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Research Paper

Structural and Magnetic Transformation in Ferromagnetic Ni-Mn-Ga Alloy

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This article covers the detailed study on the preparation and characterization of ferromagnetic Ni-Mn-Ga shape memory alloy. Annealing the polycrystalline Ni-Mn-Ga alloy at 700°C for 20 hours under argon atmosphere is found to reduce the range of transformation temperature. The differential scanning calorimeter measurement reveals that the alloy has the martensite transformation temperature at room temperature and it is less than Curie temperature. X-ray diffraction analysis witnessed the associated martensite to austenite phase transformation. Magnetic measurement has been performed using vibrating sample magnetometer. The observed narrow transformation hysteresis (around 3°C) during cooling and heating suggests that annealing Ni-Mn-Ga alloy at moderate temperature for long time, changes the characteristic temperatures of the martensite and austenite phases. From the present study it is concluded that the annealed polycrystalline Ni-Mn-Ga alloy undergoes thermoelastic martensitic transformation.

Key Words: Shape Memory Alloy; Actuator; Sensors; Austenite; Martensite; Twin Variant

1. Introduction

In recent years ferromagnetic Ni-Mn-Ga shape memory alloys have been extensively studied by various research groups [1-5] because of their considerable deformation when exposed to a magnetic field. This property is of particular interest, since the switching process can be made much faster and better controlled compared to conventional shape memory alloys. The thermo elastic phase transformation is the origin of the shape memory effect in Ni_2MnGa. Martensitic phase transformation from cubic $L2_1$ was found to occur on cooling Ni_2MnGa to -69°C[6]. Though a number of alloys undergo martensitic transformation, Ni-Mn-Ga is of particular interest. On cooling, they first become ferromagnetic at Curie temperature (T_c) and below this temperature; it undergoes martensitic transformation i.e. this alloy exhibits both martensitic and ferromagnetic characters.

The Ni-Mn-Ga Heusler alloy Ni-Mn-Ga shows two types of phase transitions. Transition from high temperature austenite to low temperature martensite is known as structural transition, and the other one from ferromagnetic austenite to paramagnetic austenite is known as magnetic transition. These two phase transitions can be overlapped in this alloy by varying composition. Moreover, microstructure of the alloy plays an important role in determining the phase transformation temperature by means of twin rearrangement. Ullakko [7] and James [8] first described the possibility for the magnetic field induced strain in Ni-Mn-Ga alloys. Following this, Ullakko [9] and Murray [10] demonstrated the 0.2% field induced strain in a single crystal Ni-Mn-Ga in the magnetic field of 800 kA/m at the temperature of –8°C. In Ni-Mn-Ga alloy, phase transformation is induced by the

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applied thermal energy (or) by the magnetic field. After phase transformation, martensites form a multivariant pattern. This multivariant minimises the transformation strain. The magnetic field induced strain [11-15] is increased in step by step manner from 0.32%, to 6% for five-layered martensite through the different composition of Ni/Mn/Ga/ and by changing the volume fraction of a particular twin variant. The giant magnetic field-induced strain of about 10% has been reported at room temperature in a seven-layered martensite orthorhombic $Ni_{49}Mn_{30}Ga_{21}$ [16], in the magnetic field of 400-640 kA/m, which is 50 times larger than the strain observed in Terfenol-D. Ni-Mn-Ga material is a complex material and the basic condition for the existence of the giant magnetic shape memory effect is 5-layered modulated martensite which has very low twinning stress and high magnetic anisotropy. It is considered that this large strain produced in this material is due to the rearrangement of the twin variant in the modulated martensite state, resulting in a macroscopic change in dimension. Theoretically it is predicted that the maximum strain of 10% can be produced and this maximum strain range is limited by the martensitic lattice parameter, i.e., (1-*c*/*a*). Till now no one reported the magnetic shape memory effect in non-modulated structure though it is having the ability to produce the strain nearly 20%.

