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S. Sandeep Nambiar
Manipal Institute of Technology

B. R.N. Murthy
Manipal Institute of Technology

Sathyashankara Sharma
Manipal Institute of Technology

A. A. Prasanna
Malnad College of Engineering

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ANALYSIS ON MAGNETOCALORIC AND STRUCTURAL PROPERTIES OF HEUSLER ALLOYS USED IN MAGNETIC REFRIGERATION

SANDEEP NAMBIAR S.[1], MURTHY BRN[2*], SATHYASHANKARA SHARMA[3] & A. A. PRASANNA[4]

[1]*Research Scholar, Department of Mechanical and Manufacturing Engineering, Manipal Institute of Technology, Manipal Academy of Higher Education, Manipal, India*

[2*]*Associate Professor- Senior Scale, Department of Mechanical and Manufacturing Engineering, Manipal Institute of Technology, Manipal Academy of Higher Education, Manipal, India,*

[3]*Professor and Head, Department of Mechanical and Manufacturing Engineering, Manipal Institute of Technology, Manipal Academy of Higher Education, Manipal, India*

[4]*Associate Professor, Department of Physics, Malnad College of Engineering, Hassan, India*

ABSTRACT

The prime importance of the majority of the research works being undertaken in the field of magnetic refrigeration is, to achieve the refrigeration at or near the room temperature in heusler alloys. The current review work surveys the magnetocaloric effects, range of temperature where the phase transformation occurs in heusler alloys and discusses their relation with the magnetic shape-memory and structural variation of the materials in accordance to the variation in its material composition. The e/a ratio of the material are considered to predict the composition of the refrigerant alloy. System having a near room temperature martensitic transformation and various compositional changes done to achieve the same are discussed thoroughly. Substitutions of constituent elements are done such that a favorable magnetic entropy change is retained and the formulation of near room temperature martensitic transformation of the alloy is formed. Around 100 existing research articles are studied to collect the information on above said parameters and displayed in a collective form in this systemic review. The review reveals that, as on date, the properties examined are martensitic transformation temperature, magnetocaloric value and structural properties. $Ni_{45}Mn_{36.5}In_{13.5}Co_5$ alloys show a martensitic transformation temperature of 294 K, which is equivalent to near room temperature; hence these can be used as a refrigerant material in conventional refrigerator system. Change in entropy at x= 4, 5 is 43 and 68 J/kg K for $Ni_{50}–xCo_xMn_{38}Sb_{12}$ alloy was observed for all the works considered for x varying from 0–7.

KEYWORDS: Heusler Alloys, Martensitic Transformation Temperature, Magnetocaloric Effect, Structural Properties & Systematic literature Review

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Original Article

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 Henriksen et al. (1990). Ozone layer has its importance as solar radiation of wavelengths that are lower than 290 nm are blocked from reaching the surface of the earth, as these layers omits certain types of ultraviolet (UV) and various other forms of radiations that have been proven to be dangerous to all living beings on earth. 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 (Aprea et al., 2016). Global importance to magnetic refrigeration has attained high priority during the recent 20 years as indicated by Coulomb (2008). The Montreal Protocol has stressed the reduction on the use of Ozone Depletion Substance (ODS) yet the greenhouse effect problem has not been solved completely.

The refrigeration technique using magnetic refrigerants has come into existence in the recent years. Its application benefits are being appreciated widely; because of its environmental friendly characteristics and assisting to effectively reduce the emission of ozone-depleting gasses from the conventional refrigeration system. Magnetic refrigeration uses magnetic materials by making use of adiabatic demagnetization.Comparatively, this method is highly efficient one and importantly environmental friendly as it helps in avoiding ozone-depleting gases. To achieve the magnetic refrigeration, a combination of high strength magnetic field source along with a material that processes a high magnetocaloric effect (MCE) is necessary. Figure 1 depicts the general mechanism involved in the production of magnetic refrigeration; the major constituents of the unit are a magnetic working body along with thermal switches and magnets. The various steps involved in the process are that the working body is made to be in contact with the heat reservoir; upper heat switch is opened and lower is closed.

- During the process of isothermal magnetization to take-up heat from the body, the working body temperature is kept higher than reservoir body.
- During the next adiabatic demagnetization step; to cool the working body the upper and lower heat switches are opened.
- During the isothermal demagnetization process, and the lower heat switch is closed with the upper one open the field reduces to zero. Temperature of the working body is lower than the heat source so as to absorb the heat.
- Adiabatic magnetization step completes the process when both heat switches are open, thus increasing the temperature of the body.

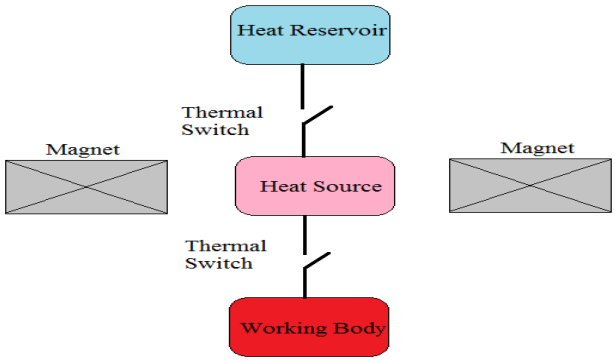


Figure 1: Schematic Diagram of Magnetic Refrigeration Production.

