NiMn-based Heusler magnetic shape memory alloys: a review

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Abstract
The use of magnetic shape memory alloys (MSMAs) in manufacturing industry has increased significantly in recent years. This is mainly due to their great interest in their potential applications in smart devices, because of the reversible distortions suffered. The well-known example of these combinations is the Heusler type. A review is given of experimental works concerning the examination of magnetic field, structural phase transitions, and the magnetocaloric impact in Heusler Ni–Mn–X (X = In, Sn, Sb) and Ni–Co–Mn–Y (Y = In, Sn, Sb) alloys. This type of compounds has excellent properties, for example, the presence of coupled magnetostructural (coincident magnetic and martensitic transitions) and metamagnetostructural phase transitions (coincident metamagnetic (ferromagnetic-antiferromagnetic) and martensitic transitions), the magnetocaloric impact (MC), and the large magnetoresistance change (MR). The conceivable difficulties and remaining problems are briefly discussed.

Keywords Heusler alloys · Martensitic transformation · Magnetic shape memory alloys · Magnetocaloric · Metamagnetic alloy

1 Introduction
In previous decades, Heusler-type magnetic shape memory alloys (MSMAs) have an increasing interest in technological applications, because of their excellent properties. These multifunctional properties include magnetic transformation [1], reversible distortion [2, 3], giant magnetoresistance (MR) [4], and extensive magnetocaloric effect (MCE) [5, 6]. These properties make them especially interesting for the creation of new magnetic sensors, actuators, and magnetic coolant for magnetic refrigeration [7–9]. The main cause of the distortion of the structure is the martensitic transformation experimented by these materials from a high-temperature ordered cubic austenite phase to a low-temperature tetragonal, orthorhombic, or monoclinic disordered martensite phase. The structural change is displacive and diffusion less. At that point, the ferromagnetic-paramagnetic transition is experienced when the Curie limit is exceeded. This structural and magnetic progress can be created by two causes: magnetic field application or temperature change. Based on diffusion less phase transformation, which is called martensitic transformation, the shape memory effect (SME) in alloys is known to be novel conduct by which a deformed alloy in the low-temperature phase recuperates its original shape by reverse transformation upon heating to the reverse transformation temperature. This impact was observed for the first time in Au–Cd alloys in 1951 and turned out to be notable with its disclosure in Ti–Ni compounds in 1963 [10, 11]. The Ti–Ni alloys are the most recognizable shape memory alloys (SMA), with applications in different fields, such as cellular-phone antennae, medical guide wires, and smart actuators. Since the strain and stress created by the SME are extremely large as compared to those created in magnetostrictive and piezoelectric materials, SMA are potential candidates for actuators, for example, motors and supersonic oscillators. Be that as it may, since the output actuation in SMA happens through temperature change for an input signal, it is difficult to get a fast response to the input signal at frequencies high than 5 Hz, because the thermal conductivity of the alloys is a rate determining factor of the response [12]. This fatal drawback limits the use of SMA as actuators. MSMAs in which a rapid output strain is obtained by the application of a magnetic field have been produced to overcome this obstacle.
The most considered MSMA\textsubscript{x} are those called Heusler alloys. These mixtures are a well-known sort of association of intermetallic mixtures containing more than 1500 members, discovered by Fritz Heusler in 1903. He has analyzed a combination of Cu, Mn, and Al is ferromagnetic, although this is not the case for all three fundamental components [13, 14]. The reason for this originates from the special crystallographic structure of the material. The Cu\textsubscript{2}MnAl was the principle Heusler compound. This combination exhibited an austenitic phase at room temperature whose structure was totally chosen 3 decades later by Bradley and Rodgers [15]. They demonstrated a cubic structure L\textsubscript{2\textsubscript{1}} with the space group F\textbar m\textbar 3 m and a lattice parameter \(a = 5.949\ \text{Å}\) and a unit cell composed of eight atoms of Cu and four atoms of Mn and Al. These alloys are ternary semiconductor or metallic materials. The last has two stoichiometries, one of type 1: 1: 1 (half-Heusler alloys) and the other of type 2: 1: 1 (full-Heusler alloys) [16]. These days, they possess a hot area of research [17]. The general stoichiometric formula of full-Heusler alloys is X\textsubscript{2}YZ. The crystal structure is illustrated in Fig. 1. The X, Y, and Z components include four distinctive fcc (face centered cubic) lattices, which are moved along the spatial diagonal. It is referred to as the L\textsubscript{2\textsubscript{1}} Heusler structure with the space group F\textbar m\textbar 3 m. The atoms X are arranged on the (0, 0, 0) and the (\(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\)) lattice, whereas, the Y and Z atoms occupy the (\(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\)) and the (\(\frac{3}{4}, \frac{3}{4}, \frac{3}{4}\)) lattices, respectively [17]. There is another structure B\textsubscript{2}, appeared in Fig. 1, for the disordered state. In this case, the Y and the Z lattices are mixed. Thus, the unit cell can be described as a bcc (body centered cubic) lattice with X atoms in the corners and Y and Z atoms with half inhabitance in the center position [17]. The class of magnetic mixtures X\textsubscript{2}YZ and XYZ has multifunctional magnetic properties, for example, magnetooptical, semi-metallic ferromagnetic element, magnetooptical effect, shape memory effect, topological covers, and magnetocaloric and magnetostructural characteristics [18–22]. For the most part, these combinations were mass polycrystalline obtained by arc melting, followed by a high-temperature annealing, or single crystals created by the Czochralski technique [23–25]. Indeed, the fast quenching by melt-spinning offers three potential focal points for making practical devices: the shape of the ribbon, the avoidance of the annealing allows a better homogenization of the phase, and the fact that it’s easy to obtain highly textured ribbons. Among the melt-spinning conditions can be mentioned the pressure of the ejection gas, the device geometry, the melting temperature, the clearance between a nozzle and the wheel surface, and the rotational speed of the wheel that influences the structure of the ribbon and their dimensions [26]. The crystallization energy occurs during the change of these parameters and the heat exchange. The melt-spinning has been completed out in several shape memory systems: Mn–Ni–Sn, Ni–Mn–In–Co, and Fe–Pd [26–28]. One of the essential cases detailed in a Heusler type combination dates back to 1999 [29].