The unique property of the Ferromagnetic Shape Memory Alloy (FSMA) is the fact that the martensitic transformation and structural transformation temperatures are extremely sensitive to the composition. The martensitic transformation and the magnetic properties of the alloys are found to depend strongly on Mn/Ga ratio and thermal treatment [17-19]. In the literatures, it is found that the very first reported Ni-Mn-Ga showed the martensitic transformation temperature of –69°C. Now numerous studies are going on around the world to raise both the martensitic and magnetic transition transformation temperatures by varying the Ni/Mn/Ga composition to meet the demands of the industry. Recent study on transformation property of polycrystalline ferromagnetic shape memory alloy evidences that the austenite grain size is the driving force to initiate the martensite transformation. The constrained propagation of the seminal martensite plate results in a lower transformation temperature in fine-grained austenite, and favours the formation of clusters of partially transformed grains. Therefore, in polycrystalline FSMA, martensite/austenite transformation is influenced by grain size [20]. The aim of our research group is to investigate the basic things responsible for the shape memory effect in polycrystalline FSMA and how it could be used in sensors and actuators in the form of thin films. The present work focuses on the investigation of structural and magnetic transformation property of a non-stoichiometric Ni-Mn-Ga alloy with excess Ni.

2. Experimental Procedure

High purity Ni (99.99% pure), Mn (99.99% pure), and Ga (99.99% pure) were taken as the raw materials for the present study. These raw materials were mixed together at room temperature with mortar and pestle. Then the mixture of these materials of 8 gm were taken in a silica crucible and melted in a tubular furnace under argon atmosphere. Initially, the sample was kept at the temperature of 700°C for 30 minutes. Then it was heated at 900°C for 40 min and at 1000°C for 60 min and finally the temperature was fixed and the sample was allowed to melt at 1025°C for 15 hours towards the through mixing of Ni/Mn/Ga and then allowed to cool at room temperature. The alloy was homogenised at 700°C for 2 days in a sealed quartz ampoule and then quenched into water. In view of minimizing the evaporation of manganese during melting, the furnace was backfilled with argon gas before keeping the sample inside the chamber. The martensitic transformation and structural transformation temperatures were measured by means of Differential Scanning Calorimeter (DSC: METTLER TOLEDO) at the cooling and heating rate of 5 K/min. Structural examination was carried out at room temperature by means of X-ray diffractometer (Rigaku RINT 2500) with CuKα radiation ($\lambda = 1.5416$ Å) recorded in the range of $20° < 2\theta < 100°$ with a step rate of $2\theta = 0.04°$. K_β was filtered with Ni. For powder XRD measurement, the ingot was crushed into fine powder, and then annealed again for 20 hrs at 750°C followed by water quenching. Surface morphology and microstructure of the particles was studied by using JEOL Scanning Electron Microscope (JSM-6390: Japan) operated at 20 kV/ 20 mA. Chemical composition was determined by the Energy Dispersive X-ray Spectrometer (EDS: INCAPenta FET-x3,) and the composition confirmed to be $Ni_{52.29}Mn_{24.59}Ga_{23.12}$. The sample is magnetically characterized using Vibrating Sample Magnetometer (VSM-5, TOEI industries) between 25°C and 105°C.

3. Results and Discussion

3.1 X-Ray Diffraction Analysis

Fig. 1 shows the X-ray diffraction pattern of the prepared NiMnGa alloy measured at room temperature. According to the measurement, all the three peaks are indexed to a body centered cubic (bcc) with lattice parameter a = 5.782 Å. It possesses $L2_1$ structure, same as that of bulk Ni_2MnGa. As the differential scanning calorimeter shows that the sample is in martensite state at room temperature, XRD measurement does not show any peak related to martensite phase. Martensite plates are sensitive to stress. Therefore, it is suspected that the stress applied at the time of crushing the ingot into fine powder could have disturbed the martensite plates. This may be the possible reason for the absence of XRD peaks, corresponding to martensite phase.

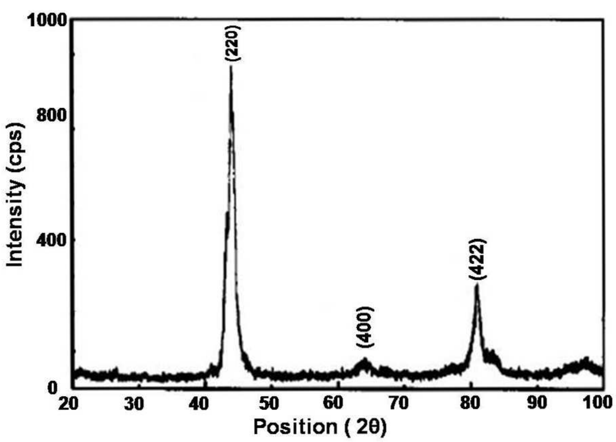

Fig. 1: X-ray diffraction pattern of the alloy shows peaks corresponding to austenite phase

