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RESEARCH ARTICLE

CHARACTERISTIC STUDY ON $Ni_{50}Mn_{45}Sn_5$ by DSC & X-RAY ANALYSIS

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ABSTRACT

The Martensitic Transformation in Ferromagnetic shape memory alloys (FSMAs) can be triggered not only by changes in temperature and stress as that of paramagnetic conventional shape memory alloys, but also by changes in the applied magnetic field. It is well known that ferromagnetic shape memory alloy has diversified utilization, but not satisfactorily use, mainly because of high cost of processing and high cost of alloying elements. Among all Heusler alloy, Ni-Mn-Sn alloy have potential properties and exhibits lower cost. In this experiment $Ni_{50}Mn_{45}Sn_5$ alloys characterize by using differential scanning calorimetric (DSC), optical microscope and X-Ray diffraction technique. The alloy undergoes the martensitic transformation from $L_2$1-type cubic structure into an orthorhombic structure.

INTRODUCTION

Ferromagnetic shape memory alloys (FSMAs) have a characteristic feature by combining shape memory effect and the bulk ferromagnetic behavior. FSMAs have considerable potential microactuator materials because they show a large recovery strain upto 10% and a high responding frequency (KHz) (Chernenko *et al.,* 1993; Wuttig *et al.,* 2000; Choi *et al.,* 2006). In this decade, many FSMAs systems have been investigated, such as Ni-Mn-Ga (Ullakko *et al.,* 1996; Wu *et al.,* 1999), Ni-Fe-Ga (Oikawa *et al.,* 2002; Liu *et al.,* 2003), Ni-Mn-Al (Fujita *et al.,* 2000), Co-Ni-Ga(Al) (Wuttig *et al.,* 2001; Oikawa *et al.,* 200) and Ni-Mn-In (Thorsten *et al.,* 2006; Thorsten *et al.,* 2007). There have been many reports on their structure, magnetic properties, martensitic transformation, magnetically controlled shape memory effect, superelasticity and magnetic-field-induced strains (MFIS). Magnetic shape memory effect in these materials involves the movement of twin boundaries which results in the growth of one of the twin variants at the expense of the other in response to an applied magnetic field below the martensitic transformation temperature (Choi *et al.,* 1770). Formation of martensite variant is accompanied by a defined shape strain; the microscopic shape of the material does not change as a whole before or after the transformation. This is due to self-accomodation of martensite formation (Bhattacharya *et al.,* 1992). A martensitic phase generally accommodates the strain associated with the transformation by slip or by a formation of twin variants that pack together in compatible orientations to minimize strain energy between the martensitic region and the surrounding untransformed, highly symmetric parent phase. By the growth of one variant of the twin at the expense of the other two is responsible to a large macroscopic recoverable strain in FSMA (Sutou *et al.,* 2004; Liu *et al.,* 2008). When finding strain for FSMA the total strain equals the sum of the parts:

$$\varepsilon^{\text{total}} = \varepsilon^{\text{elastic}} + \varepsilon^{\text{reorientation}}$$

where, $\varepsilon^{\text{reorientation}}$ is defined as $\varepsilon^{\text{reorientation}} = \varepsilon^{\text{r,max}} * \xi$. ξ and $\varepsilon^{\text{r,max}}$ are defined as variant two volume fraction and maximum reorientation strain, respectively. ξ may be found analytically from a driving force function found from Gibbs free energy using the relations of a polynomial or trigonometric hardening function. Variant two, volume fraction, the variants like applied stress, heat, magnetic anisotropy energy, and other material properties which expands the specimen when exposed to magnetic energy (Kiefer *et al.,* 2005; Karaman et al., 2007).

Highest experimented stoichiometric Ni-Mn-Ga heusler alloy involving complete substitution of Ga with Sn, where chosen from a number of candidate alloys exhibiting martensitic transformation as suggested by Wutting et. al. (Choi *et al.,* 2006). In recent study Mn- based Heusler alloys have been focus as one of the typical magnetocaloric effect material. Among them, it is found that Ni-Mn-Sn SMA is a less cost material due to lesser cost of Sn element. By considering cost, the goal of this investigation is to find a magnetic alloy exhibiting a martensitic phase transformation that would provide a large controllable displacement with the application of low magnetic field at reasonable operating temperature. In many experiment Ni-Mn-Ga alloys are widely examined for which it serves as a reference alloy. But the Husler alloys the choice of Ni-Mn-Sn alloy is due to:

a) Ni-Mn-Sn not expensive as gallium.
b) It does not contain toxic as that of gallium (Chatterjee *et al.,* 2008).

