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Mechanical and shape memory properties of $Ni_{54}Mn_{25}Ga_{21}$ high-temperature shape memory alloy

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Abstract

The mechanical properties and shape memory effect of polycrystalline $Ni_{54}Mn_{25}Ga_{21}$ (at.%) high-temperature shape memory alloy have been determined by measurement of the compressive stress–strain behavior at different temperatures. The $Ni_{54}Mn_{25}Ga_{21}$ alloy possesses a martensitic transformation temperature as high as 532 K and a tetragonal martensitic structure. The critical stress increases from 190 up to 520 MPa with increasing temperature from 293 to 633 K. When the deformation temperature increases from 293 to 523 K, the obtained recovery strain corresponding to the single martensitic state reduces from 4% to 1.6%. When deformed in a mixed state with martensite and parent phase at 538 K, it exhibits a shape recovery strain of 1.6%. Furthermore, an incomplete pseudoelasticity has been observed when deformed in the parent phase at 633 K.

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Keywords: Ni–Mn–Ga; Shape memory alloy; Martensitic transformation

1. Introduction

Ni_2MnGa is a ferromagnetic Heusler alloy with a bcc $L2_1$ structure at high temperature and shows a martensitic transformation to a complex tetragonal structure [1]. The martensitic transformation temperature (M_s) of Ni–Mn–Ga alloys is sensitive to composition [2], e.g. an increase was found in the order of 25 K/at.% for Ni substitution for Mn, while for Ni substitution for Ga, the increase is in the order of 85 K/at.% [3]. Thus, although M_s of the stoichiometric Ni_2MnGa alloy is as low as 200 K, for non-stoichiometric Ni–Mn–Ga alloys, Ni excess can easily raise M_s up to room temperature, even as high as 620 K [2,3].

Recently, Xu et al. [4,5] reported that $Ni_{54}Mn_{25}Ga_{21}$ single crystal ($M_s = 533$ K) exhibits a shape memory effect (SME) of 6% and a plasticity of 20.5% at room temperature, and an excellent phase transformation and structural stability during thermal cycles up to 10^3 times between room temperature and 623 K. Moreover, a well-pronounced superelastic effect as large as 6% caused by stress-induced martensitic transformation in some high-temperature single-crystalline Ni–Mn–Ga alloys was reported by Chernenko et al. [6]. The excellent shape memory effect and superelasticity, high thermal stability and relatively low cost have made Ni–Mn–Ga alloys as promising high-temperature shape memory alloys (HTSMAs), comparing with other HTSMAs, e.g. Ti–Ni–Hf, Cu–Al–Ni, NiAl, NiMn and Ti–Ni–Pd.

From the viewpoint of practical application, polycrystalline Ni–Mn–Ga alloys are more attractive than single crystals inspect of their extreme brittleness. Jeong et al. [7] reported a plasticity of 3.82% for polycrystalline $Ni_{53.5}Mn_{19.5}Ga_{27}$ including of an elastic strain of 2.2% and a magnetic field induced strain of 0.82%. Li et al. [8] presented the effectiveness of gain refinement on the improvement of the mechanical and SME of polycrystalline Ni–Mn–Ga HTSMA, in which a SME of 4.2% and plasticity near 10% were obtained. Moreover, Besseghini et al. [9] have shown the possibility of hot working of polycrystalline NiMnGa ingots by a special hot-rolling method.

The purpose of the present work is to investigate stress–strain behaviors and SME of polycrystalline $Ni_{54}Mn_{25}Ga_{21}$ HTSMA.

2. Experimental

Polycrystalline button ingots with nominal composition (at.%) of $Ni_{54}Mn_{25}Ga_{21}$ were prepared with high purity ele-

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ment by melting four times in an arc-melting furnace under argon atmosphere. Then alloy rods of approximately 6.8 mm in diameter were made by using a cylindrical copper mold set at the bottom of the furnace. Homogenization was performed by sealing the alloy rods under vacuum in quartz ampoules and annealing at 1273 K for 24 h, followed by water quench.

Samples subjected to the phase transformation measurement, microstructure examination and stress–strain test were cut from the middle part of the rod samples with an electro-discharge machine. Pieces of alloys with average dimensions 10 mm × 1.0 mm × 0.5 mm for optical microscope (OM) observation were mechanically polished and etched at room temperature in a solution of 2.5 g $FeCl_3$ dissolved in nitric acid and methanol (1:50 v/v). Samples for transmission electron microscopy (TEM) were prepared by first grinding to about 50 μm and then thinning using an ion mill method. TEM examinations were carried out on a Hitachi H800 microscope operated at 200 kV. X-ray diffraction (XRD) was carried out for phase identification using a Regaku D/Max 2200 PC diffractometer with Cu Kα radiation. The phase transformation temperatures of the alloy were measured by a Perkin-Elmer DSC-7 differential scanning calorimeter with a cooling/heating rate of 10 K/min. The compression tests were performed on the MTS 880 materials testing system at a cross-head displacement speed of 0.05 mm/min, and the size of the sample is 3 mm in diameter and 5 mm in length. After the compression test, the samples were heated to 673 K to examine the shape memory effect.