Throughout the years, martensitic transformations (MT) have not been found in full-Heusler alloys, with the exception of Ni\textsubscript{2}MnGa that experiences an MT and no volume change occurs over the progress [30–33]. These days, the martensitic transformation is uncovered at appropriate off-stoichiometric structures for any of the Ni\textsubscript{2}MnZ combinations (with Z = Ga, Sn, In, Sb) [34, 35]. The distinctions are that in these mixtures, in contrast with stoichiometric one, a volume change occurs during the martensitic progress, depending on the Z species [36] (see Fig. 2). The Heusler Ni–Mn–Ga combinations are the most considered alloys [37]. They demonstrate the interesting fact that they are the main ones exhibiting magnetic properties in their stoichiometric composition, whereas, other Heusler magnetic alloys show these properties only in off-stoichiometry. However, in order to overcome the generally low martensitic transformation temperature in the range between 180 and 200 K and the high cost of Ga, the search for alloys free Ga has recently attempted, specifically by displaying distinctive components, for example, In, Sn, or Sb. Krenke et al. [38, 39] inquired without Ga-free Heusler MSMA\textsubscript{x} supplanting Ga with Sn and In. They revealed a full standard examination of Ni–Mn–Sn [38] and Ni–Mn–In [39].

This article is restricted to NiMn-based Heusler magnetic shape memory alloys since it will be hard to consolidate the information from a broad number of productions on an extent of ferromagnetic compound systems, the vast majority of which just flag another piece with an enhanced magnetostructural characteristic. The principal fragment of this paper analyzes the impact of structural variation on the magnetic, and mechanical properties of various Heusler Ni–Mn–X (X = In, Sn, Sb) combinations. The second fragment of this paper deals with the connection among structure and properties of Ni–Co–Mn–Y (Y = In, Sn, Sb) systems. The structure-property correlation and furthermore the remarkable properties of Heusler combinations are investigated in various possible applications.