3.2 Transformation Temperature Measurement by DSC

Differential Scanning Calorimeter has enough sensitivity to measure the phase transition associated with heat transfer [21]. Thermoelastic martensitic transformation observed in the non-stoichiometric Ni-Mn-Ga has a particular interest in the sense of considerable change in martensitic microstructure due to thermal process. Hence, monitoring the heat flow during forward and reverse martensitic transformation temperatures can give us an accurate indication of the phase transition temperature. Twinned martensites are mobile, which is proved in temperature dependant shape memory alloys. In the martensitic phase, the alloy is deformed easily due to the easy mobility of the twin martensites. In this study, the reversibility of the transformation is confirmed by the DSC run. Fig. 2 indicates the heat flow signals during forward and reverse martensitic transformation. The measured transformation temperatures are A_s = 42°C, A_f = 45°C, M_s = 40°C and M_f = 36°C. The recorded DSC data implies that the alloy has martensite structure at room temperature. High temperature peak denoted by T_c = 110°C, corresponds to ferromagnetic transition of austenite state, which is attributed to the martensite plates of uniform thickness. Commonly the thermal hysteresis for the single crystalline FSMA is narrow, which is attributed to the martensite plates of uniform

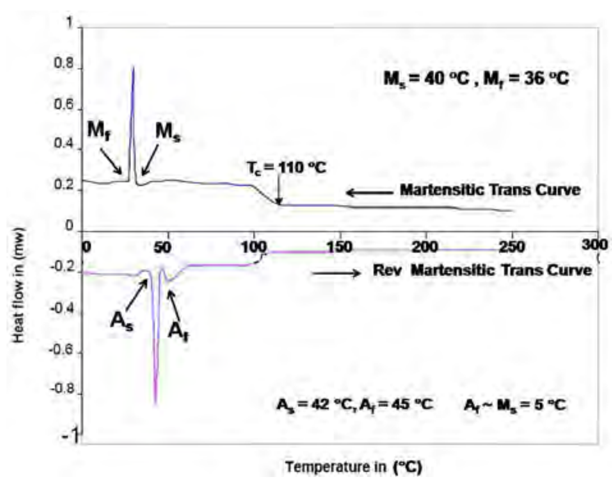

Fig. 2: DSC profile of NiMnGa sample shows the heat flow signals during forward and reverse martensitic transformation temperatures

thickness. But, it is broader for powder sample. The observed narrow thermal hysteresis (around 3°C) of the present study, suggests that annealing a polycrystalline FSMA at moderate temperature for long time can change the characteristic temperatures of the martensite and austenite phases. From the present study it is concluded that the annealed polycrystalline NiMnGa alloy may undergo thermoelastic martensitic transformation and one can get the near single crystalline property. Our observation is in close agreement with the already reported one [22].

3.3 Transformation Temperature Measurement of the Sample Using Vibrating Sample Magnetometer (VSM)

The VSM is a very powerful tool to characterize the various phase transformations, and has been widely used to analyse the thermoelastic martensitic transformation in shape memory alloys. Fig. 3 represents the temperature dependence of magnetization measured with VSM. The curve shows very sharp abrupt changes at austenitic-martensitic and magnetic transition points. Narrow austenite-martensite phase transformation indicates the high phase homogeneity. The transformation temperatures measured with VSM are A_s = 42°C, A_f = 45°C, M_s = 40°C, M_f = 36°C and T_c = 95°C. The coincidence of DSC and VSM result confirms that the sample is a ferromagnetic one. A sharp change in T_c, in the above figure is a mark of a supportive phase transition but the difference in T_c measured by VSM and DSC needs further clarification.