Due to several advantages over vapor-compression refrigeration, magnetic refrigeration has acquired major consideration (Tishin, 2007). In magnetic refrigeration process various types of heusler alloys are used as refrigerant

material. Heusler alloys are a large group of materials with more than one thousand members that is useful in producing materials of ferromagnetic and ferrimagnetic nature, shape memory alloys (SMA), energy technologies and in applications making use of magneto-caloric effect. Greater spin polarization is critical factor for the enhancement of the performance of spintronic devices such as the spin filter and the spin valve (Inomata et al., 2008). Heusler alloys are classified as Half heusler alloys and full heusler alloys. Half heusler alloys are generally composed of inter-penetrating three FCC-lattices and a 1:1:1 composition and full heusler compounds or heusler alloys have four inter-penetrating FCC-lattices with 2:1:1 composition as shown in figure 2. (Heusler, 1912, Suzuki et al., 2016).

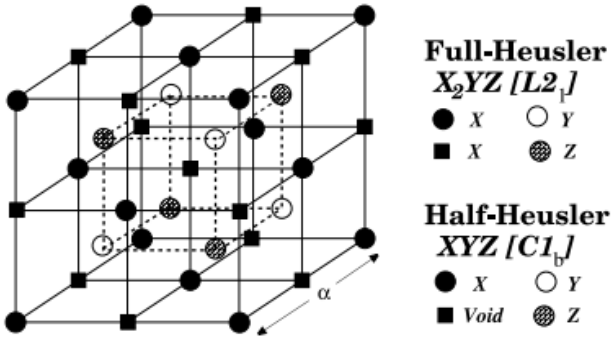


Figure 2: The Ordered $L2_1$ Phase in a Full-Heusler X_2YZ alloy, and $C1_b$ Phase in Half- Heusler XYZ Alloy (Galanakis et al., 2006).

Development of heusler alloy which is able to produce the magneto calorific effect is very important phenomenon in this field in order to attain the refrigeration at higher temperatures to apply this process for the general appliances such as refrigerators and air conditioning. From this review, it is evident that various types of two elements and three elements heusler alloys such $Ni_{50-x}Co_xMn_{38}Sb_{12}$, $Ni_{45}Mn_{42}Cr_2Sn_{11}$,$Ni_{49.4}Mn_{38.5}Sn_{12.1}$ etc. are developed and tested in this process to achieve the refrigeration at higher temperature. A complete data regarding the various combinations of heusler alloys used till date, their refrigeration temperatures, methods used to develop them, several properties of the alloys which are essential and having significant effect on the cooling process and their testing methods are collected and presented in a collective format, to provide the information at one glance to the researchers, who are interested to work in this field.

2. SYSTEMATIC LITERATURE REVIEW

2.1 Keyword Identification and Search Strategy used

Pilot study was done by using keywords for searching relevant journals and conference publishing works on heusler alloys. From the identified publications such as Physics Review, IEEE Journals, Journal of Applied Physics, Applied Physics Letters, Elsevier, Springer, and few others, an examination approach to categorize maximum related studies from the selected databanks was prepared. Although there wasn't any limit set for the publication time of these works, but it turned out to be between 1990- 2017. Each of the databases was assessed with multiple keywords done in multiple successions and the data was extracted out of it.

3. Material Preparation and Characteristics of the Alloy

From the present review work, it is observed that majority of the researchers used vacuum arc melting method for the preparation of the required alloy (Barua et al. (2013), Coll et al. (2010), Ingale et al. (2007)). Polycrystalline heusler alloys of required composition are prepared in induction melting of the elements having a purity of 99.99% of each alloying

element. The obtained samples of desired composition are annealed at a higher temperature range around 1120K and quenched in water bath. Scanning electron microscopy (SEM) is used to analyze the microstructure of the alloy. Electron image of Ni-Mn-Sn based alloy is presented in figure 3, it is observed that the alloy exhibits a single phase state without Fe addition, with 3% Fe, γ precipitates appear in the matrixin dark colored areas and it is also noticed that it is precipitated around the grain boundaries.

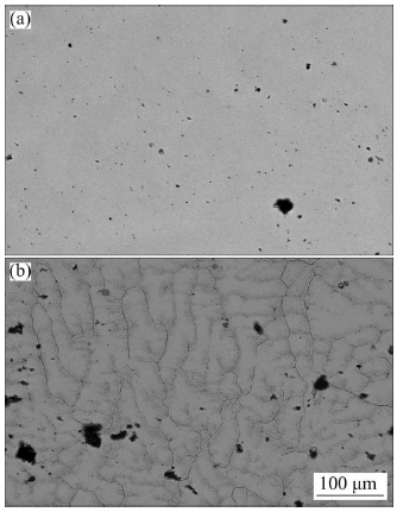


Figure 3: (a) Backscattered Electron Images of Ni-Mn-Sn, (b) Ni-Fe-Mn-Sn Heusler Alloy (Tan et al., 2017).

Bachaga et al., (2015) has used X-ray dispersive spectroscopy (EDS) equipped on SEM to determine the chemical composition of the alloy. They obtained patterns of three ribbon alloys which are determined at room temperature (R_T)as illustrated in figure 4. First two ribbons shows a 10M modulated martensitic structure and last ribbon exhibits a cubic $L2_1$ full-heusler structure.If the doping concentrationsuppresses the marten site phase, the variation in e/a ratio is the sole responsible for the deviations in the transformation temperature of the alloy. The e/a ratio should be nearer to 8.11 in order to achieve a near $R_T$martensitic transformation.Phase and crystal structure can also be estimated by referring to the same microstructure image which is obtained by EDS. XRD and Differential Scanning Calorimetry (DSC)are undertaken for determining the martensitic transformation behavior determination of the samples.