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c) Ni-Mn-Sn is less brittle than Ni-Mn-Ga (Brown et al., 2006).
d) Low transformation and Curie temperature of stoichiometric Ni-Mn-Ga than Ni-Mn-Sn.
e) The austenite and martensite phase of Ni-Mn-Sn have the same crystal structure as the corresponding phases of Ni-Mn-Ga and have the same magnetically easy axis (Choi *et al.,* 1770).
f) Ni-Mn-Sn alloys are known to have comparably high L_21/ tetragonal transition temperature as that of Ni-Mn-Ga.
g) Stoichiometric of Ni-Mn-Sn alloys reveals similar magnetostrictive behavior with respect to temperature as that of Ni-Mn-Ga alloys(Choi *et al.,* 1770).
h) Ni-Mn-Ga alloys are insufficient for FSMA actuators (Sutou *et al.,* 2004).

$Ni_{50}Mn_{45}Sn_5$ FSMs is a ternary intermetallic compound, which has the cubic L_21-type structure. In this structure, the Ni ion occupy at the site of the cube corners (8c-site), and Mn and Sn ions are in the alternate body centers of the successive cubes (4a- and 4c- sit, respectively) (Koyama *et al.,* 2006), as shown in Figure 1.

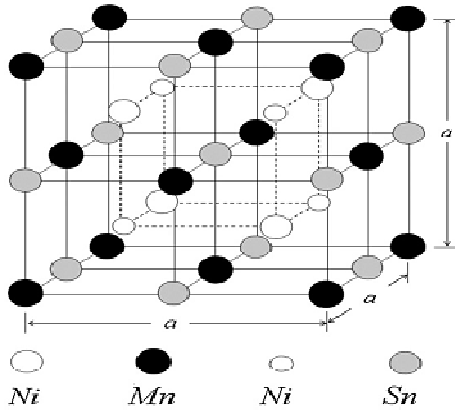

Figure 1. Unit cell of Ni2MnSn FSMA. Different atomic sites are presented by bellow symbols

MATERIALS AND METHODS

A ternary polycrystalline $Ni_{50}Mn_{45}Sn_5$ Heusler alloys were prepared by using Ni, Mn and Sn elements having their commercial purity 99.95%, 99.9%and 99.99% respectively. The melting and boiling point of the different elements used in alloy preparation as shown in Table-1. For melting of this alloy nonconsumable arc under high purity atmosphere (99.996%) is used. For the preparation of alloy ingot, the melting chamber was evacuated to a pressure of 1×10^{-5} torr and then was purged with pure argon. The process of evacuation and purging was repeated three times. The melting was carried out in an argon atmosphere and at a chamber pressure of nearly 500Mtorr. The entire melting process was repeated several times in order to get complete homogenization of the alloy. Then the alloy was cast into a rod form. The composition has been reported to form a martensite at room temperature (Ms= 337k) with martensitic Curie temperature, Tc close to room temperature (287K). The ingot was sealed in a quartz ampoule filled with helium gas and solutionized at 1000^{o}C for 24 hour for homoginization. The martensitic transformation and phase in these alloys successfully characterized by using Optical Microscopy, X-Ray Diffraction and Differential Scanning Calorimerty.

Table 1. Melting and Boiling point of different element of Ni-Mn-Sn alloys

Element	Melting Point (^{o}c)	Boiling Point (^{o}c)
Mn	1245	2150
Ni	1435	2730
Sn	232	2270

RESULTS AND DISCUSSION

Differential Scanning Calorimetry

To characterize the material behavior, it is important to identify the regions where the martensite phase exists at the transformation temperatures under zero stress. The magnetic shape memory effect is only present in regions consisting of stable martensite. These regions of stability however, are temperature dependent. The alloy absorbs, or emits, heat over a small change in the specimen temperature, when there is a phase transformation occurs in the material. The forward and reverse martensitic transformation of $Ni_{50}Mn_{45}Sn_5$ is shown in figure-2. In this figure number-1 represent as forward martensitic transformation and number-2 represent reverse martensitic transformation. The temperature was raised from 300^{o}C to 500^{o}C and lower from 500^{o}C to 300^{o}C at a rate of 5^{o}C/min, while the baseline heat flow rate vs. temperature was recorded by the data acquisition computer. Martensitic start temperature (M_s), Martensitic finish temperature (M_f), austenitic starte temperature (A_s) and austenitic finish temperature (A_f) are 423.02^{0}C, 403.73^{0}C, 428.36^{0}C and 452.99^{0}C respectively. Here martensite starting temperature is higher and it is due to the lower percentage of Sn in that alloys (Martynov *et al.,* 1992).