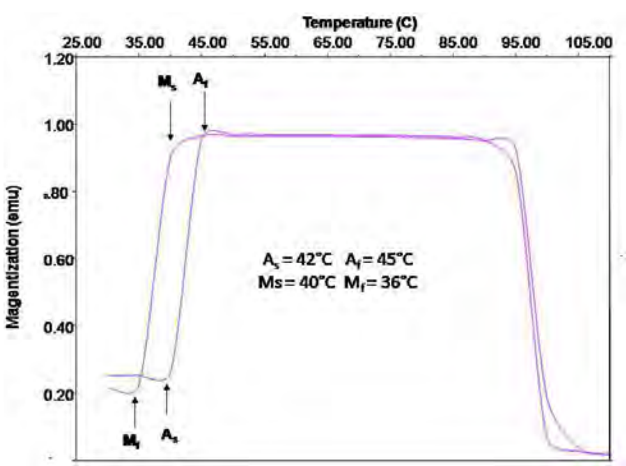

Fig. 3: Typical temperature dependant magnetization curve measured by VSM

3.4 Composition Analysis and Microstructure of the Alloy

EDS spectrum, shown in the inset of Fig. 4 depicts the result of composition analysis of the prepared sample. It consists of a number of peaks which belong to Ni, Mn and Ga. It is evident that the synthesized NiMnGa alloy contains only Ni, Mn and Ga. No other signals corresponding to any impurity has been recorded. It confirms that the material is highly pure without any impurity.

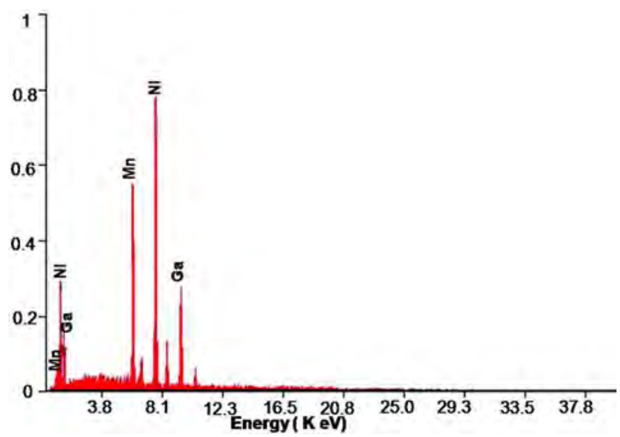

Fig. 4: EDS spectrum of the alloy shows that the prepared sample contains only Ni, Mn and Ga and there is no other impurity

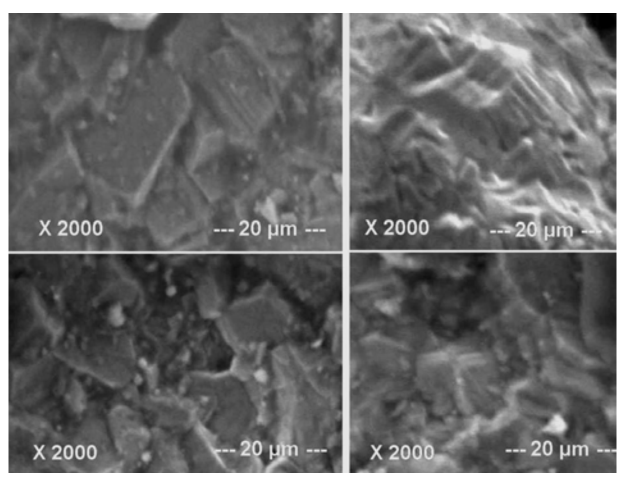

Fig. 5: SEM image of the alloy displays the presence of martensite plates

3.5 Microstructure of the Alloy

Microstructure of the alloy is illustrated in the Fig. 5. Close observation of the SEM image reveals that all the grains are having martensite plates. These martensite plates are essential for an alloy to exhibit the magnetic shape memory effect and also it should be thin. Typically, this type of plate martensite is formed at the time of quenching the sample from melt condition.

4. Conclusion

The martensitic and magnetic transformation properties of $Ni_{52.29}Mn_{24.59}Ga_{23.12}$ magnetic shape memory alloy have been investigated. The alloy shows the martensitic transformations below Curie temperature ($M_s = 40°C$, $M_f = 36°C$, $T_c = 95°C$). From the present study it is concluded that the near single crystalline property can be obtained in a polycrystalline sample if it is subjected to heat treatment at moderate temperature. Further improvement in the material property of this composition, in the form of thin film, is expected to make this alloy a potential candidate for certain micro-damper and energy dissipation mechanism.

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