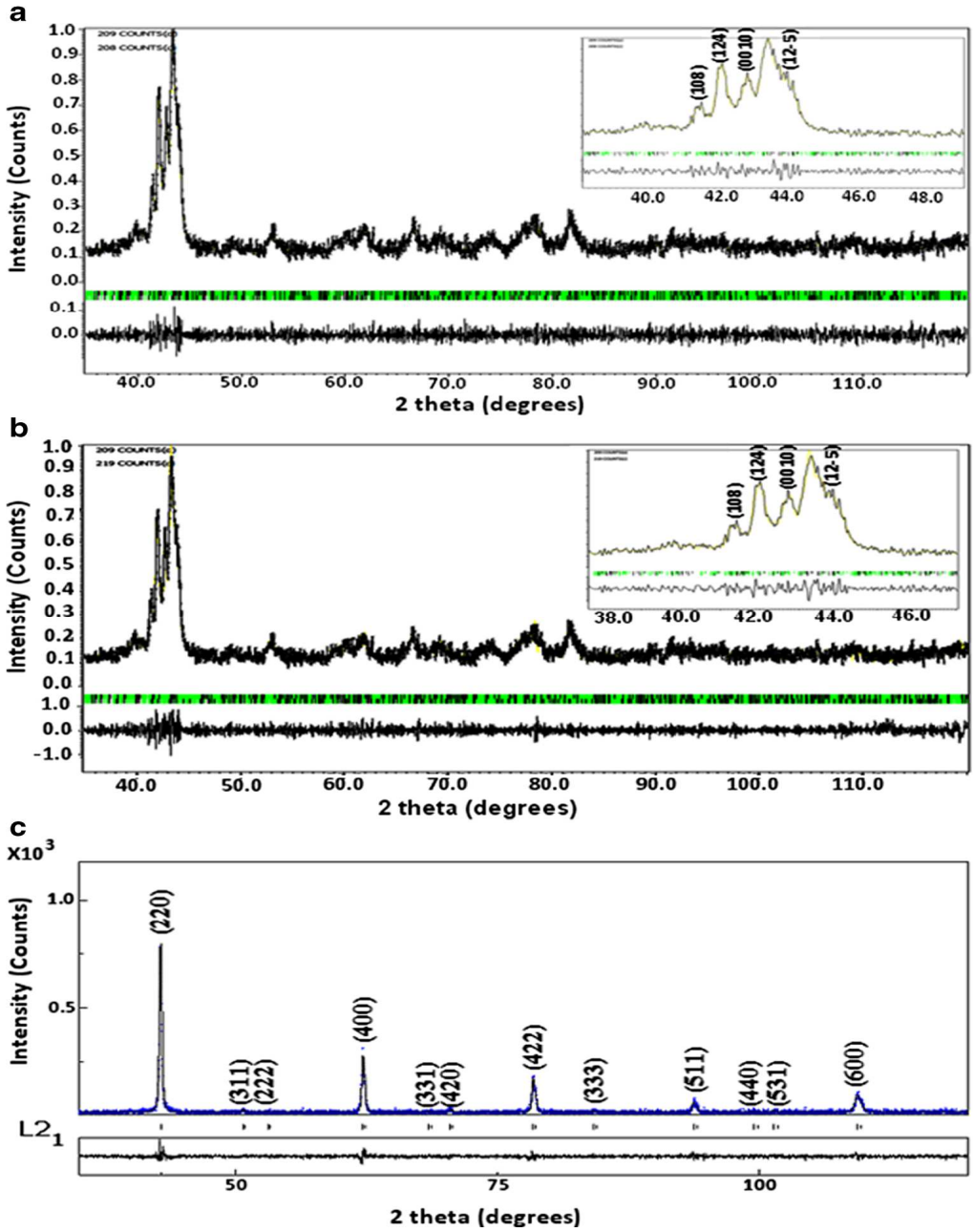


Figure 4: XRD of Ni – Co-Mn Heusler Alloy (Bachaga et al., 2015).

4. Magnetic Entropy Change

The definition of MCE is the variation in temperature of a magnetic material caused by the change in current magnetic state. The magnitude of it can be written directly in terms of its temperature difference between two magnetic states, or indirectly with respect to the change in specific heat, or the variation in magnetic entropy when a varying magnetic field is being applied to it. Maxwell equation is generally used in calculating the isothermal magnetic entropy change of a material on a given applied magnetic field.

$$\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B \quad \ldots\ldots \quad . (1)$$

The terms S, B, T, and M represent entropy, magnetic field induction, temperature, and magnetization respectively in equation 1 (Tishin et al., 2003).Magnetocaloric materials can be separated into two sections:

- First order phase transition (FOPT),
- Second order phase transition (SOPT).

MCE is mainly based on phase transition order. From various works on heusler alloys it is seen that first-order materials have the magnetic entropy change value (ΔS_m) greater than the second order. The temperature peaks are narrower in case of first order.In second-order transition type ferromagnetic to paramagnetic transition occurs nearer to martensitic transformation temperature (Tc). During the change of phase there is almost no synchronicity between dissimilar phases and the magnetization reaches a very low value which is almost equal tozero. But in first order, materials tend to experiences the synchronicity of dissimilar phases and exhibit rapid change of magnetization. Maximum MCE isattained in the region where there is a transitionof first-order especially when the magnetic transition as well as structural transition is occurred (Titov, 2015).

