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Structure and shape memory effect in a $Ni_{54}Mn_{25}Ga_{20}Gd_1$ alloy with a high transformation temperature

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ABSTRACT

$Ni_{54}Mn_{25}Ga_{20}Gd_1$ (at.%) alloy with a high transformation temperature has been obtained by substituting 1 at.% Gd for Ga in a ternary $Ni_{54}Mn_{25}Ga_{21}$ shape memory alloy. The microstructure and phase transformations in the $Ni_{54}Mn_{25}Ga_{20}Gd_1$ alloy have been investigated by SEM, TEM, XRD and DSC. The results show that the microstructure of the $Ni_{54}Mn_{25}Ga_{20}Gd_1$ alloy consists of matrix and hexagonal Gd $(Ni,Mn)_4Ga$ phase, and martensitic transformation start temperature (M_s) is 491 K. The compressive strength and the compressive strain are about 958 MPa and 16%, respectively. The complete recovery is obtained from the $Ni_{54}Mn_{25}Ga_{20}Gd_1$ alloy as the pre-strains are no more than 3%. The maximum shape memory strain is achieved in $Ni_{54}Mn_{25}Ga_{20}Gd_1$ alloy with pre-strain of 4%, and the shape memory strain and recovery ratio are 1.9% and 87.5%, respectively. The two-way shape memory effect is also observed in $Ni_{54}Mn_{25}Ga_{20}Gd_1$ alloy.

1. Introduction

High-temperature shape memory alloys (HTSMAs) have attracted much attention in high-temperature filed, such as aerospace, nuclear power, fire, oil and gas exploration, etc. Current HTSMAs systems include Cu-based alloys, NiAl, NiTi-based alloys (NiTiHf, NiTiZr, NiTiPd, etc.)[1–7], but until now some problems have remain unresolved. The brittleness of NiTiZr and NiTiHf limits their practical use [1,2]. NiAl and Cu-based HTSMAs are considered unstable [4,5] because of precipitate phase formed at high temperature, which are detrimental to the shape memory effect. As for the NiTiPd alloys, their full recovery strains have been increased to 5.5% by proper thermomechanical treatment [6], but the high cost of precious metal Pd hinders its application. In recent years, Ni–Mn–Ga shape memory alloy receives more and more interests for its large magnetic field-induced strain and high response frequency [8]. It is also expected to become an excellent candidate of the high-temperature shape memory alloys by adjusting the composition [9]. Xu et al. reported that a HTSMA was developed, and a SME of 6.1% was observed in $Ni_{54}Mn_{25}Ga_{21}$ single crystal with martensitic transformation temperature higher than 250 °C [10]. This SME remains almost unchanged even after 1000 thermal cycles. Unfortunately, the extreme brittleness of the polycrystalline Ni–Mn–Ga alloys limits their practical applications. There has been growing interest in improving the ductility of Ni–Mn–Ga alloys by adding the fourth element. Zhao et al. reported that by adding rare earth Tb or Sm elements, the bending strength of NiMnGa alloys could be increased to some extent [11,12]. Ma et al. found out that the addition of Cu and Cr significantly improved the compressive ductility of the alloy [13,14]. Gao et al. discovered that the addition of Gd, Dy and Y substituting Ga significantly improved the compressive ductility and martensitic transformation temperature of the $Ni_{50}Mn_{29}Ga_{21}$ alloy [15–18]. The fact that has been confirmed rare earth addition can toughen Ni–Mn–Ga shape memory alloys. In the present paper, the rare earth Gd was added into the $Ni_{54}Mn_{25}Ga_{21}$ high-temperature shape memory alloy to improve its mechanical properties. The microstructure, crystal structure, phase transformation behavior, and SME of the $Ni_{54}Mn_{25}Ga_{20}Gd_1$ alloy have been investigated.

