Martensitic transformation behavior and structural characteristics of annealed Ni-Mn-Sn-Fe-In Heusler alloy

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Abstract. Ni-Mn based heusler alloy with Ni$_{50-x}$Fe$_x$Mn$_{30}$Sn$_{20-y}$In$_y$ where 1<=$x<=$4; 2<=$y<=$8 are studied for their structural as well as mechanical characteristics using various testing facility such as field emission scanning electron microscope, energy dispersion spectrometry, differential scanning calorimetry and Vickers hardness equipment. From the general understanding the materials are to display a transformation of austenite-martensite. The materials are seen to be showing this transformation in and around near room temperature. The optical and FESEM imaging of the specimen show that during annealing heating to high temperature to longer time, the diffusion kinetics are activated at faster rate so that the dendritically structure is annihilated to develop well distributed grain structure. The coarser dendrites seems to be broken and fine grain, well dispersed phases are formed. X-ray diffraction confirms the peak split and martensitic transformation in the system of alloys. DSC results confirm the martensitic transformation around room temperature.

Keywords: Heusler alloys, Martensitic transformation, magnetic refrigeration

1. Introduction

The ever-increasing human use of refrigeration and related activities such as various vapor compression refrigeration and air conditioning techniques have resulted in depletion of the ozone layer. Conventional refrigerators and air conditioners use chlorofluorocarbons (CFC) as their refrigerant gases. Such substances have been proven to be causing a large level of depletion to the ozone layer over the years. Thus, there is a high need to find better refrigeration system that does not make use of these ozone-depleting gases and hence form a safer living environment.

The one such substitution to the existing refrigeration system is magnetic refrigeration. Magnetic refrigeration system is being the future as it is a new age technology that does not produce harmful substances like in vapor-compression technology. The refrigeration technique using magnetic refrigerants has come into existence in the recent years. Magnetic refrigeration uses magnetic materials by making use of adiabatic demagnetization [1]. To achieve the magnetic refrigeration, a combination of high strength magnetic field source along with a material that processes a high temperature of the body.
Heusler alloys exhibit martensitic transformation of first order, in which the initial austenitic phase of the material is sheared in a diffusion less process. This martensitic transformation in the alloy is of great importance as the process involves the materials ability to withhold the characteristics when it is made to undergo deformation in martensitic state and for it to retransform when heated to its austenitic state. The most common stoichiometric of heusler alloys are \( X_{2}YZ \) in \( L_{2}1 \) structure. When a heusler alloy is magnetic they show a magnetic shape memory effect in them. Here the alloys tend to show a large strain in them when the strain is applied in the martensitic state \([2,3]\).

The ability to have the martensitic transformation in the alloys and for that to occur near room temperature is of great interest for application prospects. Hence an alloy system with \( \text{Ni}_{50-x}\text{Fe}_{x}\text{Mn}_{30}\text{Sn}_{20-y}\text{In}_{y} \) where \( 1 \leq x \leq 4; 2 \leq y \leq 8 \) is identified which shows a martensitic transformation near room temperature \( \text{On having checked with the e/a ratio of the alloy to have a martensitic transformation the following set of alloys have been identified.} \)

When a decrease in Curie temperature \( (T_{c}) \) is seen with slight increase of e/a. Above this concentration, the system is in a martensitic state at room temperature \( (R_{t}) \), and then there is a decrease in \( T_{c} \), decreases rapidly with increasing e/a. This sudden change in the e/a dependence of the Curie temperature is attributed to a change in the ferromagnetic exchange mechanism in the martensitic phase with respect to that in the austenitic state.

The number of valance electron per atom for Ni, Mn, Sn, Fe and In are i) 10\((3d^{8}, 4s^{2})\), ii) 7\((3d^{5}, 4s^{2})\), iii) 4\((5s^{2}, p^{2})\), iv) 8\((3d^{6}, 4s^{2})\) and v) 3\((5s^{2}, p^{1})\) respectively.

The electron to atom ratio \( (e/a) \) using the electron concentration of the outer shells for each chemical component of the is given by the equation;

\[
e/a= \frac{10x(Ni \text{ at.}%)+7x(Mn \text{ at.}%)+4(Sn \text{ at.}%)+8x(Fe \text{ at.}%)+3x(In \text{ at.%})}{Ni \text{ at.%}+Mn \text{ at.%}+Sn \text{ at.%}+Fe \text{ at.%}+In \text{ at.%}}, \quad \ldots \ldots (1.1)
\]

Using the equation 1.1 the electron to atom \( (e/a) \) ratio of all the alloys are calculated and further tabulated in the form of a plot to determine a martensitic transformation temperature nearer to room temperature as shown in figure 1.

