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Structural and magnetic characterization of martensitic Ni₂MnGa polycrystalline ferromagnetic shape memory alloy

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ABSTRACT

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Ferromagnetic shape memory alloys (FSMAs) are keenly investigated due to their Shape Memory Effect (SME), high frequency response and large magnetic field-induced strain. Polycrystalline Ni_{53.2}Mn_{24.6}Ga_{22.1} alloy was synthesized by arc-melting technique. X-ray diffraction revealed that annealed alloy at 1073 K exhibit a well-defined 5M structure .Scanning Electron Microscope image confirms the twinned martensite plate with magnetic domain walls. It is worthy to notice that a high saturation magnetization of 65 (emu/g) and martensitic transformation temperature of T_M (334 K) are found by Vibrating Sample Magnetometer and Differential Scanning Calorimetry.

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Introduction

Ni₂MnGa FSMAs are prominent candidate for new class of actuator and sensor materials that deform under a magnetic field. FSMAs are materials which exhibit large changes in shape and size in magnetic field [1-2]. The key factor behind this phenomenon is a thermoelastic structural phase transition called martensitic transformation (MT). The high temperature austenitic parent phase is transformed into low temperature martensitic phase (Cubic-Tetragonal or Orthorhombic/monoclinic). This leads to the formation of a new class of actuators showing higher frequency and higher response. These materials exhibit a large strain of 6-10% [3-4] when subjected to magnetic field due to the reorientation of twin variants in martensitic phase. The possible martensite structures are explained by Pons and U. Gaitzsch et al. [5-6] and are indicated as 5M, 7M, and NM, respectively. All these structures are derived from the cubic $L2_1$ Heusler phase, which is the equilibrium at high temperature (austenite) phase for both stoichiometric and off-stoichiometric compounds.

In conventional SMAs, which are paramagnetic, the martensitic transformation underlying the SME is induced by changes in temperature or stress or both. In spite of the large strain achieved, the activation of the thermo elastic SME is slow and inefficient because it depends on the transportation of heat, i.e. heating, especially cooling of the sample. On the other hand, FSMAs alloys have more recently emerged as an interesting addition to this class of materials. In particular, Ni-Mn-Ga has generated immense interest because of very large strain in a moderate magnetic field (1 Tesla). Moreover, in Ni-Mn-Ga the actuation is much faster than in conventional SMA. The MT in FSMAs can be triggered not only by changes in temperature and stress, but also by changes in the applied magnetic field.

Many FSMA systems have been developed such as Ni₂MnGa [7], Ni₂MnAl [8], Co–Ni–Ga (Al) [9, 10], and Ni–Fe–Ga [11], Fe-Pd [12], Fe-Pt [13], Ni-Mn-In [14], Ni-Mn-Sn [15]

and Ni-Mn-Sb [16]. There are many reports on their structure, magnetic properties, martensitic transformation, magnetically controlled shape memory effect, super elasticity and MFIS. Among these, Ni₂MnGa is one of the prototypical FSMAs; the martensitic temperature is reported to be around 210 K, while the Curie temperature (T_C) is around 370 K [17]. At present, SMAs can perform at a temperature below 390 K, but few industries such as robotic, automotive, aerospace, require SMAs that operate at higher temperatures. However, Cu-Ni-Al, Ti-Pt and Ni-Ti-based alloy, Zr based quasi binary [18, 19], Ta-Ru [20-22] and Nb-Ru [22] have been intensively studied and the results have been documented in [23-26]. At high temperature, Cu-based and NiAl HTSMAs are considered unstable because equilibrium phases which are detrimental to SME and the precipitate. Moreover, Ni-Ti-Zr and Ni-Ti-Hf are too brittle for practical use. Therefore, this study is attempted to explore HTSMA with presence of shape memory effect related martensitic transformation.

The main purpose of the present paper is to study the martensitic phase transformation behaviors and micro-structural properties of high temperature polycrystalline Ni–Mn–Ga alloy. **Experimental Procedure**

 $Ni_{53.2}Mn_{24.6}Ga_{22.1}$ was preferred to the stoichiometric Ni_2MnGa to increase the transformation temperature much higher than room temperature. Polycrystalline Ni-Mn-Ga alloy has been prepared using conventional arc melting technique in argon atmosphere. High purity raw elements Nickel (99.99%), Manganese (99.8%) and gallium (99.99%) were used and melted. To ensure better homogeneity in the samples, ingots were inverted and melted again and process was repeated four times. The composition of the resultant powder was found to be $Ni_{53.2}Mn_{24.6}Ga_{22.1}$ using inductively coupled plasma optical emission spectroscopy (ICP-OES) technique. The ingot was annealed for 24 hrs at 1073 K using high temperature furnace for homogeneity. The powder X-ray diffraction (Raigaku RINT)

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2500) measurement has been carried out to study the crystal structures using Cu K α radiation in the angle 0° < 2 Θ < 90° with a step of 0.05° and a holding time of 2 s for each step at room temperature. The transformation temperatures have been measured using a differential scanning calorimeter (DSC), model Q100 (M/s TA Instruments, USA) under constant heating and cooling rates of 5 K min-1. Microstructure analysis was systematically studied by means of Scanning Electron Microscope (SEM-ZEISS). The magnetic properties of the alloy were investigated using Vibrating Sample Magnetometer (VSM-883 A).