3. Results and discussion

The result of differential scanning calorimetry (DSC) indicates that the M_s, M_f, A_s and A_f temperatures of the $Ni_{54}Mn_{25}Ga_{21}$ alloy sample are 532, 504, 571 and 608 K, respectively. Fig. 1 shows the optical morphology and TEM images of the $Ni_{54}Mn_{25}Ga_{21}$ alloy samples at room temperature (293 K). It is seen that $Ni_{54}Mn_{25}Ga_{21}$ sample is composed of equiaxed grains about 200 μm in size. Martensite with twin structure is the single phase can be observed. The TEM bright-field image indicates an internal microstructure of the finer martensitic twins. Fig. 2 shows the powder XRD curve of $Ni_{54}Mn_{25}Ga_{21}$ sample at 293 K. This diffraction curve

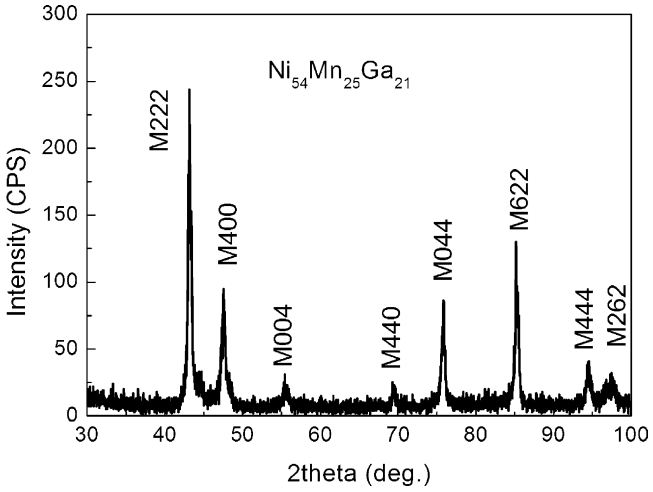

Fig. 2. Powder XRD curve of $Ni_{54}Mn_{25}Ga_{21}$ alloy at 293 K.

exhibits a typical non-modulated martensite of tetragonal structure, which has usually been found in Ni excess Ni–Mn–Ga alloy [3,8], and no other phase is detected. The lattice parameters of $a = 0.7656$ nm, $c = 0.6633$ nm and the tetragonality ratio (c/a) of 0.8664 are calculated from the XRD result. This result is similar to those of $Ni_{53.1}Mn_{26.6}Ga_{20.3}$ ($a = 0.765$ nm, $c = 0.660$ nm and $c/a = 0.863$) and $Ni_{59.0}Mn_{19.4}Ga_{21.6}$ alloys ($a = 0.765$ nm, $c = 0.665$ nm and $c/a = 0.869$) with non-modulated martensite structure reported by Pons et al. [10].

The compressive stress–strain behaviors of $Ni_{54}Mn_{25}Ga_{21}$ samples deformed to a total strain of 8% at different temperatures are shown in Fig. 3. Based on the relationships between the deformation temperatures and the transformation temperatures, the structural states of $Ni_{54}Mn_{25}Ga_{21}$ alloy can be confirmed as martensite at 293 K ($<A_s$, Fig. 3a) and 523 K ($<A_s$, Fig. 3b), as the mixed state of martensite and parent phase at 578 K (between A_s and A_f, Fig. 3c) and as the parent phase at 633 K ($>A_f$, Fig. 3d). Remarkable differences can be seen among four compressive stress–strain curves of $Ni_{54}Mn_{25}Ga_{21}$ samples at various temperatures.

From the compression stress–strain curve of $Ni_{54}Mn_{25}Ga_{21}$ alloy deformed at 293 K as shown in Fig. 3a, it is seen that the initial elastic deformation stage terminates at a strain of 2% and a