![Figure 1. T vs e/a plot in Ni-Mn-Sn based alloys from [10-11]](image-url)
The martensitic transformation to occur in the material and for it to show a phase transition the heusler alloys are to be subjected to annealing at a temperature range from $800^\circ - 900^\circ C$\cite{4}. Majority of the studies suggest the specimen be annealed in a vacuum condition to prevent oxidation on the surface of the specimen. While the working on Mn$_2$FeGe heusler alloy with Marble’s reagent for 30 seconds and was able to find grain boundaries for the sample\cite{5}. Studied on NiMnGa-Co based heusler alloy\cite{4} suggested that to be able to identify the microstructure using Marble’s reagent as an etchant. Marbles reagent was also been used to study in various other works as well where the major composition of heusler alloys were Ni-Mn-Sn [6-7].

2. Experiment

A 5 g weight ingots were prepared in a vacuum arc melting furnace in an argon atmosphere in a water-cooled Cu crucible. Ni (99.99%), Mn (99.99%), Sn (99.99%), In (99.99%), Sn (99.99%) concentration of the alloys were weighed and the alloys were prepared. The vacuum unit with rotary and diffusion pumps can attain a vacuum of $10^6 m$ bar. Copper hearth and the electrodes have their temperature reduced by using cold circulating water from the chiller. Once the master alloys are subjected to complete melt these are then solidified. These can be then re melted by turning the around using the tweezer mechanism. The melting followed by solidification later the 'turn over' of the specimen and then final re-melting process is continuously repeated for multiple times such that a compositional homogeneity of the specimen is attained.

![Figure 2. Alloys prepared from raw materials after vacuum arc melting.](image)

Figure 2 shows the alloys where 1, 2, 3& 4 indicate Ni$_{49}$Fe$_1$Mn$_{30}$Sn$_{18}$In$_2$, Ni$_{48}$Fe$_2$Mn$_{30}$Sn$_{16}$In$_4$, Ni$_{47}$Fe$_3$Mn$_{30}$Sn$_{14}$In$_6$ and Ni$_{46}$Fe$_4$Mn$_{30}$Sn$_{12}$In$_8$ respectively.

The alloys thus formed were subjected to annealing at 750 $^\circ C$ for 24 hours by compact closing the specimen in a special attachment and placing inside the furnace this is to prevent any surface oxidation. A rectangular sample bar, freshly cut from middle part of a disc from Ni$_{50-x}$Fe$_x$Mn$_{30}$Sn$_{20-y}$In$_y$ alloys by an electro discharge machining, has been used to measure the XRD pattern of the sample. The diffractometer was operated at 40 kV and 30 mA with a curved graphite monochromator. A continuous $\theta$-$2\theta$ scanning was carried out over the diffraction angle $2\theta$ in the range $10^\circ < 2\theta < 90^\circ$, which covers the range of the characteristic diffraction peaks from the present alloy samples. The data were measured at room temperature and at selective temperatures in the range 298-400 K. High temperature studies performed at varied temperatures allowed determining the lattice expansion and/or a phase transformation from a martensite to an austenite structure of an alloy. Step scans in the $35^\circ < 2\theta < 70^\circ$ range were carried out for the different alloy samples at a slow scan rate of 0.02$^\circ$/min with a preset time of 2-4 s. A long counting time over a narrow angular range measures the XRD peak positions.
from a sample very preciously. The XRD patterns so obtained on the various Ni<sub>50</sub>-xFe<sub>x</sub>Mn<sub>30</sub>Sn<sub>20</sub>-yIn<sub>y</sub> alloys prepared in this work were compared with the standard patterns for the identified crystalline phases in such alloys.

To determine if there is any correlation between the compositional dependence and mechanical hardness of the Ni<sub>50</sub>-xFe<sub>x</sub>Mn<sub>30</sub>Sn<sub>20</sub>-yIn<sub>y</sub> alloy, Vickers hardness (Hv) was conducted at three different points on cross section cut parallel to disc, at upper, lower and midpoint. The Hv was conducted by using a Vickers hardness tester at a load of 200 gf. The indentation by diamond indenter at an angle of 136° between opposite faces is subjected to a load of 1 to 200 gF. This is done between a dwell time of 10 to 15 seconds.

Polycrystalline samples of 20 mg where further cut from the samples for it to undergo calorimetric studies. For conducting Differential Scanning Calorimetry (DSC) the specimen was initially grounded with grit paper of 2500 size such that a complete thermal contact is present. The measurement was done in a cooling and heating rate of -70 to 127 °C at 10 °C /min. in METTLER-TOLEDO DSC. The typical cooling and heating rate in the instrument is 0.5 degree/min. The measurement were carried out in a fine air cooling system. The 20 mg sample was encapsulated in an aluminum cup with a lid an then placed in the DSC cell.