Results and Discussion

Crystal structure of Ni-Mn-Ga FSMA

The crystal structure of the martensite is an important factor that affects the magnetic and mechanical properties of ferromagnetic Ni-Mn-Ga alloys [27, 28]. Figure 1 shows the Xray diffraction pattern of Ni53.2Mn24.6Ga22.1 alloy at room temperature. The Ni_{53.2}Mn_{24.6}Ga_{22.1} alloy was annealed at 1073 K to have tetragonal structure, which can be seen from the three main peaks such as (222), (400), and (440) are marked. From these prominent peaks, the lattice parameters of the crystal are calculated as a=b=0.5941 & c= 0.5618 which confirms the martensite tetragonal structure. These values are close to the earlier reported values [29, 30]. It is reported that the e/a ratio is plaving a vital role in determining structure. Electron-to atom (e/a) ratio at e/a < 7.7, a modulated structure occurs, whereas for e/a >7.7 the non-modulated structure is stable [31]. However e/a ratio for present alloy is 7.705. The e/a ratio is calculated by assuming the valence electrons 10 for Ni (3d8, 4s2), 7 for Mn (3d5, 4s2), and 3 for Ga (4s2, 4p1), respectively. The single phase tetragonal structure with a reflection of (222), (400), and (440) peaks are corresponding to typical modulated structure (i.e. c/a<1). The basic unit cell of 5M phase structure is often approximated to a tetragonal or monoclinic structure [32-34].



Figure. 1. XRD pattern of Ni_{53,2}Mn_{24.6}Ga _{22.1} Polycrystalline alloy

Phase Transformation

The transformation temperatures were measured by using Differential Scanning Calorimeter (DSC-Perkin Elmer) with heating and cooling rates of 5 K min-1. The resulting DSC measurement shows the forward (cooling) and reverses (heating) martensitic transformations and displayed in Fig. 2 for Ni_{53.2}Mn_{24.6}Ga _{22.1} polycrystalline alloy. It can be seen that exothermic and endothermic peaks in the cooling and heating DSC curves respectively, represents the appearance of phase transformation. The martensite start temperature (M_s) and its finishing temperature (M_f) during cooling and the austenitic start temperature (A_s) and its finishing temperature (A_s) and t

334 K, it is calculated using $T_M = (A_f + M_S)/2$ [35]. As reported by Tong and Wayman [14], in thermoelastic martensitic transformations, the transformation hysteresis is defined by the temperature difference between A_f and M_s . Similarly, the temperature difference between A_s and M_f is also taken as transformation hysteresis. Here, the transformation hysteresis defined as $DTH = A_f - M_s$. It is found that DTH = 15K.



Figure. 2. DSC curve of Ni_{53,2}Mn_{24.6}Ga _{22.1} polycrystalline allov

Scanning electron microscopy

The microstructure of polycrystalline $Ni_{53.2}Mn_{24.6}Ga_{22.1}$ alloy was analyzed using high-resolution scanning electron microscope at room temperature and shown in Fig. 3a. As seen in Fig. 3a, there is no evidence of impurity and fracture. It is very important to take great concern in handling and polishing the sample to protect it from 'damaging' of the structural arrangement of magnetic domains. The twinned martensitic crystal structure plays an important role during the rearrangement of the twin variants. It is well known that a series of plane parallel twin constitutes the simplest of martensite structures. It is observed, the sample consists of twinned martensite with magnetic domain walls extending over many twins.



Figure. 3a). SEM image of Ni_{53.2}Mn_{24.6}Ga _{22.1} polycrystalline allov



b) Inset of figure 3a showing the twin variant Magnetic Studies

M Vs H is plotted for the prepared $Ni_{53,2}Mn_{24,6}Ga_{22,1}$ polycrystalline alloy. The ferromagnetic hysteresis loop of the specimen was recorded at room temperature in magnetic field range of +20 kOe to -20 kOe. Ni-Mn-Ga alloys has easy and

hard axis of magnetization which depends on the crystallographic direction. Generally c-axis is the easy axis of magnetization. The analysis of the curve is shown that the annealed Ni–Mn–Ga polycrystalline alloys exhibit good soft magnetic properties. The crystal structure of material plays a vital role in determining the magnetic moment of the material. The characterized results show narrow hysteresis loop, low coercivity and high magnetic-saturation value. Ferromagnetic nature is observed even at the low magnetic field. The values of coercivity and saturation magnetization are calculated to be 29.24 Oe and 65emu/g.



Figure. 4. Magnetization hysteresis loop for Ni_{53.2}Mn_{24.6}Ga _{22.1} polycrystalline alloy

Conclusion

It is confirmed the 5M modulated tetragonal structure at room temperature. The SEM image confirms the martensitic plate. High martensitic transformation temperature was achieved in $Ni_{53.2}Mn_{24.6}Ga_{22.1}$ polycrystalline alloy for high temperature applications such as robotic, automotive, and aerospace.

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