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Characterization and properties of ferromagnetic shape memory alloys

*F. Ahmad Khalid**, *S. Zameer Abbas*

Faculty of Materials Science and Engineering, GIK Institute of Engineering Sciences and Technology, Topi, KPK, Pakistan

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ABSTRACT

Ni–Mn–Ga shape memory alloys are employed for applications in actuators and sensing devices. These alloys exhibit ferromagnetic shape memory effect with large reproducible strains in moderate magnetic fields. This work presents a study of the effect of composition and annealing treatment on the microstructure and magnetic properties in Mn-rich off-stoichiometric Ni–Mn–Ga alloys. Modulated martensitic structure ($c/a<1$) with hierarchical twins was found at room temperature in alloys with Mn≥28 at.% whereas the alloy containing higher Ga (>22 at.%) revealed austenitic structure at room temperature. Ferromagnetic nature of the alloys was confirmed by the magnetization curves. It is demonstrated that a maximum of 400 parts per million strain was measured in the alloy with 7 M martensitic structure at room temperature.

1. Introduction

Ferromagnetic shape memory alloys are well-known to exhibit short response time and large reversible strains owing to high stability of ferromagnetic martensite, modulated structure, high magnetocrystalline anisotropy (MCA) and high saturation magnetization [1,2]. For high temperature applications, high T_C is also an important requirement [3]. Ni–Mn–Ga ternary alloys are characterized by high frequency actuation and large strains that is typical for giant strains in single crystals at ambient temperatures [4]. Various types of martensitic phases occur in Ni–Mn–Ga alloys depending upon composition and thermomechanical treatment.

These alloys also display thermally induced shape memory effect, magnetic field assisted superelasticity, and magnetocaloric effect in addition to magnetic shape memory effect [5,6]. The main applications of ferromagnetic shape memory alloys include actuators, proportional fluid valves, linear motors and sensors [7]. Attempts have also been made to produce metallic foam and composite materials for light weight and vibration damping components [8–10].

Generally these alloys are difficult to produce owing to large variation in the melting points of Ni, Mn and Ga which are 1455 °C, 1246 °C and 29.6 °C respectively [11]. Stoichiometric Ni2MnGa alloy solidifies (starts to melt at ~1380 K) into cubic B2 structure where Ni occupies the body centered site, and Mn and Ga are distributed among the corner sites of the unit cell [12]. It is reported that in these alloys during solidification, B2 phase undergoes an ordering transformation to $L2_1$ structure, which, further transforms to a thermoelastic martensite at a lower temperature (below room temperature for a stoichiometric composition) [12]. Furthermore, the modulated martensite in the near stoichiometric Ni–Mn–Ga alloys is known to produce magnetic field induced strain that is essential for commercial applications [13]. The necessary condition for magnetic field induced strain is that the stress required to move the twin boundaries should be less than the stress produced on the twin boundaries by an applied magnetic field. For large magnetic

* *Corresponding author*. Tel.: +92 938 271858; fax: +92 938 271880.
E-mail address: khalid@giki.edu.pk (F.A. Khalid).

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fields the magnetic stress τ_{mag} saturates to $\tau_{max \cdot mag}$. In order to make magnetic field induced strain (MFIS) possible a high value of magnetocrystalline anisotropy (K_U) is also required. For perfectly oriented single crystals $\tau_{max \cdot mag}=K_U\, s^{-1}$ where s^{-1} is the twin shear as reported in [14].

It is demonstrated that twinning stress increases with a decrease in the temperature below transformation temperature, therefore, maximum strain is expected near the transformation temperature in the martensitic state. It also reduces the amount of total strain produced and increases the reversibility [15]. Therefore, 100% reversibility depends upon the processing parameters and test conditions. A reduction in the maximum strain from 6% (at 223 K) to 5% (at 307 K) was reported in [16]. In previous work [17] difference in composition, structure (lattice parameters), defects and grain size of the alloys are the factors that influence the maximum strain is reported. The magnetomechanical training helps to reduce the number of variants and remove any locking mechanisms thus increasing the value of strain achieved in a magnetic field.

This study presents the progress on development of ferromagnetic alloys and analysis of microstructural phases and magnetic properties of homogenized and annealed off-stoichiometric polycrystalline Ni–Mn–Ga alloys that has not been fully reported previously.