High resolution microscopic images were recorded to study sizes, shapes, and surface topologies in distinct microscopic features and their distributions in the alloys. Room temperature structural analysis of the specimen was carried out with x-ray diffraction technique while the microstructure of the specimen was identified using FESEM. For this Polishing of specimen and etching for microstructure analysis was done. The specimen was subjected to polishing with various grades of emery paper and finally 3-micron and 1-micron diamond polishing to form a mirror like finish on the surface. From various studies on literature it was found that the Marble’s reagent was the optimal etchant that is to be used on heusler alloys in order to obtain the microstructure of it. The composition of the reagent is 10 g CuSO<sub>4</sub> with 50 ml hydrochloric acid with 50 ml water with drops of H<sub>2</sub>SO<sub>4</sub> to increase its activity. The specimens were subjected to etching for 20 seconds as per various literature [8-9].

3. Results

The x-ray diffraction was conducted in two sets of specimens. One of the specimens (Ni<sub>49</sub>Fe<sub>1</sub>Mn<sub>30</sub>Sn<sub>18</sub>In<sub>2</sub>) was split into equal halves and subjected to annealing while the other was the as-cast heusler alloy. This was done for estimating the annealing and to determine the effect it shows on the characteristics of heusler alloy. The XRD patterns of the Ni<sub>50</sub>-xFe<sub>x</sub>Mn<sub>30</sub>Sn<sub>20</sub>-yIn<sub>y</sub> where 1<=x<=4; 2<=y<=8, recorded in the range 20º≤2θ≤90º of the diffraction angle 20 as shown in figure.3, intrigue distinct changes in number and/or relative intensities of the peaks when there is a change in the alloying elements content in this alloy series. XRD pattern of only six peaks arises in a pure tetragonal L<sub>1</sub>0 martensite phase with lattice parameters a = 0.7808 nm, c = 0.6954 nm. A minor change of the Ni-content with Sn fades away the superlattice in a bit strain free fcc-L<sub>2</sub>1. This is a result of a surface reinforced densification in one phase that bounds the other in a composite structure.
Figure 3. XRD pattern in Ni$_{49}$Fe$_{1}$Mn$_{30}$Sn$_{18}$In$_{2}$ alloy

The x-ray diffraction pattern of the alloys taken at room temperature shows that the sample has the Heusler crystal structure in figure 3. There is also a hint of peak splitting that can be seen which has happened in the most intense peak. This also gives the indication of martensitic transformation in the specimen. Although while enlarging the peak from figure 4 it is seen that their clear conclusive evidence of peak splitting which are generated due to the martensitic transformation. The multiple splits like pattern shown are formed maybe due to dominant split seen. While in case of as cast specimen as well there is a hint of peak splitting seen as in figure 5 but it cannot be taken as a conclusive evidence regarding the martensitic transformation occurring in the material.

Figure 4. Enlarged XRD for annealed sample

Figure 5. XRD pattern in non-Annealed as cast sample
Hence, the pattern here infers austenitic phase, however, it can only be concluded after a confirmatory result it obtained from DSC studies.

Figure 6. Microstructure of annealed specimen

The microstructure of annealed specimen is being shown in figure 6. The specimens are annealed in furnace for a period of 48 h to breakdown the dendritical structure. During annealing heating to high temperature to longer time, the diffusion kinematics are activated at faster rate so that the dendritical structure is annihilated to develop well distributed grain structure. The coarser dendrites seem to be broken and fine grain, well dispersed phases are seen.

Figure 7. Microstructure of as cast specimen

The microstructure of the as cast Heusler alloy is shown in figure 7. It shows the dendritical structure with coarser dendrites of both phases. The two phases seem to be almost uniformly dispersed. The second phase (phase 2) quantity seems to be less compared to first. The dendrites generally show inhomogeneity in the chemical composition in the microscopic level from location to location or dendrites to dendrites. The dendritic structure generally shows inhomogeneity in the properties throughout.
FESEM study on Ni-Mn alloy confirms the breakdown of the dendritic structure in the alloy as seen in figure 8. While in case of as cast alloy there is continued larger dendritic structure in the alloy. The annealing in furnace for a period of 48h on the alloy has resulted to breakdown the dendritical structure.