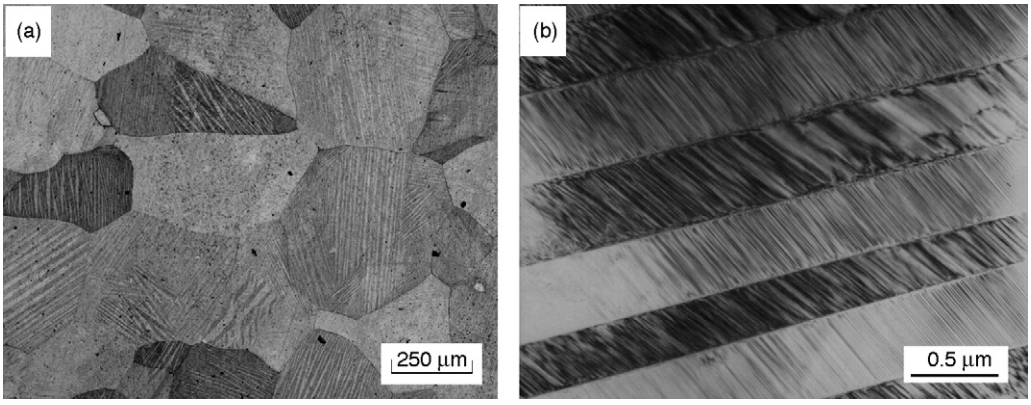

Fig. 1. Optical morphology (a) and TEM bright-field image (b) of $Ni_{54}Mn_{25}Ga_{21}$ alloy.

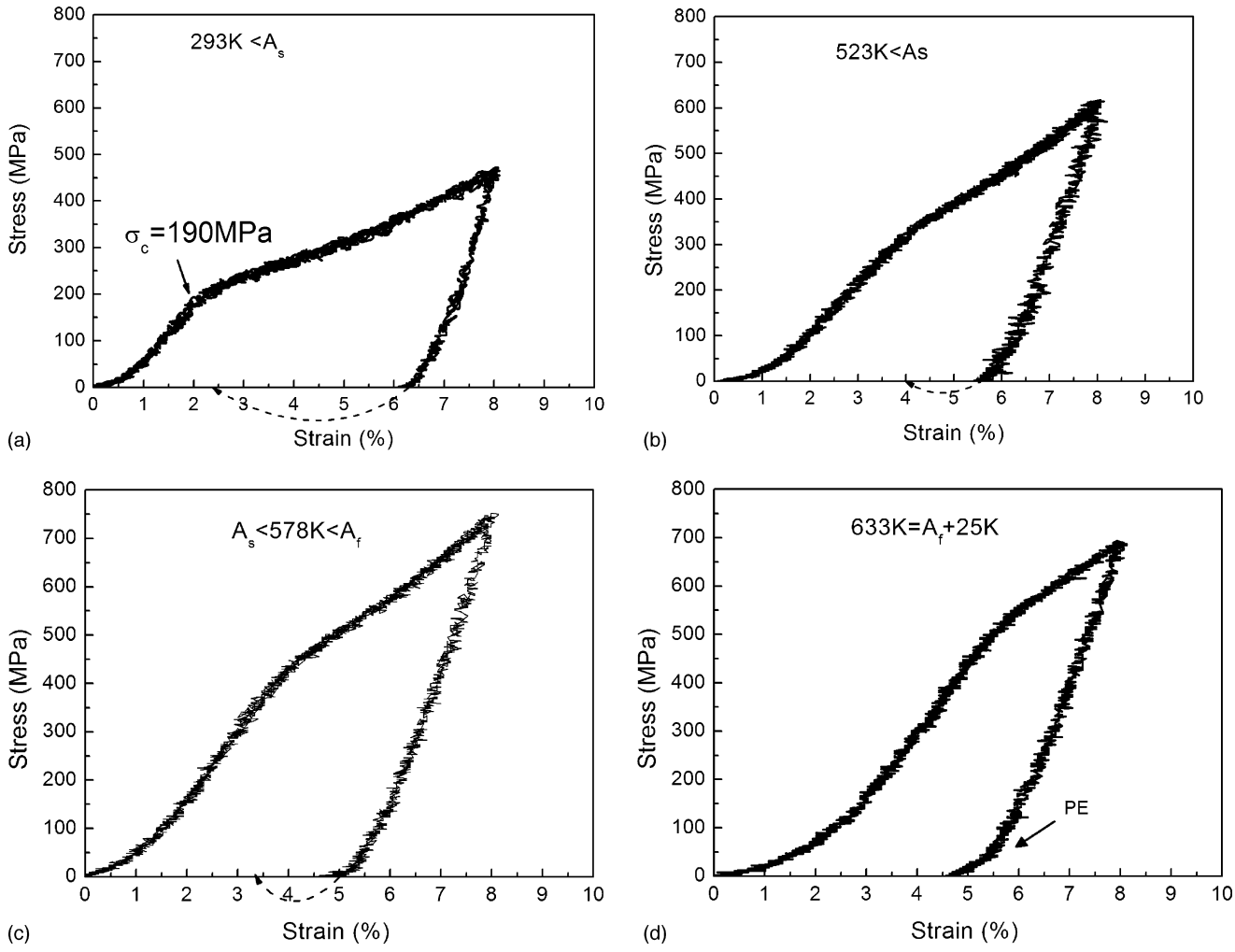

Fig. 3. Compression curves of $Ni_{54}Mn_{25}Ga_{21}$ alloy at different temperatures to a total strain of 8%, (a) at 293 K < A_s, (b) at 523 K < A_s, (c) at A_s < 578 K < A_f and (d) at 663 K > A_f. The dash line means the recovery strain upon heating.