2. Experimental

The nominal compositions of the alloys studied were $Ni_{54}Mn_{25}Ga_{21}$ and $Ni_{54}Mn_{25}Ga_{20}Gd_1$ (at.%). High-purity starting element nickel (99.99%), manganese (99.95%), gallium (99.99%) and gadolinium (99.95%) were melted in a non-consumed vacuum arc furnace under argon atmosphere for preparation of $Ni_{54}Mn_{25}Ga_{21}$ and $Ni_{54}Mn_{25}Ga_{20}Gd_1$ 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 phase transformation temperatures were determined by Perkin-Elmer diamond differential scanning calorimetry (DSC) with heating and cooling rate of 20 K/min. The phase structure of the alloys was identified by an X'Pert PRO MPD diffractometer with CuKα radiation (XRD). The microstructures of the alloys were examined using an XJP-6A optical micrographs and a MX2600FE scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscopy (EDS) analysis system and a FEI TECNAI G2 20 STWIN 200 kV transmission electron microscope equipped with a double-tilt cooling stage (TEM). Thin-foil specimens for TEM characterization were mechanically polished to about 80 μm

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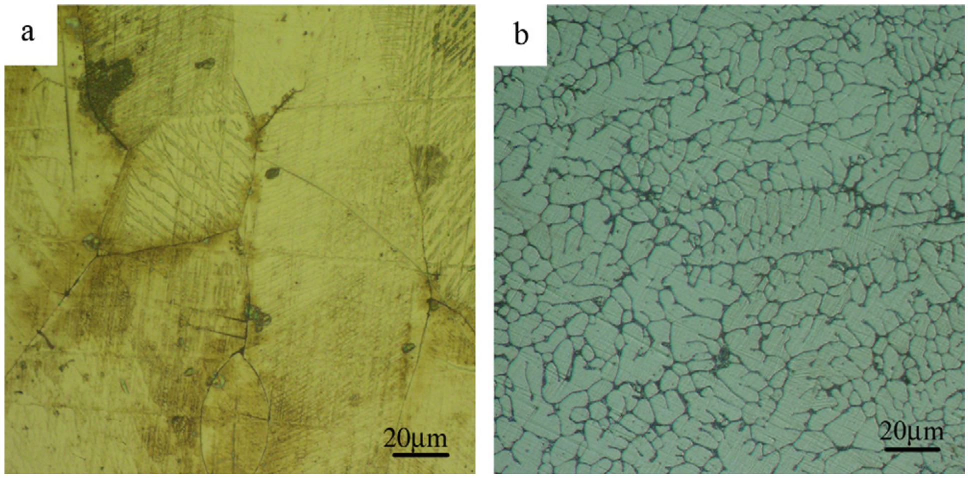

Fig. 1. Optical micrographs of solution treated (a) $Ni_{54}Mn_{25}Ga_{21}$ and (b) $Ni_{54}Mn_{25}Ga_{20}Gd_1$ alloys.

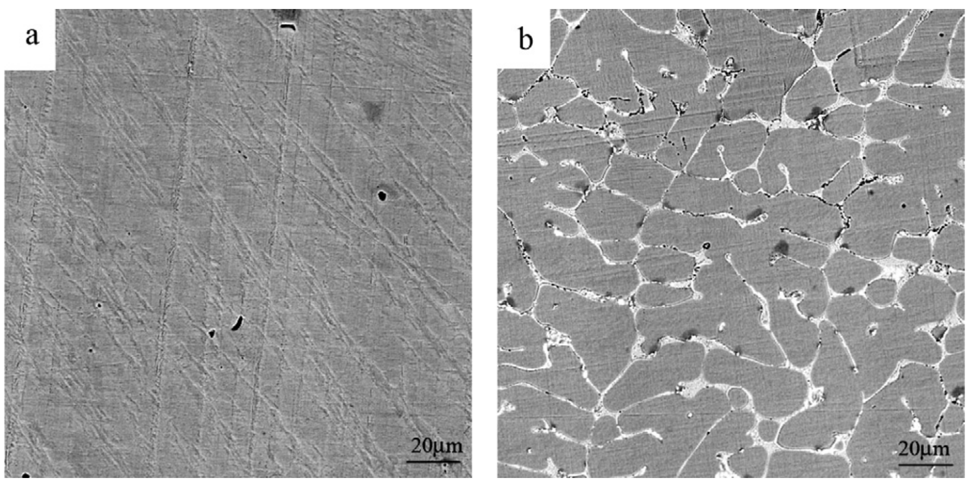

Fig. 2. Backscattered electron images of solution treated (a) $Ni_{54}Mn_{25}Ga_{21}$ and (b) $Ni_{54}Mn_{25}Ga_{20}Gd_1$ alloys.