Composition of the alloy was checked using the EDX analysis technique. Table 1 depicts the composition of the alloy at varying x and y values. The results envisage the homogenous alloying all the four composition. $\text{Ni}_{50-x}\text{Fe}_x\text{Mn}_{30}\text{Sn}_{20-y}\text{In}_y$ where $1 \leq x \leq 4; 2 \leq y \leq 8$

| x  | y  | Ni  | Mn  | Sn  | In  | Fe  |
|----|----|-----|-----|-----|-----|-----|
| 1  | 2  | 37.4| 26.63| 31.27| 3.93| 0.77|
| 2  | 4  | 37.04| 26.52| 27.28| 7.04| 1.12|
| 3  | 6  | 37.0| 26.91| 23.59| 10.68| 1.37|
| 4  | 8  | 36.88| 26.92| 20.91| 13.74| 1.75|

The values are accurate within ±0.1% error

On understanding the results from Vickers hardness test the outer region of the as-cast alloy, which was cooled effectively faster in a bulk structure, is a primarily softer austenite phase as seen in figure 9. During cutting from a master alloy disc, a compressive stress its lower surface faces would breed a surface hardening only. The hardness propagates with local strain relieves as a carrier in the small martensite strips split-up and self-accommodate in a modified pattern as what is illustrated with the FESEM images. This excremental result envisages that a thermal gradient sensitively controls the evolution of the microstructure in the martensite strips of small crystallites in association to the dynamics of the atoms at the bulk alloy surfaces. As the nucleation and propagation of cracks can be suppressed by tailoring the microstructure. In the martensite phase, since the free energy at the
interfaces between the martensite strips is higher than that in the interior of strips, the interfaces obstruct the dislocation motion in strengthening the alloy of small crystallites. Large piled-up interfaces available in the martensite phase due to the sub strips of nano crystallites significantly contribute this process resulting in large average HV value 2.64 GPa at the upper cross section and the lower cross section having the value 2.54 GPa as shown in Table 2. In the composite phase, the austenite fraction suppresses the number density of martensite multistrip or interfaces so that the HV-value stands smaller. Dramatic increase in HV-value to 3.321 GPa incurs in the austenite alloy because there are no martensite-martensite or martensite-austenite interfaces. A nominal fall in the HV-value in the other austenite alloy (x = 4 and y=8).

Table 2: Vickers microhardness measured for Ni$_{50-x}$Fe$_x$Mn$_{30}$Sn$_{20-y}$In$_y$ alloy where 1<=x<=4; 2<=y<=8 at Upper (U), central (C) and lower (L) cross section of alloy disc.

| x  | y  | U   | C   | L   |
|----|----|-----|-----|-----|
| 1  | 2  | 2.513 | 3.058 | 2.627 |
| 2  | 4  | 3.102 | 3.530 | 3.237 |
| 3  | 6  | 2.125 | 2.711 | 2.264 |
| 4  | 8  | 2.647 | 2.714 | 2.736 |

![Figure 9](image-url)  
Figure 9. Vickers microhardness (HV) showing martensite and phase softening at the expense of strains in Ni$_{50-x}$Fe$_x$Mn$_{30}$Sn$_{20-y}$In$_y$ crystallites. The data were measured on upper (U), central (C) and lower (L) cross-sections from an alloy disc.

The results of the DSC analysis indicate that heat output over -70 to +120 °C was carried out. The results of four alloys Ni$_{49}$Fe$_{1}$Mn$_{30}$Sn$_{18}$In$_{2}$, Ni$_{48}$Fe$_{2}$Mn$_{30}$Sn$_{16}$In$_{4}$, Ni$_{47}$Fe$_{3}$Mn$_{30}$Sn$_{14}$In$_{6}$ and Ni$_{46}$Fe$_{4}$Mn$_{30}$Sn$_{12}$In$_{8}$ as indicated as 1,2,3 and 4 respectively shows that the peak value of Ap in M-A transition is displaced off in the austenite start as As and austenite finish as Af. The martensitic start and finish are indicated as Ms and Mf respectively shown in figure 10. It seems that the transitions have occurred above room temperature; one is close to room temperature. The peaks are not dominant due to sharp shift at the point of reversing temperature in the measurement. On plotting a separate the cooling and heating data it is interpreted accordingly.
Figure 10. DSC curve for Heat flow vs Temperature(°C) for the alloys where 1, 2, 3& 4 indicate Ni$_{49}$Fe$_{1}$Mn$_{30}$Sn$_{18}$In$_{2}$, Ni$_{48}$Fe$_{2}$Mn$_{30}$Sn$_{16}$In$_{4}$, Ni$_{47}$Fe$_{3}$Mn$_{30}$Sn$_{14}$In$_{6}$ and Ni$_{46}$Fe$_{4}$Mn$_{30}$Sn$_{12}$In$_{8}$ respectively.

4. Conclusion

- There is a peak splitting seen in both annealed and as cast specimen.
- While enlarging the XRD plot of both annealed as and as cast specimen it shows otherwise. Hence annealed specimens were considered for further analysis.
- From the results of the microstructure, it suggests the formation of martensitic transformation phase in the alloy and thus the desired magnetocaloric effect could be found on further analysis of the specimen.
- Result justifies the annealing process and its breakdown of dendritical structure during annealing at longer time.
- The microhardness test results also justify the M-A transition in the material.
- It seems that the martensitic transitions have occurred above room temperature, post heat treatment process.

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