4.1 Ni-Mn-Sn Based Compounds and its Magnetic Entropy Change

Krenke et al. (2007) studied the compositions of Ni-Mn-X heusler alloys where X is substituted as Sn element.For $Ni_{50}Mn_{37}Sn_{13}$element, the entropy change is found to be at 20 J/kg K at 5 T magnetic fields and it is presented in figure 5. It is noted from the figure that, either Fe or Co addition causes e/a ratio to decrease andtherefore lowers the temperature corresponding to the peak position of ΔS_m.On substituting nickel element with iron and cobalt and increasing its concentration results in T_M to decrease.Substituting 1 % of Fe results in overall reduction ofentropy change. On substituting 3 wt.% Fe leads to an increase in ΔSm by about 30 J/kg K at 5 T.

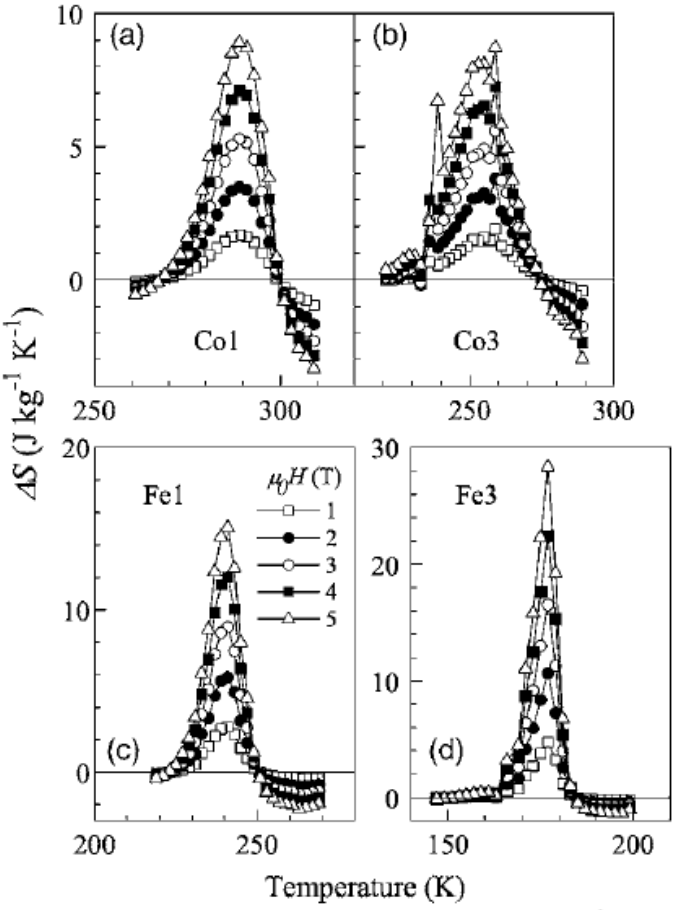


Figure 5: The Entropy Change of a) Co1; b) Co2; c) Fe1; and d) Fe2 (Krenke et al. 2007).

Nayak et al. (2010) carried out work on $Ni_{50-x}Co_xMn_{38}Sb_{12}$alloy and on the basis of the results obtained, theymade few conclusions such as: on varying the values for x from 0–7, M_T tends to decrease and there is no transition beyond and at x=8. Change in entropy (ΔS_m) for x value varying between 4 and 5 are 43 and 68 J/kg K respectively. 34% of magnetoresistance is observed for x when it is at 7. The magnetocaloric effect and the magnetoresistance can be varied accordingly with varying composition on Ni/Co composition. A large peak was observed in DSC and heat capacity values and hence confirms the transition from austenite to martensitic phase. High MR as well as MCE was found at the transition region. Thus, it can be said that the composition of the current alloy can be used for various magnetic refrigeration related applications. Wang et al. (2008) studied $Ni_{45}Mn_{42}Cr_2Sn_{11}$alloy and they predicted that, when theMn is substituted by Cr there is a rapid decrease in the martensitic transition temperature.In their work, Wang et al. (2007) have determined that, ΔS_mvalue was 15 J/kg K in a magnetic field of 10 kOe for$Ni_{43}Mn_{46-x}Cu_xSn_{11}$ series. In this series when there is increment inthe Cu concentration, there is a shift in $T_M$to a higher temperature. Under a low applied magnetic field of 10 kOe, ΔS_m +14.1, 18.0, and 15.8 J /kg K for x=1, 2, and 3, respectivelylarger MCE and MR values are seen in the result from the same work.This property is made use in various practical applications. Kainuma et al. (2010) detected a ΔS_m of 22.2 J /kgK for $Ni_{43}Co_7Mn_{39}Sn_{11}$ set of alloys. The ductility of the material is said to increase with the use of powder metallurgy technique than plasma arc technique.

Hu et al., (2001) recognized that, with the controlling of the constituent element of Ni-Ga-Mn helps in obtainingΔS_m in a wide range of temperature and the same is depicted in figure 6. For the given 5 T magnetic field, two

peak values were observed for $\Delta S_{m.}$ The highest peak of 18.0 J/kg K is observed at 300K temperature. When $\Delta S_m$is presented in volumetric units with various compositions which are: i) 146 mJ/cm^3 - $Ni_{52.6}Mn_{23.1}Ga_{24.3}$, ii) 136 mJ/cm^3 - $Gd_5Si_2Ge_2$, iii) 77 mJ/cm^3 -Gd, respectively, under field of 5 T. The cooling-power per unit volume is an important parameter for a magnetic refrigerator.

