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The mechanism clarification of Ni–Mn–Fe–Ga alloys with excellent and stable functional properties

S.Y. Yang [a,*], Y. Liu [b], C.P. Wang [a], Z. Shi [a], X.J. Liu [a,*]

[a] Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen 361005, China
[b] School of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore 639798, Singapore

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ABSTRACT

The functional properties, thermomechanical stability, ductility and shape memory effect of four types of two-phase NiMnGa-based high-temperature shape memory alloys were investigated, including $Ni_{56+x}Mn_{25}Ga_{19-x}$ ($x = 1, 2, 3, 4$), $Ni_{56}Mn_{25-y}Fe_yGa_{19}$ ($y = 4, 8, 12, 16$), $Ni_{56}Mn_{25-z}Co_zGa_{19}$ ($z = 4, 6, 8$) and $Ni_{56}Mn_{25-w}Cu_wGa_{19}$ ($w = 2, 4, 8$) alloys. It is found that $Ni_{56}Mn_{25-y}Fe_yGa_{19}$ alloys ($y > 4$) exhibit the most excellent thermomechanical stability with no γ' precipitates after thermomechanical cycling. Results further show that different alloying elements (Ni/Co/Cu/Fe) have different effects on the mechanical properties of both γ phase and corresponding two-phase NiMnGa-based alloys, which are closely related to the thermomechanical stability, ductility and shape memory effect of these alloys. The strength of Ni–Mn–Ga alloys decreases obviously with the addition of Fe, and the ductility of the alloys is effectively improved due to the formation of the most ductile γ phase with the lowest strength in $Ni_{56}Mn_{25-y}Fe_yGa_{19}$ alloys. Particularly, Fe addition significantly improves shape memory effect of Ni–Mn–Ga alloys. As a result, two-phase $Ni_{56}Mn_{25-y}Fe_yGa_{19}$ alloys exhibit the most excellent and stable functional properties as potential high-temperature shape memory materials.

1. Introduction

Recent investigations have shown that the ductility of polycrystalline Ni–Mn–Ga shape memory alloys (SMAs) can be effectively improved through formation of ductile fcc γ phase by either increasing the concentration of Ni content or by alloying with elements such as Co, Cu and Fe [1–5]. These "modified" two-phase NiMnGa-based alloys are found to possess a good combination of moderate ductility, shape memory effect (SME) and high martensitic transformation (MT) temperature, which form a promising new class of low-cost high-temperature shape memory alloys (HTSMAs). When technical application is concerned, being potential HTSMAs, the thermal stability of these two-phase NiMnGa-based alloys have been investigated [6]. The previous results showed that two-phase Ni–Mn–Fe–Ga HTSMAs exhibited the excellent thermal cycling stability [6]. However, many practical applications require that SMAs can function stably at high temperatures with several thermomechanical cycles, requiring that HTSMAs have to possess stable and reliable the stability of MT and SME. To date, due to their poor ductility, the thermomechanical cycling tests of ternary polycrystalline Ni–Mn–Ga SMAs can hardly be carried out and have never been reported. On the other hand, addition of alloying elements (Ni/Co/Cu/Fe) into Ni–Mn–Ga alloys can significantly improve their ductility [1–5], thus making it possible for us to assess their thermomechanical cycling stability. This article is to present the results of thermomechanical cycling of two-phase NiMnGa-based SMAs and the effect of alloying elements (Ni/Co/Cu/Fe) on their thermomechanical stability and SME.

Previous investigations have shown that alloying elements (Ni/Co/Cu/Fe) play a critical role in determining the ductility and SME of two-phase NiMnGa-based alloys [1–5]. The improvement in alloy ductility is due to the formation of ductile γ phase. Results further show that the volume fraction, distribution and morphology of γ phase and its mechanical properties play an important role in the ductility and SME of these two-phase HTSMAs. However, to date, the attempts to achieve an optimized combination of ductility and SME through alloying are mainly from a trial-and-error approach. Therefore, for effective alloy design, we also need to systematically investigate the effect of γ phase on the ductility and SME of these alloys in order to gain in-depth understanding.

In the present study, in order to obtain two-phase microstructures (i.e. martensite and γ phase) with various amounts of γ phase, four types of two-phase NiMnGa-based HTSMAs were prepared based on single martensite $Ni_{56}Mn_{25}Ga_{19}$ master alloy (denoted as Ni56 in this study) and alloyed with different amounts of Ni/Co/Cu/Fe [1–4]. The designations and chemical compositions

* Corresponding authors. Tel.: +86 18059243800; fax: +86 592 2187966.
E-mail addresses: yangshuiyuan@xmu.edu.cn (S.Y. Yang), lxj@xmu.edu.cn (X.J. Liu).