![Fig. 1 Schematic illustration of the L\textsubscript{2\textsubscript{1}} and the B\textsubscript{2} structure of a Heusler alloys with the chemical composition X\textsubscript{2}YZ. The X, Y, and Z atoms, which are shown in red, blue, and green respectively, occupy different sublattices. Reproduced from reference [17]](image-url)
2 Characteristics and properties of Heusler Ni–Mn–X (X = In, Sn, Sb) alloys

Recent research concerning the new MSMA’s of the Ni–Mn–X (X = In, Sn, Sb) alloys appears instead of the Ni–Mn–Ga alloy. This is due to the presence of a coupled magnetostructural transition in non-stoichiometric compositions. The magnetostructural change of these new Heusler alloys is joined by a magnetocaloric effect and giant magnetoresistance [5, 6, 36, 40, 41].

2.1 Structure and phase change of Heusler Ni–Mn–X (X = In, Sn, Sb) alloys

The magnetostructural transitions are shown in the Ni–Mn–X (X = In, Sn, Sb) alloys, which are joined by a magnetocaloric effect and giant magnetoresistance [41–57]. Takenaga et al. [41] exhibited that Ni2Mn2−xSnx alloys near to stoichiometry (x = 0.3) have a cubic structure of type Heusler L21 with a parameter of 6 Å. They have demonstrated that a slight increase in the level of Mn atoms in these alloys leads to the presence of a basic progress austenite-martensite during a temperature change. Hernando et al. [42] studied the magnetostructural development of Heusler NiMnSn and NiMnIn alloys. They showed that the alloys are monophase and that ferromagnetic L21 austenite is a high-temperature parent phase. In addition, at a low temperature, the austenite is converted into a martensite with a system-dependent symmetry modulated structure (orthorhombic 7 M, monoclinic 10 M, and monoclinic 14 M). Krenke et al. [37] studied the structural change in Ni0.2Mn0.5−xSnx alloys. They have shown that the structure of martensite is of the 10 M, 14 M, or L10 type, whereas, that of austenite is of the L21 type, on the basis of the Sn composition. In addition, they are showing that both phases are ferromagnetic in Ni0.5Mn0.5−xSnx alloys. For the Heusler Ni0.5Mn0.5−xInx alloys, they experience martensitic transformations in the scope of 0.05 ≤ x ≤ 0.16, while, in the 0.16 ≤ x ≤ 0.25 range, the alloys retain the cubic stage. At the point when x = 0.16, the magnetic field-induced structure transformation (MIST) occurs, and martensitic change moves 42 K in the 5 T field [38]. The structural change in Heusler Mn50Ni50−x(Sn, In) alloys is studied in references [43–45]. These studies have shown that the martensitic transformation (from austenite with cubic L21 structure to martensitic phase with 14 M modulated monoclinic structure) was detected in Mn50Ni50−xSn, and Mn50Ni50−xIn samples. Yiwen et al. [49] studied the structural change in Mn50Ni50−xSn (x = 7–10) alloys. The martensite phase is recognized to be modulated...
monoclinic 6 M; however, the austenite is with L21 cubic structure. At the moment when the Sn content is 7–9%, there is no obvious magnetization difference related to martensitic transformation, since the martensitic transition happens from a paramagnetic austenite to powerless magnetic martensite. For the ribbons with Sn content of 10%, the martensitic transformation occurs from ferromagnetic austenite to brittle magnetic martensite. Khan et al. [50] have demonstrated that Heusler Ni50Mn37Sn13 ingots and is a 14 M orthorhombic martensite, the orthorhombic structure is 10 M modulated for Ni50Mn25+. Martensite. Khan el al. [50] have demonstrated that Heusler formation occurs from ferromagnetic austenite to brittle magnetic. For transformation, since the martensitic transformation happens from a martensitic stage, decrease straightly with the expansion of x. Which of such structures stabilize in the martensitic transformation of the Ni–Mn–X alloys depends on the composition. The phase diagrams of Ni–Mn–based Heusler alloys are shown in Fig. 3. In these phase diagrams, the magnetic and martensitic phase change temperatures are plotted as a function of the valence electron concentration per atom (e/a) for Ni–Mn–Ga, Ni50Mn40–xInx, Ni50Mn40–xSnx, and Ni50Mn40–xSbx alloys [33]. It very well may be seen that the structure changed from cubic→10 M→14 M→L10 with an increasing (e/a) and temperature, in Fig. 3(a–c). But in Fig. 3(d), the alloy follows the next sequence cubic→4 O–sevenfold (mixture)→L10. The 4 O modulated structure is also observed, for the Sn alloy [33].