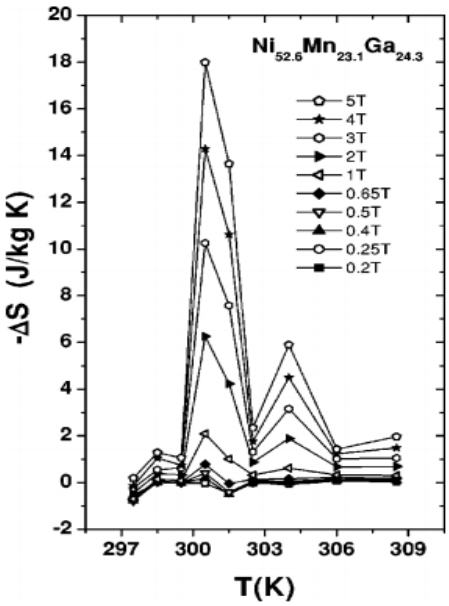


Figure 6: Magnetic Entropy vs Temperature Plot (Hu et al., 2001).

Jing et al. (2009) have found that a large ΔS_m of 37.1 J/kg K and magnetic field variation up to a value of 50 kOe for $Ni_{48}Co_2Mn_{38}Sn_{12}$ alloy. With Co concentration being increased, the martensitic transition moves to a lower temperature and the magnetic entropy change falls to the lower level. Ma et al. (2010), identified two peaks in the plot of temperature vs entropy change between the temperature ranges of 260 - 320K for Ni-Mn-Co-Sn material, thus indicating the presence of an intermediate phase. The combined effect of MCE and MR can be made use in wide range of magneto-refrigeration applications. The study by Ghosh et al. (2013), on $Ni_{47.5}$–$xCo_xMn_{37.5}Sn_{15}$ alloy shows a ΔS_M of 9.5 J/kg K at x at 3.5 due to a variation of 1.5 T magnetic fields. Although a large transformation value is obtained, it is not the indication of its high cooling capacity. It is observed that 18.7 J/kg K ΔS_M is shown for a magnetic field of 5 T and this value is attained for a set of alloys with composition of $Ni_{41}Ti_1Co_9Mn_{39}Sn_{10}$. Qu et al. (2017) worked on Ni-Mn-Sn alloy and identified a reversible ΔS_M characteristic under a 5 T applied field. The alloy exhibits neither toxic nor expensive properties at the transformation phase thus making it suitable for various potential room temperature magnetic refrigeration applications. Sharma et al. (2006) observed a ΔS_M of 2 J/kg K around 220 K for Ni-Mn-Sn alloy at 225 K. The shape memory effect at a given temperature in the alloy gets affected by the path navigated on H-T curve phase space to reach the required temperature.

Hernando et al. (2008) found ΔS_M of 4.1 J/kg K at 20 kOe for Ni-Mn-Sn alloy at structural transition. Low ΔS_M due to first-order nature with hysteretic losses reduces the refrigeration capacity of the material. Guo et al. (2013) worked on $Ni_{45}Co_5Mn_{40}In_xSn_{10}$ alloys and identified the peak values under a field change of 3 T. The observed peak values are: i) 22.5 J/kg K at x= 2, ii) 19.8 J/kg K at x=4, iii) 18.3 and 18.3 J/kg K for x= 6, 8 respectively. Muthu et al. (2010) found that ΔS_M of 32 J/kg at 5 T field in the x = 3, at the peak transformation temperature of 180 K. The refrigerant capacity (RC) in the alloy declines with Indium substitution.

4.2 Ni-Mn-In based Compounds and Change in Magnetic Entropy Change

Bourgault et al. (2010), in their research article over heusler alloys, stated that ΔS_Mvalue of 30 J/Kg K at 7 T magnetic fields was observed during the transition of first order at 355 K for $Ni_{45}Co_5Mn_{37.5}In_{12.5}$ alloy. Pathak et al. (2016) in their study on $Ni_{50}Mn_{34}CoIn_{15}$ alloy identified the changes in magnetic entropy in between the temperature ranges of 264 to 296 K, and later there is a negative ΔS_Mat 296–356 K. Thus both magnetizing and demagnetizing processes is used in magnetic refrigeration forefficiency improvement. Similar results were also comprehended by Niemann et al. (2010) that the inverse MCE at ΔS_M of 8.8 J/Kg K in 9 T at 353 K for Ni-Mn-Co-In alloy. According to Per Liu et al. (2006) at 303K, 5T, ΔS_M was reported to be around 29 J/Kg K for Ni-Mn-Co-In alloy. Recarte et al. (2010) in their study on Ni-Mn-Co-In alloy have attained maximum $\Delta S_M$of 7 J/kg K at 245 K and in between 225 and 245 Krange for 40 and 60 kOe respectively. Stern-Taulats et al. (2014) found that $\Delta S_M$of 25 J/kg Kis induced in a reversible manner under consecutive application and removal 6aT magnetic field in Ni-Mn-In alloy while, for the same alloy Bhobe et al. (2007)also got equivalent25 J /kg K entropy change for 5 T field at room temperature.The narrow difference between the structural and magnetic transition temperature and alteration of T_M by magnetic field are remarkable properties that the present alloy exhibits. Oikawa et al. (2006) also worked on the above said alloy and achieved ΔS_M value of 3 J /kg K at 9 T and hence made a conclusion that, an antiferromagnetic like transformation was observed to a ferromagnetic transformation.

5. Martensitic Transformation Temperature in Heusler Alloy

A diffusionless FOPT austenitic and martensiticphase in a material is termed as martensitic transition. High-temperature phase with face-centered cubic (FCC) lattice $L2_1$ is termed as an austenite phase (AP), and martensitephase (MP) is a low-temperature phase with a body-centered cubic lattice $L1_0$. The transition temperature is generally been defined by valence electron concentration (e/a),and they are in relation to its valence structure. (Kim et al., 2006, Liu et al., 2003).