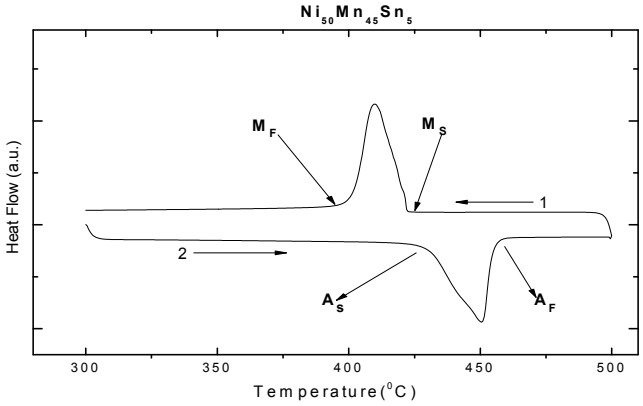

Figure 2 Martensitic Transformation For sample $Ni_{50}Mn_{45}Sn_5$

Microstructure of Martensite in different specimen

Figure-3 (a) shows the martensitis structure of $Ni_{50}Mn_{45}Sn_5$ FSMA and figure-3(b) shows the magnified martensitic boundary, which leads to motion during transformation. The martensitic transformation possesses well defined characteristics which is associated with an inelastic deformation of the crystal lattice with no diffusive process involved. The phase transformation results from a cooperative and collective motion of atoms on distances smaller than the

lattice parameters. The absence of diffusion makes the martensitic phase transformation almost instantaneous. The reconstruction of martensitic domains is possible only in the case when their boundaries are mobile, i.e., if the martensite transformation is a thermoelastic one. Since the crystal lattice of the martensitic phase has lower symmetry than that of the parent austenitic phase, several variants of martensite can be formed from the same parent phase crystal. The large strain can either be caused by a magnetic field-induced structural reorientation (usually by twin boundary motion) shown in figure-3(d) or by a magnetic field-induced phase transformation (usually a martensitic phase transformation) shown in figure-3(c). The magnetic field-induced phase transformation is correctly referred to as MSM effect or as magnetically induced martensite/austenite (Tsuchiya *et al.,* 2000). Some of the picture of NiMnSn sample taken from Optical Microscope are given below:

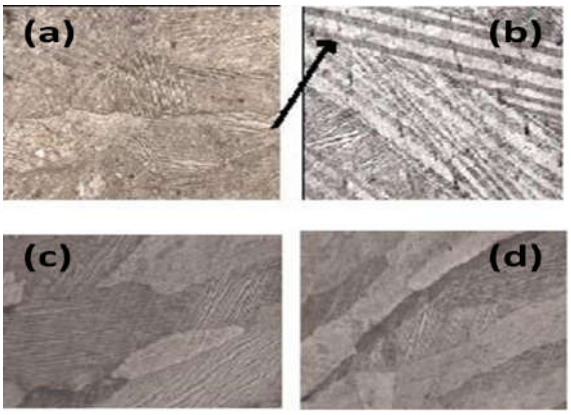

Figure 3 (a) A number of Martensitic layers present in $Ni_{50}Mn_{45}Sn_5$, (b) enlarged martensitic layer at 50X magnification showing martensitic layer boundary, (c) morphology of different orientation of martensite withen the grain at 20X magnification and (d) showing the twin boundaries present.

X-Ray Diffraction

The obtained sample was confirmed to be a single phase with the L_21 structure by XRD measurements at room temperature. The XRD experiment with CuKα radiation was made at $20° \leq 2\Theta \leq 80°$ with a step size of 0.01°. Here the reflections by $K\alpha_1$and $K\alpha_2$ radiations are observed. Bragg peaks denote the Miller Indices (hkl value), which confirm that the phase has L_21 structure and 4O structure as shown in figure-4.

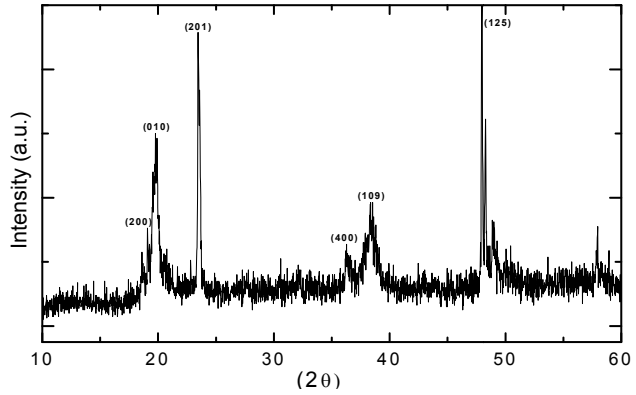

Figure 4. XRD pattern for $Ni_{55}Mn_{45}Sn_5$ alloy

CONCLUSIONS

The behavior of Ni-Mn-Sn alloys reported in this literature has better properties than other Heusler alloy. The higher martensitic transformation temperature of NiMnSn alloys leads to work under higher working temperature than NiMnGa alloys. The $Ni_{55}Mn_{45}Sn_5$ FSMAs undergoes the martensitic transformation from L_21-type cubic structure into an orthorhombic structure.

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