The correlation analysis between the width of the composition zones and species X, in the phase diagrams, describes the structural and magnetic changes. It’s also noted that the crystalline structure of martensite depends on the conditions of elaboration. For example, Santos et al. [51] observed a 7 O orthorhombic martensite in a Ni50Mn50Sn15 alloy with melt spinning technique; while, Muthu et al. [52] found an 4 O orthorhombic martensite, in Ni50Mn37Sn13 alloy obtained with arc melting technique. Hernandez et al. [42] reported that the orthorhombic structure is 10 M modulated for Ni50Mn37Sn13 ingots and is a 14 M orthorhombic martensite modulated for Ni50Mn37Sn13 ribbons.

### 2.2 Properties of Heusler Ni–Mn–X (X = In, Sn, Sb) alloys

The understanding of the possible appearance of the magnetostructure transition and inverse MCE is essential to study presence of the magnetic exchange interaction between the martensitic and austenitic phases in these alloys resulting in the presence of magnetization jumps. Krenke et al. [53] studied for the first time the inverse MCE in alloys: Ni50Mn35Sn15 and Ni50Mn37Sn13. The measurements ΔS_m were performed and based on the Maxwell relation. The maximum variation of the entropy is equal to ~ 15 J kg−1 K−1 at T_m = 185 K for the Ni50Mn35Sn15 alloy and for the Ni50Mn37Sn13 alloy was ~ 20 J kg−1 K−1 at T_m = 305 K, upon the change in the magnetic field ΔH = 5 T. The magnetostructural behavior and the magnetocaloric properties of the Mn50.5–xNi41Sn8.5x alloys with (x = 0, 1, and 2) were studied by Ghosh et al. [54]. They showed that the entropy change ~ 11.85 J kg−1 K−1 was obtained for x = 0 at 270 K under a magnetic field of 1.5 T. They demonstrated that the net refrigerant capacity was evaluated at ~ 44.82 J kg−1 for a similar example, which turned out to be larger than that of other Ni–Mn–Sn alloys. This causes the obtaining of a magnetoelasticity of about 33% for these alloys within the sight of 8 T attractive field contrasts. Caballero-Flores et al. [55] considered the thermomagnetic properties and magnetocaloric effect in Heusler Ni50.3Mn36.5Sn13.2 alloy ribbons. They showed that the maximum value of entropy about ~ 17.3 J K−1 kg−1 for an applied magnetic field of 3 T. The inverse magnetocaloric impact of bulk Ni2+xMn1.4−xSn0.6 (x = 0, 0.06, 0.12, 0.18) Heusler alloys is researched by Ray et al. [56] (see Fig. 4). They demonstrated that the change in magnetic entropy at first extended with abundance Ni focuses up to x = 0.12 in any case, then a drastic fall in value is observed for the sample x = 0.18, but, the relative cooling power (RCP) value is increased continuously with the excess Ni concentration. The effect of Sn content on mechanical, magnetization, and shape memory behavior in NiMnSn alloy is researched by Aydogdu et al. [57]. It was revealed that the Ni50Mn40Sn10 alloy have a good shape memory effect with 2.1% recoverable strain and completely reversible superelasticity at high temperatures (190 °C).
Ni_{50}Mn_{39}Sn_{11} alloy failed at 650 MPa and 7% during compressive deformation. Tan et al. [58] studied impacts of fractional substitution of Fe element for Ni element in the structure, martensitic transformation, and mechanical properties of NiFeMnSn alloys. They demonstrated that the mechanical properties of Ni–Mn–Sn alloy can be essentially improved by Fe addition. The Ni_{47}Fe_{3}Mn_{38}Sn_{12} alloy has accomplished a maximum compressive strength of 855 MPa with a fracture strain of 11%.