From figure 7, it is understood that the alloy shows diverse T_M and T_C values over x=13-15 when the valence electrons per atom e/a value varies from 8.0 to 8.2. The T_C^Areduces slightly on e/increases up to 8.1, the martensite state extends at room temperature, and its T_C^A decreases swiftly with increasing the e/a value. The change in the e/a dependence on TC point is credited to a change in the ferromagnetic exchange from the austenitic state.

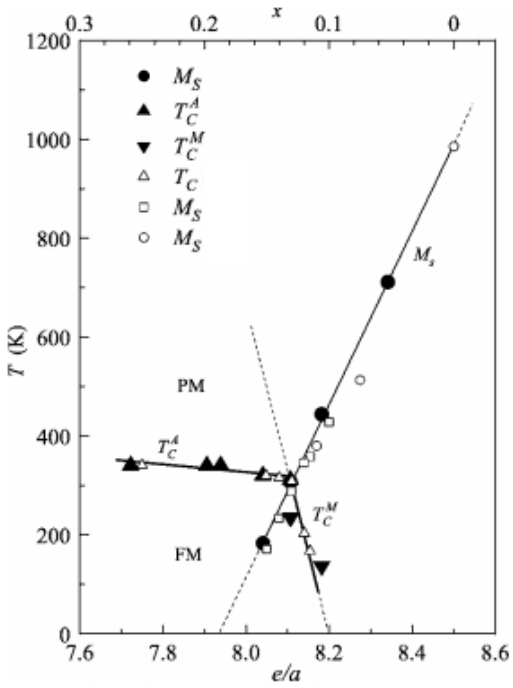


Figure 7: Variations in the TM, T_C^M and T_C^A -Values in the Marten Site and Austenite Phases as a Function of e/a (Krenke et. al, 2005).

Nucleation and succeeded growth in martensitic phase region is generally seen as indirect martensitic transformation, during transition the medium is a combination of two phases. Martensitic start and Martensitic finish (Ms/Mf) and Austenitic start and Austenitic finish (As/Af).Upon heating, the marten site phase becomes unstable and converts to the parent austenite phase at temperature termed as martensitic temperature (TM).There is a hysteresis between forward and reverse transformation processes in cooling followed by heating through the TM point, with no change in the chemical composition, but considerably large change in the heat and volume. Supercooling is necessary for nucleation of the marten site phase and, consequently, the marten site reaction is usually a thermal process with a particular starting point Ms and the finish point Mf. In the reverse process, the marten site phase starts transform back to the austenite phase at point As and completes at temperature Af. The average transformation temperature is described by the equation $T_M = 1/2(Ms + Af)$ (Kumar et al., 2008). A concurrence of the marten site and magnetic transitions near room temperature is promising for magnetic refrigeration applications. A hysteresis with a large heat change arises from an increase/decrease of the elastic and surface energies in the transformation (Sutou et al., 2004).

5.1 Ni-Mn-Sn Based Alloys and its Martensitic Transformation Temperature

Gao et al.(2009) suggested Cu substitution for Mn, in NiMn based alloy. When the Cu concentration is varying from 2 to 5 there is a drop in TM from 220 K to 120 K. TM is reported to disappear with further increase in Cu. Zhang et al. (2004), in their work on $Ni_{50}Mn_{36}Sn_{14}$ alloys identified that the transformation temperatures increasesfrom 196 to 249 K as the carbon content increases in Ni-Mn-Sn-C alloy. Maziarz et al., (2013) states that when Sn substituted by Al substitution reaches the transformation temperature and reverse temperature at 49 to 43K respectively. For $Ni_{50}Mn_{39}Sn_{11}$alloy as per Yuhasz et al., (2009) the samples show a martensitic transformation temperature of 379 K while if the samples are being annealed during the material preparation the martensitic transformation temperature tends to reach 400 K.

5.2 Ni-Mn-Ga Based Alloys and its Martensitic Transformation Temperature

Kishi et al., (2003) stated that the transformation and reverse temperature are estimated at 297and 367 K for Co-Ni-Ga alloy which are identical to Ni-Mn-Ga alloy due to unclear reasons as per their study. Vasil'ev et al., (1999) estimated the transformation temperature to be around 300K in $Ni_{21}xMn12_xGa$ alloy with varying substitution for x, thus the compositional dependence of martensitic transformation was seen. As per Gao et al.,(2006) martensitic transformation temperature increases with e/a ratio increase in ternary Ni-Mn-Ga alloys. It can also be applied to the case of the quaternary Ni-Mn-Ga-Gd alloys on a small range. Li et al. (2015) states that Ni-Mn-Ga alloy undergoes transition temperature at 200 K; which raises the maximum magnetic-field-induced strain. Li et al., (2003) studied on$Ni_{55.8}Mn_{18.1}Ga_{26.1}$ alloys and show that the martensitic transition temperature of 202 K.