and twinjet electropolished with an electrolyte of nitric acid and methanol (3:7 in volume) at around 258 K. The mechanical properties and shape memory effect were studied by compressive tests in an Instron-5569 universal mechanical testing machine. The sample dimensions are Φ 4 mm × 6 mm and deformation rate is 0.2 mm/min.

3. Results and discussion

Fig. 1 shows the optical micrographs of solution treated $Ni_{54}Mn_{25}Ga_{21}$ and $Ni_{54}Mn_{25}Ga_{20}Gd_1$ alloys. It is evident that the crystal sizes of Ni–Mn–Ga–Gd alloys are refined from 90 μm to 15 μm by adding rare earth Gd. Fig. 2 shows the backscattered electron images of the $Ni_{54}Mn_{25}Ga_{21}$ and $Ni_{54}Mn_{25}Ga_{20}Gd_1$ alloys. It can be seen that the $Ni_{54}Mn_{25}Ga_{21}$ alloy exhibits a single-phase structure, whereas the $Ni_{54}Mn_{25}Ga_{20}Gd_1$ alloy contains a brightly imaging second phase along the grain boundaries. The compositions of the matrix and second phase of the experimental alloys measured by EDS are listed in Table 1. It can be seen that only 0.2 at.% Gd is detected in the matrix, which means the solid solubility of Gd in the matrix is very low. The Gd addition results in the formation of the Gd-rich phase along the grain boundaries. As shown in Table 1, the Mn content in the matrix of $Ni_{54}Mn_{25}Ga_{20}Gd_1$ alloy is increased, and the Ga content is decreased. The Gd-rich

Table 1
The EDS results of the $Ni_{54}Mn_{25}Ga_{21}$ and $Ni_{54}Mn_{25}Ga_{20}Gd_1$ alloys (at.%).

Composition	Phase	Ni	Mn	Ga	Gd
$Ni_{54}Mn_{25}Ga_{21}$	matrix	54	25.5	20.5	–
$Ni_{54}Mn_{25}Ga_{20}Gd_1$	matrix	53.9	26.3	19.6	0.2
	second phase	57	20	12.5	10.5

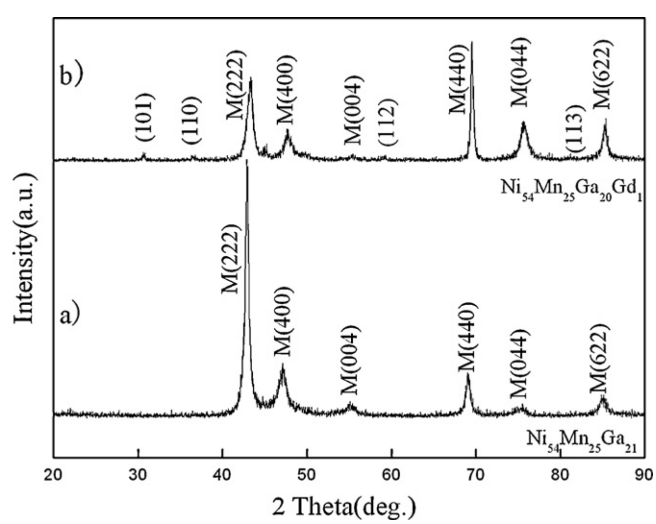

Fig. 3. X-ray diffraction pattern of $Ni_{54}Mn_{25}Ga_{21}$ and $Ni_{54}Mn_{25}Ga_{20}Gd_1$ alloys at room temperature.