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# Effect of pre-strain on martensitic transformation of Ni<sub>43</sub>Mn<sub>43</sub>Co<sub>7</sub>Sn<sub>7</sub> high- temperature shape memory alloy

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#### 1. Introduction

High-temperature shape memory alloys (HTSMAs), as a kind of important shape memory alloys (SMAs), have attracted significant attention for their potential application at high temperatures (above 100 °C) [1–3]. During the last decades, several HTSMAs have been developed, including Cu-, NiAl-, TiNi- and Zr-based alloys [4-6]. However, for each alloy system there exist different disadvantages which limit their application. Therefore, it is necessary to develop new alloy systems. It has been reported that NiMn alloy containing 5-10% Ti and Al is also a promising HTSMAs with transformation temperature up to 400 °C [7.8]. Shape memory effect, microstructure and martensitic transformation behavior of NiMnTi(Al) allov have been studied by Potapov et al. [7,8]. However, the brittleness of such alloys becomes an obstacle for further development. Recently, some compositional NiMnGa alloys with a Ni or Mn content higher than the stoichiometric Ni<sub>2</sub>MnGa have been confirmed to undergo transformation at high temperature [9-12]. Ma et al. [13] found Ni<sub>56</sub>Mn<sub>21</sub>Co<sub>4</sub>Ga<sub>19</sub> alloy has greatly improved hot workability and ductility (about 8% tensile strain), high martensitic transformation temperature ( $M_s = 412$  °C) and recoverable strain of 2.1% under a residual strain of 4.3%. Since that, NiMn-based HTSMAs attract a lot of attention once more. However, the  $\gamma$  phase formed in such alloys usually deteriorates shape memory effect due to the impedance effect on the reorientation of martensitic variant [9].

#### ABSTRACT

In the present work, the effect of pre-strain on martensitic transformation of  $Ni_{43}Mn_{43}Co_7Sn_7$  (at.%) alloy was investigated. The results show that  $Ni_{43}Mn_{43}Co_7Sn_7$  alloy undergoes a martensitic transformation at 288 °C upon cooling. The thermal cycling does not affect the transformation behavior of the alloy, indicating the good thermal stability. The reverse transformation of the deformed martensite is pre-strain dependent. When the pre-strain is higher than 7.5%, the reverse transformation occurs in two-stage manner upon first heating due to the nonuniform martensite deformation. In contrast, during the first martensitic and second reverse transformation, the pre-strain shows little effect on the transformation temperatures.

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Very recently, the present authors found that the doping of both Co and Sn into NiMn is effective in preparing HTSMA [14]. The transformation temperature of Ni<sub>43</sub>Mn<sub>41</sub>Co<sub>7</sub>Sn<sub>9</sub> alloy can reach up to 200 °C [14]. Based on this alloy, by adjusting the ratio of Co to Sn, another HTSMA (Ni<sub>43</sub>Mn<sub>43</sub>Co<sub>7</sub>Sn<sub>7</sub>) with higher  $M_s$  is presented in the work. It is generally accepted that the pre-strain significantly influences martensitic transformation behavior in most of the shape memory alloys [15]. In the present work, microstructure and martensitic transformation of a Ni<sub>43</sub>Mn<sub>43</sub>Co<sub>7</sub>Sn<sub>7</sub> alloy was investigated. The emphasis was placed on the effect of pre-strain on the transformation behavior.

#### 2. Experimental procedures

An alloy with the nominal composition of  $Ni_{43}Mn_{43}Co_7Sn_7$  (at.%) was prepared by arc melting under an argon atmosphere using highpurity elements. The button ingot was melted five times and cast into a chilled copper mold to obtain a master rod with a diameter of 10 mm and a length of 60 mm. The rods were sealed in quartz tubes under a vacuum and then annealed at 900 °C for 6 h followed by quenching into ice water for chemical homogeneity.