For Ni2-Mn-Ga alloy as per Vasil'Ev et al., (1996) the transformation temperature is around 202K.The results interpret the dependence of temperature on the efficiency of direct conversion of electromagnetic and acoustic waves in the alloy. Rao et al., (2007) studied on $Ni_{55}Mn_{20.6}Ga_{24.4}$ and the transformation temperature is near room temperature, atoms of Ni occupy corners of cube forming a body-centered cubic (bcc) with center of the cube occupied by Mn and Ga elements. On cooling, the cubic structure transforms to a martensitic structure at TM temperature. As per Mandal et al., (2009) due to the dependence of composition to that of the transformation temperature for $Ni_{2+x}Mn_{1-x}Ga$, where x is 0.16 to 0.26 in steps of 0.02. We see that with the increase in x there is an increase in martensitic transformation temperature of the material from 260 to 445K. As per González-Legarreta et al., (2015) for the alloys $Ni_{47}Mn_{41}In_{12}$, $Ni_{45}Mn44In_{11}$, $Ni_{48}Mn_{39}In_{13}$the martensitic transformation temperatures are 300 and 302K and there tends to be a shift with increasing e/a ratio of the material. According to Khan et al., (2012) in $Ni_{50}Mn_{37+x}Sb_{13-x}$alloy where x=1, the martensitic transformation temperature is at 300K irrespective of changes made in e/a ratio in composition of the material. In both the cases T_M decreases with increasein Cr or Ni concentration. Thisindicates that, for a well-developed T_M monotonically following e/a does not apply to Mn rich Heusler alloys.

Fabbrici et al. (2009), in his research article presented the information regarding the martensitic transformation temperature of various heusler alloys which is tabulated in table 1.

Table 1: Heusler Alloys and their Martensitic Transformation Temperature form Fabbrici et al. (2009)

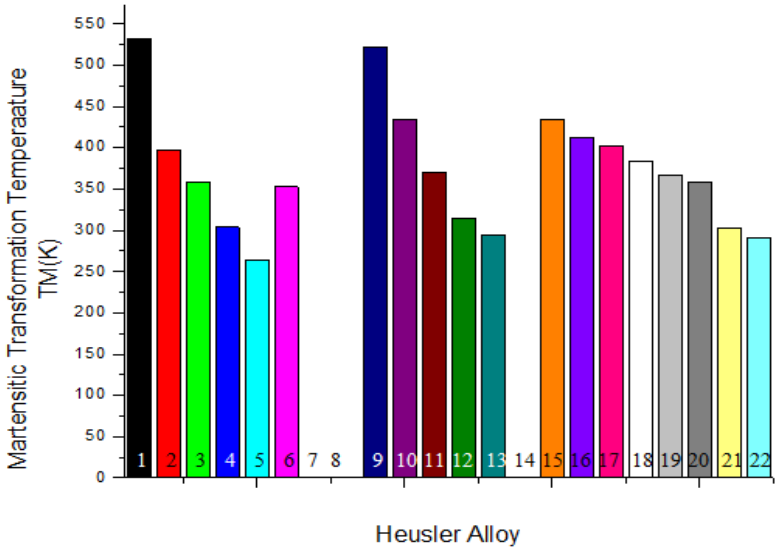
Heusler Alloys	T_M in K
$Ni_{43}Co_7Mn_{32}Ga_{18}$	420
$Ni_{41}Co_9Mn_{32}Ga_{18}$	421
$Ni_{50}Mn_{30}Ga_{20}$	376
$Ni_{45}Co_5Mn_{31}Ga_{19}$	353
$Ni_{43}Co_7Mn_{31}Ga_{19}$	384

It is seen from the table, as the Co content in the alloy composition isincreasedthe transformation temperature tends to disappear out of the measuring range. By varying the doping of Co suitably it is possibleto make a reverse magnetostructural transformation that can be varied in accordance with its composition and can be used for various application prospects.

5.3 Ni-Mn-In based Alloys and its Martensitic Transformation Temperature

Heusler alloys and their martensitic transformation temperature were studied by Ito et al. (2007) in their article. Here

around 22 alloys of various compositions have been considered and their transformation temperature is shown in figure below.



1. $Ni_{50}Mn_{40}In_{10}$
2. $Ni_{50}Mn_{37}In_{13}$
3. $Ni_{50}Mn_{36}In_{14}$
4. $Ni_{50}Mn_{35}In_{15}$
5. $Ni_{50}Mn_{34.5}In_{15.5}$
6. $Ni_{50}Mn_{34}In_{16}$
7. $Ni_{50}Mn_{33.5}In_{16.5}$
8. $Ni_{50}Mn_{25}In_{25}$
9. $Ni_{45}Mn_{40}In_{10}Co_5$
10. $Ni_{45}Mn_{39.5}In_{11.5}Co_5$
11. $Ni_{45}Mn_{37.5}In_{12.5}Co_5$
12. $Ni_{45}Mn_{36.5}In_{13.5}Co_5$
13. $Ni_{45}Mn_{36.6}In_{13.4}Co_5$
14. $Ni_{45}Mn_{36.5}In_{13.5}Co_5$
15. $Ni_{42.5}Mn_{39.5}In_{10.5}Co_{7.5}$
16. $Ni_{42.5}Mn_{38.5}In_{11.5}Co_{7.5}$
17. $Ni_{42.5}Mn_{38}In_{12}Co_{7.5}$
18. $Ni_{42.5}Mn_{37.8}In_{12.2}Co_{7.5}$
19. $Ni_{42.5}Mn_{37.7}In_{12.3}Co_{7.5}$
20. $Ni_{42.5}Mn_{37.6}In_{12.4}Co_{7.5}$
21. $Ni_{42.5}Mn_{37.5}In_{12.5}Co_{7.5}$
22. $Ni_{42.5}Mn_{39.5}In_{12.6}Co_{7.5}$

Figure 8: Heusler Alloys and their Martensitic Transformation Temperature from Ito et al. (2007).