Stern-Taulats et al. [59] studied the magnetic caloric effect in a low-hysteresis Ni_{51}Mn_{33.4}In_{15.6} metamagnetic shape memory (see Fig. 5). They noted that the maximum variation of entropy in the martensitic transition region \( T_m = 304 \) K under the variation of the magnetic field equal to 5 T is \( \Delta S_m = 15 \) J kg\(^{-1}\) K\(^{-1}\). Thus, that the magnetocaloric effect is inverse, which is consistent with the fact that the transition temperatures pass to lower values under an applied magnetic field. Rosa et al. [60] showed the annealing influence on the martensitic transition and the magnetic entropy change in a Ni_{45.5}Mn_{38.0}In_{11.5} shape memory alloy. They showed that the annealing at 873 K was the best choice for high entropy variation; however, the other annealing at 973 and 1073 K. The giant elastocaloric impact of directionally solidified Ni–Mn–In magnetic shape memory alloys is researched by Huang et al. [61]. It was uncovered that the Ni_{48}Mn_{35}In_{17} alloy has a good reversibility of the giant elastocaloric with 1.4% recoverable strain. These adiabatic stress-strain curves present fully recoverable superelasticity of about 1.1% transformation strain.

Khan et al. [62] reported the inverse magnetocaloric effect in ferromagnetic Ni_{50}Mn_{37+x}Sb_{13-x} Heusler alloys and observed the best extent of the inverse MCE. The maximum estimation of \( \Delta S_m \) is 20 J kg\(^{-1}\) K\(^{-1}\) in Ni_{50}Mn_{38}Sb_{12} at 297 K for a magnetic field change of 5 T as compared to the concentrations \( x = 0.5 \) (\( \Delta S_m (T_m = 284 \) K) = 15.0 J kg\(^{-1}\) K\(^{-1}\)) and \( x = 0 \) (\( \Delta S_m (T_m = 273 \) K) = 18.2 J kg\(^{-1}\) K\(^{-1}\)). The exploratory investigations of magnetocaloric effect in Ni_{50–x}Mn_{38+x}Sb_{12} alloys with \( x = -1, 0, 1, \) and 2 performed by Feng et al. [63] (see Fig. 6). An extensive reversible negative above room temperature was founded. The most extreme estimation of \( \Delta S_m \) is 5.21 J kg\(^{-1}\) K\(^{-1}\) in Ni_{49}Mn_{39}Sb_{12} at 347 K for a magnetic field change of 5 T.

The mixture Co with Ni–Mn–X (X = In, Sn, Sb) alloys has a significant influence on the magnetic and mechanical properties, more precisely on the behavior of the magnetization. The Cobalt concentration also greatly affects the magnetic properties of these alloys.
3 Characteristics and properties of Heusler Ni–Co–Mn–Y (Y = In, Sn, Sb) alloys

In Heusler Ni–Mn–X alloys, the attractive coupling between the closest Mn particles is probably to be antiferromagnetic. However, by doping Co to supplant a piece of the Ni particles, the attractive coupling of Mn–Mn must be initiated for to be ferromagnetic. In this way, the expansion of Co for Ni builds the Curie point, the magnetic moment of the austenitic stage, and the magnetization at the MT. A remarkable behavior of the Ni–Co–Mn–Y alloys is the possibility of inciting the opposite transformation by an attractive field and the related metamagnetic shape memory impact, i.e., the recuperation of a past strain by means of field-initiated inverse MT.

3.1 Characteristics and properties of Ni–Co–Mn–In alloys

Recent studies demonstrate that the substitution of Nickel by Cobalt in Heusler Ni–Mn–In alloys firmly influences magnetocaloric and magnetic properties. Besides, Co-doping will not only improve magnetization of the magnetic phase of Ni–Mn–In, yet additionally enhance fundamentally upgrade metamagnetic properties, including the metamagnetic shape memory impact and the magnetocaloric effect. The Ni–Co–Mn–In alloys have numerous favorable advantages of the application, for example, the composition does not contain rare earths or harmful components, super-elastic deformation, great protection from oxidation, simple make, high machining, and high adiabatic temperature change at low field [64]. Huang et al. [65] detailed that the extensive reversible MCE in a Ni49.8Co1.2Mn33.5In15.5 magnetic shape memory alloy was acquired with a 7 M monoclinic structure. They demonstrated that the extensive reversible magnetic entropy change of 14.6 J kg\(^{-1}\) K\(^{-1}\) and a wide operating temperature window of 18 K under 5 T were all the while accomplished, connected with the low thermal hysteresis (8 K) and large magnetic-field-induced move of change temperatures (4.9 K T\(^{-3}\)) that prompt to a narrow attractive hysteresis (1.1 T) and little normal magnetic hysteresis loss (48.4 J kg\(^{-1}\) under 5 T) as well. This difference in parameters is critical for enhancing the magnetocaloric performance.