critical stress (designated as σ_c) of 190 MPa, which corresponds to the start point of the reorientation of martensite. The value of critical stress (σ_c) is much higher than that of Ni–Mn–Ga single crystal in non-modulated tetragonal martensite structure corresponding to a typical value of 10–20 MPa [11,12]. Then the deformation process from 2% to 8% corresponds to the reorientation of martensite, although it exhibits unlike a stress plateau, which perfectly appeared in the deformation of single crystal Ni–Mn–Ga alloy [4,11,12]. Finally, a permanent strain of 6.0% is remained after unloading. The dash line implies a partial recovery upon heating and the obtained recovery strain is 4.0% associated with a residual strain of 2.4%. Fig. 3b shows the deformation and recovery behaviors of $Ni_{54}Mn_{25}Ga_{21}$ alloy deformed in martensitic state at 523 K. This process is also composed of reorientation of martensite and shape memory recovery similar to the thermomechanical behaviors as mentioned above. It is noted that the sample exhibits a higher critical stress of 310 MPa and lower recovery strain of 1.6% comparing to the sample deformed at 293 K. The low recovery strain of the latter is due to the relative high critical stress leading to a lager plastic deformation upon loading.

Fig. 3c shows the compression stress–strain behavior of $Ni_{54}Mn_{25}Ga_{21}$ alloy at 578 K. The deformation mechanism appears more complicated than those implicated in Fig. 3a and b, because the sample is in mixed state of martensite and parent phase rather than a single martensitic phase. During the deformation above the critical stress before unloading, the internal mechanism may be attributed to the martensitic reorientation or to the co-occurrence of martensitic reorientation and the stress-induced martensite transformation. The recovery strain is obtained as 1.6% comparable to that in Fig. 3b, and no pseudoelasticity can be observed.

Fig. 3d shows the compression stress–strain behavior of $Ni_{54}Mn_{25}Ga_{21}$ alloy at 663 K. This deformation temperature is 25 K higher than A_f and prefers to a single parent phase of the sample. So, the critical stress at 663 K indicates the deformation of the parent phase or the stress-induced martensite transformation (SIM). It is clearly seen that the unloading curve is deviated from the usual linear elastic change. This may suggestion an incomplete pseudoelasticity due to the SIM. The residual strain as much as 4.7% presents that severe plastic deformation forms upon loading.

Table 1
Shape memory properties of $Ni_{54}Mn_{25}Ga_{21}$ HTSMA deformed at different temperatures to a total strain of 8%

Temperature	Structural state	σ_c (MPa)	Permanent strain (%)	Recovery strain (%)	Residual strain (%)	Recovery ratio (%)
$293\,K < A_s$	M	180	6.4	4.0	2.4	63
$523\,K < A_s$	M	310	5.6	1.6	4.0	29
$A_s < 578\,K < A_f$	M + P	440	5.0	1.6	3.4	32
$663\,K > A_f$	P	520	4.7	0	4.7	0

M: martensite; P: the parent phase; σ_c: critical stress.

The mechanical and shape memory properties of the $Ni_{54}Mn_{25}Ga_{21}$ alloy deformed at different temperature are summarized in Table 1. It is seen that the critical stress of $Ni_{54}Mn_{25}Ga_{21}$ alloy increases with increasing temperature from 293 to 633 K, indicating a higher critical stress in parent phase than in martensite phase, which is consistent with the results on $Ni_{53.1}Mn_{26.6}Ga_{20.3}$ and $Ni_{51.2}Mn_{31.1}Ga_{17.7}$ single crystals in Ref. [6]. However, this result is contrary to the temperature dependence of critical de-twinning stress of non-layered tetragonal martensite of $Ni_{52.8}Mn_{25.7}Ga_{21.5}$ single crystal in Ref. [11]. Thus, more studies should be carried out to clarify the inner mechanism.

4. Conclusion

The compressive stress–strain behaviors and SME of polycrystalline $Ni_{54}Mn_{25}Ga_{21}$ high-temperature shape memory alloy have been investigated. $Ni_{54}Mn_{25}Ga_{21}$ alloy possesses a martensitic transformation temperature as high as 532 K and a tetragonal martensitic structure. The critical stress increases from 190 up to 520 MPa with increasing temperature from 293 to 633 K. When the deformation temperature increases from 293 to 523 K, the obtained recovery strain corresponding to the single martensitic state reduces from 4% to 1.6%.

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