From the plot it is clear that transformation temperature tends to decreases with an increase in the composition of the element, while the Tc of the parent phase is independent of variation in indiumconcentration. It is seen that there is an increase in temperature Tc with an increases in the addition of Co concentration. Transformation temperature illustrates a trend of decrease at the critical concentration there is a change in magnetism of the material from paramagnetic to ferromagnetic. In the Ni-Mn-In and Ni-Co-Mn-In serieswith varying composition the reduction in austenite to marten site temperature transformation induced by a magnetic change in field was confirmed. These results obtained from the experiment and that of the results that are obtained from Clausius–Clapeyron equation are in correlation.The transformation temperatures of the set of alloys are all-around 300K.

6. STRUCTURAL PROPERTIES

6.1 Mn-Based Heusler Alloys

According to Li et al (2007) for $MnFe_{1-x}Co_xGe$ with the increase in value of x from 0 to 1 at the step of 0.1 there is an increase of curie temperature Tc from 159 to 345K and the elements were initially in the space group of P63/mmc until x=0.8. As per Tegus et al. (2002) in $Mn_5Ge_{3-x}Sb_x$ alloys it also show an increasing Tc with the P63/mcm space group with the variation in the x. Zhao et al., (2006) show that in case of $Mn_5Ge_{3-x}Si_x$ alloy Tc tends to decrease with increase in x and the space group remains the same. Lin et al. (2006) showed that the samples have the Ni_2In type structure (hexagonal, space group P63/mmc) for $x < 0.8$ and in the TiNiSi-type structure (orthorhombic, space group Pnma) for x at 0.85. The Mn-Fe-Co-Ge alloy crystallizes in Ni_2In-type, butiota of orthorhombic phase traces was present. The lattice parameter

decreases and c increases, but the unit cell volume becomes smaller with increasing of Co contents.

Zhang et al. (2006) studied on $LaMn_{2-x}Fe_xGe_2$ at x= 0.1, 0.15, 0.2 with l4/mmm space group.Tohei et al. (2004) recognizeda decreasing trend in Tc for $Mn3_{-x}Co_xGaC$ and it had a Pm3m space group. As per Morikawa et al.,2004 in $Mn_{1-x}As_{0.75}Sb_{0.25}$ alloy, with x= 0, 0.03, 0.05 had a P63/mmc structure with a decreasing in Tc. The lattice parameters and the curie temperature of alloy materials in the series mentioned above decreases,when the value of x is increased. Large change in entropyof magnetism is observed in these alloys nearerto room temperature. Silicon substitutions in Mn_5Ge_3 alloys do not tend to show a variation in its crystal structure. The article also confirms that, the substitution of silicon produces two types of effects on MCE. Firstly, there is a declinein magnetic-entropy change when the content of silicon is increased, and secondly the magnetocaloric effect peak becomes broadened.

7. CONCLUSIONS

With the knowledge obtained from this review article, following conclusions can be drawn.

- Majority of the researchers used vacuum arc melting furnace with inert gas and some did multiple heating on it,in order to obtain a stable composition. In certain works, sintering technique was used to improve the ductility of the material. In some cases, the alloys are made to undergo annealing at higher temperature to tune the martensitic transformation temperature to a desired level.
- MCE is mainly based on phase transition order; first-order materials have the magnetic entropy change value (ΔSm) greater than the second order one. The temperature peaks are narrower in case of first order. In second-order transition type, ferromagnetic to paramagnetic transition occurs nearer to martensitic transformation temperature (Tc). During the change of phase, there is almost no synchronicity between the dissimilar phases and the magnetization reaches a very low value, which is almost equal to zero. Maximum MCE is attained in the region, where there is a transition of first-order especially when the magnetic transition as well as structural transition is occurred. Change in entropy at x= 4, 5 is 43 and 68 J/kg K for $Ni_{50}–xCo_xMn_{38}Sb_{12}$ alloy was observed for all the works considered for x varying from 0–7.
- The ability of the alloy to have a martensitic transformation temperature near room temperature is of prime importance for magnetic refrigeration application. Even though, this is purely achievable by proper tuning of the composition of the alloy according to e/a ratio. The parent alloy composition is a very important factor, in order to tune the magnetocaloric and forward & reverse magnetoresistance properties of the alloy. In alloys with composition of $Ni_{43}Co_7Mn_{32}Ga_{18}$, $Ni_{41}Co_9Mn_{32}Ga_{18}$, $Ni_{45}Co_5Mn_{31}Ga_{19}$, $Ni_{43}Co_7Mn_{31}Ga_{19}$it is seen that increase in certain composition of the alloy leads to vanishing of transformation temperature form the desired range which is not desirable.$Ni_{45}Mn_{36.5}In_{13.5}Co_5$ alloys show a martensitic transformation temperature of 294 K, which is equivalent to near room temperature; hence these can be used as a refrigerant material in conventional refrigerator system.
- Compounds crystallizing in the orthorhombic Fe_3C structure, tetragonal $ThCr_2Si_2$-type structure and hexagonal Mn_5Si_3-type structure with space group P63/mcm are all observed in the works of various authors. Large entropy change of magnetism is observed in these alloys nearer to room temperature. Si substitutions in Mn_5Ge_3 alloys have zero effect on the crystal structure of the alloy.

This review paper provides the basic and necessary information regarding the methods of alloy preparation, magnetocaloric effects of various heusler alloys used so far, martensitic transformation temperature of different types of heusler alloys considered in magnetic refrigeration process till date. This will also provideknowledge of the crystal structure of the Mn based heusler alloys. With this collective information about various structural and compositional characteristics of the alloys, one can get the knowledge to develop alloys of desired properties for suitable applications.

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