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Table 1
Designations and chemical compositions of studied alloys.

System	Designation	Chemical formula	Chemical composition (at.%)
Ni	Ni57	$Ni_{56+x}Mn_{25}Ga_{19-x}$ (x = 1, 2, 3, 4)	$Ni_{57}Mn_{25}Ga_{18}$ (x = 1)
	Ni58		$Ni_{58}Mn_{25}Ga_{17}$ (x = 2)
	Ni59		$Ni_{59}Mn_{25}Ga_{16}$ (x = 3)
	Ni60		$Ni_{60}Mn_{25}Ga_{15}$ (x = 4)
Fe	Fe4	$Ni_{56}Mn_{25-y}Fe_yGa_{19}$ (y = 4, 8, 12, 16)	$Ni_{56}Mn_{21}Fe_4Ga_{19}$ (y = 4)
	Fe8		$Ni_{56}Mn_{17}Fe_8Ga_{19}$ (y = 8)
	Fe12		$Ni_{56}Mn_{13}Fe_{12}Ga_{19}$ (y = 12)
	Fe16		$Ni_{56}Mn_9Fe_{16}Ga_{19}$ (y = 16)
Co	Co4	$Ni_{56}Mn_{25-z}Co_zGa_{19}$ (z = 4, 6, 8)	$Ni_{56}Mn_{21}Co_4Ga_{19}$ (z = 4)
	Co6		$Ni_{56}Mn_{19}Co_6Ga_{19}$ (z = 6)
	Co8		$Ni_{56}Mn_{17}Co_8Ga_{19}$ (z = 8)
Cu	Cu2	$Ni_{56}Mn_{25-w}Cu_wGa_{19}$ (w = 2, 4, 8)	$Ni_{56}Mn_{23}Cu_2Ga_{19}$ (w = 2)
	Cu4		$Ni_{56}Mn_{21}Cu_4Ga_{19}$ (w = 4)
	Cu8		$Ni_{56}Mn_{17}Cu_8Ga_{19}$ (w = 8)

of studied alloys are given in Table 1. In this work, in order to achieve an optimization between thermomechanical stability, ductility and SME of the alloys, we have systematically characterized the γ phase (including volume fraction, distribution, morphology and ductility), the strength of the alloys and γ phase, the precipitate, and have correlated them to the thermomechanical stability and SME of the alloys.

2. Experimental procedure

Four types of two-phase NiMnGa-based HTSMAs were prepared by arc melting (Table 1). The purities of the nickel, manganese, gallium, iron, cobalt and copper were 99.9%, 99.7%, 99.99%, 99.9%, 99.9% and 99.9%, respectively. Each button of about 40 g was remelted five times to ensure the homogeneity. The ingots were then sealed into vacuum quartz ampoules and annealed at 900 °C for 36 h followed by quenching into ice-water.

Cylindrical specimens (ϕ3 mm × 5 mm) were cut from the center of the quenched buttons and were subjected to thermomechanical cycles. Before each thermal cycle, the sample was compressed to a pre-strain of 6% using INSTRON 5569 at a crosshead speed of 0.2 mm/min, and then followed by one thermal cycle through phase transformation temperatures. Thereafter, the sample was again deformed to 6% under compression followed by the second thermal cycle. Such thermomechanical procedure was repeated for four times and, before the fifth thermal cycle, the sample was not pre-strained. The thermal cycling tests were performed on a Thermomechanical Analyzer (TMA 2940, TA Instruments) at a rate of 10 °C min^{-1} for both heating and cooling. The temperature range for thermal cycling was between 300 °C and 800 °C for alloys of Ni system, Cu system and Co system, between 200 °C and 700 °C for Fe4 alloy, between 100 °C and 600 °C for Fe8 alloy, between 50 °C and 600 °C for Fe12 and Fe 16 alloys, respectively, depending on the transformation temperatures of each alloy. The SMEs were calculated using the dimensional change of the samples before heating and after reverse transformation after the removal of length change due to thermal expansion, as highlighted by the colored arrowed bars in Fig. 1. The details of the calculation are as follows. The lengths of the specimens were measured before loading (l_0), after unloading (l_1) and after thermomechanical cycling (l_2). The residual strain after unloading (ε_r) and the SME (ε_{SME}) were calculated as: $\varepsilon_r = (l_0 - l_1)/l_0 \times 100\%$, and $\varepsilon_{SME} = (l_2 - l_1)/l_0 \times 100\%$, respectively. The recoverable rates were calculated as: $R = (\varepsilon_{SME}/\varepsilon_r)$.