The impact of the atomic order on the martensitic transformation entropy change has studied in a Ni–Mn–In–Co metamagnetic shape memory alloy by Monroe et al. [66]. It is affirmed that the entropy change advances as a result of the variations on the degree of L2\(_1\) atomic order brought by thermal treatments, although, in opposition to what happens in ternary Ni–Mn–In. The entropy change value between around 40 and 5 J\(^{-1}\) kg\(^{-1}\) K\(^{-1}\) can be acquired in a controllable for a single alloy under the fitting maturing process, which drawing out the possibility of appropriating tune the magnetocaloric effect. For the Heusler Ni\(_{45}\)Co\(_3\)Mn\(_{37}\)In\(_{13}\) alloy at 1 T [67], when martensitic transition happened, the most extreme difference in magnetization \(\Delta M = 90\ \text{A m}^2\ \text{K}^{-1}\) was gotten. The martensitic structure is 6 M structure modulated with \(a = 0.4393\ \text{nm}, b = 0.5572\ \text{nm}, c = 1.296\ \text{nm}, \beta = 93.83^\circ\).

Kainuma et al. [2] examined the attractive field-actuated shape recuperation by reverse phase transformation of Ni\(_{45}\)Co\(_3\)Mn\(_{36}\)In\(_{13.4}\) alloy. The structure has cubic L2\(_1\) structure with \(a = 0.5978\ \text{nm}\), and the Curie temperature is \(T_C = 382\ \text{K}\). After cooling, a martensite stage change happens at a particular martensitic transformation temperature around room temperature, joined by large magnetization change (\(\Delta M\)). Li et al. [68] revealed that the vast reversible MCE in a Ni\(_{45.3}\)Co\(_{5.1}\)Mn\(_{36.1}\)In\(_{13.5}\) alloy was obtained with an austenite L2\(_1\) cubic structure. Furthermore, a substantial reversible \(\Delta S_M\) above room temperature was observed. The most extreme estimation of \(\Delta S_M\) is 16.7 J kg\(^{-1}\) K\(^{-1}\) for a magnetic field change of 5 T.

As of late, the mechanocaloric impact (including barocaloric effect and elastocaloric effect) and magnetocaloric effect in Heusler Ni–Co–Mn–In alloys have progressively pulling in consideration [69–71]. Liu et al. [5] revealed the inverse MCE amid the attractive field-initiated strains in Ni\(_{45.3}\)Co\(_{5.1}\)Mn\(_{36.1}\)In\(_{13}\) alloy. They mentioned the temperature change is imperative to such an extent that \(\Delta T_{ad} = -6.2\ \text{K}\) at 317 K in \(\Delta H = 1.9\) due to large reverse MCE. Although, the giant \(\Delta T_{ad}\) is getting just in the main stacking of field, but it strongly decreases after the cycle runs out of the field. Among the elements that reason the decrease of \(\Delta T_{ad}\), the hysteresis is the fundamental factor in this first-arrange progress. The irreversible energy loss caused by hysteresis altogether decreases the efficiency in magnetic refrigeration applications.

In Heusler Ni\(_{49.26}\)Mn\(_{36.08}\)In\(_{14.66}\) combination, an external pressure displaces the martensitic change temperature \(T_f\) by 2 K kbar\(^{-1}\) [72], while, for the Ni\(_{45.3}\)Mn\(_{36.7}\)In\(_{13}\)Co\(_{5.1}\) alloy, this expansion of \(T_f\) is 4.4 K kbar\(^{-1}\), which is considerably more articulated. It’s in this manner additionally critical to show that converse MCE materials, for example, Ni–Mn–Co–In exhibit an ordinary barocaloric impact. The magnetic hysteresis is illustrated in Fig. 7. It can be impressively decreased if the sample is charged without bias stress but demagnetized under an external hydrostatic pressure of 1.3 kbar. Moreover, the theoretical calculations give that the efficiency of a magnetocaloric material can be improved by all the while and precisely changing the magnetic field and the pressure, with respect to an apparatus in which just the magnetic field can be adjusted [73].

In Ni–Co–Mn–In system, a relatively flawless shape recuperation strain of about 3% can be acknowledged by applying both steady and single pulsed magnetic fields of 7 T [74]. This sort of shape memory alloy is known a metamagnetic shape memory alloy since it is caused by a metamagnetic change.