The microstructure of the alloys was examined by optical microscope. The X-ray diffraction (XRD) was carried out on a PANalytical Xpert'pro diffractometer using Cu K $\alpha$  radiation. The phase transformation behavior of the alloys was studied using a Perkin Elmer Diamond differential scanning calorimetry (DSC). The heating and cooling rate was 20 °C /min. In order to examine the effect of pre-strain on the transformation behavior, the samples were pre-compressed to a specific strain  $\varepsilon$  at room temperature (25 °C) and then placed in DSC for complete thermal cycling (the first step is heating). The compression

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tests were performed on an Instron-3365 materials testing system at a cross-head displacement speed of 0.05 mm/min. The size of the samples for the compression test was  $2 \text{ mm} \times 2 \text{ mm} \times 4 \text{ mm}$ .

#### 3. Results and discussion

Fig. 1 shows the XRD pattern and optical micrograph of Ni<sub>43</sub>Mn<sub>43-</sub>Co<sub>7</sub>Sn<sub>7</sub> alloy at room temperature. The diffraction peaks can be indexed a martensite with a tetragonal structure by the following lattice parameters: a = b = 0.7803 nm, c = 0.6941 nm. In comparison with the XRD results in other NiMn-based alloys [7], it is shown that Ni<sub>43</sub>Mn<sub>41</sub>Co<sub>7</sub>Sn<sub>7</sub> alloy undergoes a transformation from B2 parent phase to the tetragonal martensite. The optical image shown in Fig. 1 (b) exhibits a typical martensite microstructure, which is confirmed by the XRD result in Fig. 1(a).

Fig. 2(a) shows the transformation behavior of the annealed  $Ni_{43}Mn_{43}Co_7Sn_7$  alloy after different thermal cycles. The sample shows a typical martensitic transformation with a hysteresis of 15 °C, which is 9 °C smaller than that of NiMnTi alloy [8]. The start and finish temperatures are determined to be  $M_s = 288$  °C and  $M_f = 242$  °C for the forward transformation and  $A_s = 268$  °C and  $A_f = 303$  °C for the reverse transformation, respectively. Transformation peaks T<sub>A</sub> and T<sub>M</sub> are 292 °C and 271 °C, respectively. DSC measurements of the transformation behavior over 5 consecutive thermal cycles show that the thermal cycling does not affect the transformation behavior of the alloy, indicating the good thermal stability.

Fig. 2(b) shows the transformation behavior of the annealed  $Ni_{43}Co_7Mn_{43}Sn_7$  alloy subjected to 10.1% deformation, in which the superscripts denote the transformation sequence, subscript M for the forward martensitic transformation and A for the reverse martensitic



Fig. 1. (a) XRD pattern and (b) optical image of  $\rm Ni_{43}Mn_{43}Co_7Sn_7$  (at.%) alloy at room temperature.



**Fig. 2.** Transformation behavior of the annealed  $Ni_{43}Mn_{43}Co_7Sn_7$  alloy after (a) different thermal cycles, the number of thermal cycles is indicated and (b) deformation to 10.1%.

transformation. Upon the first heating, two transformation peaks were detected, where the corresponding characteristic transformation temperatures are called  $T_A^{1-1}$  and  $T_A^{1-2}$ , respectively. In addition,  $T_{A}^{2}$ ,  $T_{M}^{2}$  and  $T_{M}^{1}$  represent the characteristic temperatures of transformation peaks for the second reverse transformation, the second and the first forward martensitic transformation, respectively. It is observed that both  $T_A^{1-1}$  and  $T_A^{1-2}$  shift to high temperature compared with that of the undeformed sample (Fig. 2(a)), implying the martensite is stabilized by the deformation. In the second cycle, the reverse transformation occurs in a manner similar to that of the undeformed sample, which indicates that the stabilization is a onetime effect. For the forward martensitic transformation, on the other hand, little difference is observed between the first and second cycle. During the subsequent thermal cycles, the transformation behavior of the deformed sample keeps stable as the undeformed one shown in Fig. 2(a).

For SMAs, the stored elastic energy caused upon cooling against the forward transformation assists the reverse transformation. If such elastic energy is relaxed the reverse transformation temperature will be changed. It has been accepted that, in polycrystalline SMAs, the stored elastic energy will be relaxed by twin boundaries movement and by slip by the movement of dislocation resulting from the predeformation[16]. Such relaxation is a one-time effect. Thus only the reverse transformation was affected in the first heating cycle by prestrain.

DSC curves of the samples subjected to different pre-strains for the first heating, first cooling and second heating cycles are shown in Fig. 3(a-c). Upon the first heating, when the deformation is lower

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