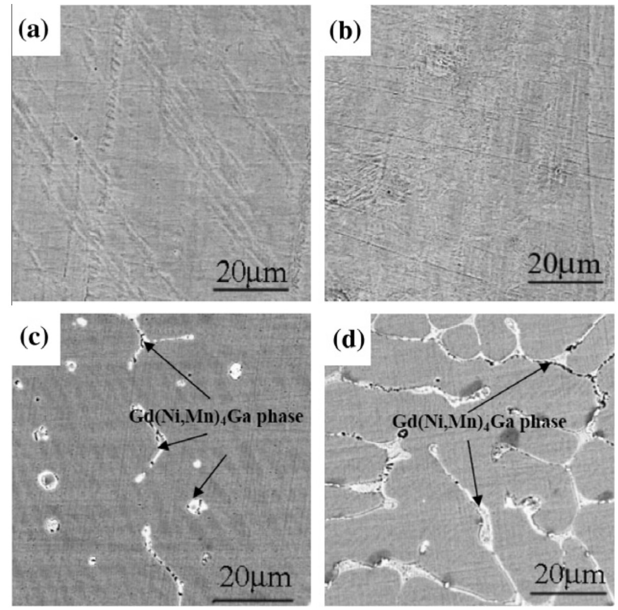

Figure 1. Backscattered electron images of solution-treated $Ni_{54}Mn_{25}Ga_{21-x}Gd_x$ alloys: (a) $x = 0$; (b) $x = 0.1$; (c) $x = 0.3$; (d) $x = 0.5$.

Figure 2 shows the effect of temperature on strain and the compressive stress–strain curve of $Ni_{54}Mn_{25}Ga_{20.7}Gd_{0.3}$ alloy with 6% pre-strain. The recovery of deformed martensite during the first heating starts at 280 °C, which is termed the martensitic reverse transformation starting temperature (A_s) as shown in Figure 2. A compressive strain recovery (ε_{sme}) of 3.6% was measured after heating to 350 °C for 1 min. In the following thermal cycle, the specimen exhibits a reversible two-way memory strain of $\varepsilon_{tw} = 2.9\%$. It can be observed that A_s in the first thermal cycle is 70 °C higher than that during the second heating. This phenomenon is attributed to the fact that plastic deformation relaxes the elastic strain energy stored during thermoelastic martensitic transformation, leading to a decrease in the driving force of the martensitic reverse transformation [18]. Consequently, the A_s temperature increases. It can be seen that the transformation temperatures of deformed specimen in the second transformation cycle corresponds to those of underformed specimen ($A_s = 210$ °C, $A_f = 231$ °C) [16], implying that

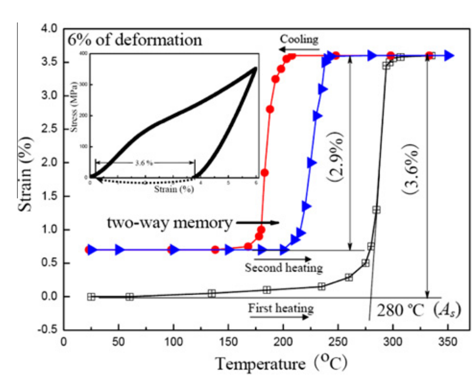

Figure 2. The effect of temperature on strain and the compressive stress–strain curves of $Ni_{54}Mn_{25}Ga_{20.7}Gd_{0.3}$ with 6% pre-strain.