After thermomechanical cycling, several plate-shaped specimens were further cut from the thermomechanically tested specimens for microstructural observations by optical microscope (OM) using Leica DMI 5000 M. Samples for microscopic observation were mechanically polished and chemically etched in a solution of 99 ml methanol + 2 ml nitric acid + 5 g ferric chloride. In this work, the each phase compositions were determined using an energy-dispersive X-ray spectrometer (EDX) analysis directly from these phases, and each composition data presented is an average value of five measurements. The mechanical properties were carried out by tensile tests using a Galdabini Sun 2500 machine at a crosshead speed of 0.2 mm/min. The gauge size of the tensile specimen was 3 mm wide, 0.5 mm thick and 7 mm long. In the present study, the volume fractions of γ phase and martensite were obtained by the previous investigation in Ref. [6], in which they were experimentally determined by the optical imaging and analysis system using Leica DMI 5000 M.

3. Results

3.1. Transformation temperatures after thermomechanical cycling

Fig. 1 is the TMA curves of partial two-phase NiMnGa-based alloys during four thermomechanical cycles, including Ni57 and Ni60 alloys in Ni system, Cu2 and Cu8 alloys in Cu system, Co4 and Co8 alloys in Co system, Fe4 and Fe12 alloys in Fe system. In order to understand the effect of thermomechanical cycling on the transformation temperatures, the 5th TMA test was carried out without applying a pre-strain after four thermomechanical cycles. The results of the 5th TMA cycle are highlighted in the insets in each figure, where M_{s5}, M_{f5}, A_{s5} and A_{f5} are the starting and finishing temperatures for martensite and austenite transformations respectively. The austenite starting temperatures (A_{s5}) during the 5th cycle are summarized in Table 2. For comparison, the austenite starting temperatures (A_s) of the samples without pre-strain (determined by DSC) [1–4] are also given in Table 2. The shifts in austenite transformation temperature after thermomechanical cycling ($\Delta T^5_{As} = A_{s5} - A_s$), are presented in Table 2. The effect of alloying element (Ni/Co/Cu/Fe) on ΔT^5_{As} is shown Fig. 2.

From Fig. 2, it can be observed that the temperature shifts are different for different types of alloys. It is noted that there are two types of shifts in transformation temperatures. The first one is $\Delta T^5_{As} < 0$, which includes alloys in Ni system, Co system, Cu system and Fe4 alloy. These alloys exhibit a large decrease in A_s temperatures after thermomechanical cycling. The second one is $\Delta T^5_{As} > 0$, which includes alloys of Fe system ($y > 4$). Moreover, for the alloys of Fe system with more than 8 at.% Fe, ΔT^5_{As} decreases with increasing Fe content and nearly reaches to zero for 16 at.% Fe addition. These results are somehow similar to the observations on the same alloys after pure thermal cycling [6]. However, for Fe4 alloy the difference in temperature shift (ΔT^5_{As}) is significant: it is −37 °C after thermomechanical cycling, whereas there was no apparent change after pure thermal cycling [6].

3.2. SME during thermomechanical cycling

The residual strains (ε_r), shape memory effects (ε_{SME}) and recovery rates (R) are summarized in Table 3. Fig. 3 presents the effect of Ni/Co/Cu/Fe content on the SME during four cycles. It can be observed that the SME differs significantly among different types of alloys. In Ni, Co and Cu systems, when $x \leqslant 2$, $z = 4$ and $w \leqslant 4$, these alloys possess relatively good SMEs. However, with further increasing Ni/Co/Cu content ($x/z/w$), including Ni59, Ni60, Co6, Co8 and Cu8 alloys, the SME becomes very poor (<1%). Even after the 1st cycle, the SME nearly vanishes in Co8 and Cu8 alloys. On the other hand, in some alloys of Fe system, good SME is observed, however, it decreases with increasing Fe concentration. Overall, alloys from Fe system possess the best SME as compared to other alloy systems.

3.3. Microstructure evolution during thermomechanical cycling

Fig. 4 shows the microstructures of Co8, Cu8, Ni60, Fe4, Fe12 and Fe16 alloys after thermomechanical cycling. Comparing with the initial microstructures prior to thermomechanical cycling [6], the martensite grain boundaries become coarse as indicated by the red arrows in Fig. 4. A large amount of precipitates are present in Co8, Cu8 and Ni60 alloys as shown by the white arrows. The precipitates distribute in martensite as well as at the boundaries between different martensite variants in Co8, Cu8 and Ni60 alloys and also in γ phase in Ni60 alloy. These results suggest that the thermomechanical cycling has high tendency to cause the formation of precipitates. It is also noticeable that a large amount of