2. Experimental Procedure

High-purity nickel, manganese and gallium elements were used to make three different alloy compositions. These alloy buttons were arc melted and cast into cylindrical rods of 9 mm diameter in a water cooled copper mold. The ingots were vacuum sealed in quartz tubes and homogenized. The alloys were homogenized at 1000 °C for 24 h followed by furnace cooling. These alloy samples were then annealed at 600 °C for 10 h prior to testing and examination. Crystal structure and phases at room temperature were determined by Philips PW3710 X-ray diffractometer with Cu K_α radiation. Electron microscopy and compositional analysis was done by using Philips XL30 scanning electron microscope with an attached energy dispersive spectrometer (EDS). The transformation temperatures of the Ni–Mn-Ga alloys were determined by Perkin Elmer differential scanning calorimeter (DSC) model-7 using a scan rate of 10 °C/min. Magnetization loops were obtained using Lakeshore 450 vibrating sample magnetometer (VSM). Training of the samples were done by placing the sample under a static load of 6 kg in the longitudinal and then in the transverse direction for a time of 10 s. The process was repeated 3 times. A short magnetic field training was also applied by placing the samples axially in a moderate magnetic field of 300 kA/m for 5 s and then placing it in a transverse direction to the same magnitude of magnetic field for 5 s. This procedure was repeated three times. Magnetic field induced strain was measured at room temperature by attaching a strain gauge (EP-08-250BF-350) along the periphery of the cylindrical samples with the terminals connected to a P3500 strain indicator of Vishay Instruments. The sample was held by a rubber damper attached to a wooden screw in a wooden sample holder as shown in Fig. 7. The assembly was placed between the poles of an electromagnet (Lakeshore 450 VSM). The field was applied transverse to the cylindrical axis of the sample. These measurements were performed in a magnetic field strength starting from zero to 1200 kA/m with intervals of 80 kA/m. The samples used were 9 mm in diameter and ~6 mm in height.

3. Results and Discussions

3.1. *Transformation Behavior*

The chemical compositions and electron concentration (e/a) values determined in the alloys are given in Table 1. The number of valence electrons per atom for Ni, Mn, Ga atoms are 10 ($3d^8$, $4s^2$), 7($3d^5$, $4s^2$) and 3($4s^2$, $4p^1$), respectively [5]. The electron to atom ratio (e/a) was calculated using the electron concentration of the outer shells for each element of the Ni–Mn–Ga alloy. The following expression is used to calculate e/a ratio as described in detail in [5].

$$e/a = [10x_{Ni} + 7x_{Mn} + 3x_{Ga}]/[x_{Ni} + x_{Mn} + x_{Ga}]$$

x= atomic percent of the element

Fig. 1 shows the DSC curves of three samples of alloys in homogenized and annealed conditions. It appeared that the transformation temperatures in Ni–Mn–Ga alloys are very much dependent upon the electron concentration i.e., e/a ratio.

Considering the DSC curves of the alloys, shown in Fig. 1, the transformation temperatures decreased with decrease in e/a due to decline in the concentration of both Ni and Mn. T_M (martensitic transformation) and T_C (curie transformation) coincide at an e/a ratio of ~7.67 as in alloy 1. Decreasing e/a ratio below 7.67 resulted in an increase in T_C and a decrease in T_M values. Annealing near the ordering temperature is expected to the decrease the temperature range in which the structural transformation takes place thus improving the shape memory behavior [18].

The martensitic transformation temperature dropped from 355 to 335 K due to decrease in the e/a (from 7.67 for alloy 1 to 7.58 for alloy 2). Currie temperature (T_C) appears as a step like feature in the DSC curves. In alloy 3 (Fig. 1), the step at 373 K in the heating curve represents T_C, indicating transition from a ferromagnetic to a paramagnetic state in the alloy. On cooling, the paramagnetic to ferromagnetic transition occurred at 369 K. The phase transition in alloys 2 and 3 occurred in the ferromagnetic state since the T_C is above the structural transformation range. The martensitic transformation which did not occur in alloy 3 (Fig. 1) has occurred below 320 K. The curie temperature of alloy 1 is not identified in the DSC curve but considering similar compositions reported in the literature [19], it is assumed to be within the transformation temperature range.

Table 1 – Chemical composition and e/a ratio of the alloys.

Alloy	Ni (at.%)	Mn (at.%)	Ga (at.%)	e/a
1	50.6	28.3	21.1	7.67
2	48.0	30.6	21.5	7.58
3	48.1	28.1	23.8	7.49