Feng et al. [75] examined the improvement of mechanical property and large shape recuperation of sintered Heusler
Ni45Mn36.6In13.4Co5 alloy. The mechanical properties of Ni45Mn36.6In13.4Co5 bulk sintered at 873 K with 60 MPa compressive stress are improved comparing with the as-cast ingot with same nominal composition. The strain and compressive fracture strength of it are 14% and 1200 MPa, respectively. While, the strain and compressive fracture strength of bulk sintered at 1073 K with 40 MPa are 9.5% and 800 MPa, respectively. The presence of texture benefits the strength and plasticity of it. The recoverable strain is 11.4% and 7.0% for the sample sintered at 873 K with α fiber texture ([100]/ND) under different compressive pre-strain and 7.8% for sample sintered at 1073 K without obvious texture, while, the recoverable strain is only 5.3% for the as-cast ingot with same pre-strain. All the recoverable strain of sintered sample is larger than 90%, while, that of the as-cast ingot is only 66.7%. This demonstrates that the improvement of mechanical property and texture both have effect on the expansion of recoverable strain.

3.2 Characteristics and properties of Ni–Co–Mn–Sn alloys

The Ni–Co–Mn–Sn system is another MSMA system pursued by the Ni–Co–Mn–In system. The Ni–Co–Mn–Sn system is a phenomenal possibility for a magnetic shape memory alloy for practical applications since it contains no costly segments and magnetic elements can be acquired. Also, good mechanical properties play an important role in the practical application of Ni–Mn–Sn MSMA. To completely comprehend the multifunctional properties of these alloys, it is very important to study in detail their magnetic and mechanical properties and their basic changes. Nevertheless, despite several examinations that have concentrated principally because of Co-addition to the magnetocaloric impact [76, 77], there have been a couple of methodical and definite investigations of composition-dependent magnetobasic change in this system.

Deltell et al. [78] considered the structural and thermal behavior of melt-spun alloys of the Ni–Mn–Sn–Co system. They indicated that the martensitic structure comprised of 4 O orthorhombic in samples with a higher (Mn/Sn) proportion and 14 M monolayers with 7 modulated layers in samples with a lower (Mn/Sn) proportion. Also, a change in the martensitic crystalline structure of 14 M to 4 O occurs with the decrease of the martensitic transition temperature. They suggested that the internal pressure be incited by the firmly situated microstructure, which prompts to the decrease of the progress temperature due to a refined martensite plate and to the formation of thick martensitic variants of different orientation. In addition, it has also been found that the partial substitution of Ni by Co shifts martensitic change to bring down to lower temperatures in Ni–Mn–Sn–Co compounds [77].

For compositional improvement purposes behind MSMAs, a recent investigation of the phase diagram of the Ni–Co–Mn–Sn alloy in the high-temperature range has established [79]. Be that as it may, the phase diagram in the low temperature extend has never been investigated. The foundation of the complete phase diagram of the Ni–Co–Mn–Sn alloy system is vital for understanding the temperature-dependent composition, practical properties, and physical phenomena in this compound (see Fig. 8). Cong et al. [80] detailed that the magnetic properties and both the temperature and magnetic-field-induced structural transformations in the Ni50–xCo4MnxSn11 (0 ≤ x ≤ 10) multifunctional alloys over a large temperature range from 500 K down to 10 K was performed. It’s uncovered that, with expanding x, the martensitic transformation temperatures first decrease slowly when 0 ≤ x ≤ 4 and then decrease rapidly when 5 ≤ x ≤ 8; no martensitic transformation was observed in the alloys with 9 ≤ x ≤ 10. The attractive properties of these alloys are very sensitive to their chemical composition. They noted from dependent on the outcomes of attractive and basic advances, the total phase diagram of the Ni50–xCo4MnxSn11 (0 ≤ x ≤ 10) alloy system, from high
temperature down to 10 K, is set up. This phase diagram can be used for the plan of multifunctional alloys with particular properties. Li et al. [81] contemplated the stage progress and magnetocaloric properties of the Mn$_{50}$Ni$_{42-x}$Co$_x$Sn$_8$ (0 ≤ x ≤ 10) alloys. They showed that the martensite has a b2/m monoclinic structure, which the austenite has a L21 cubic structure. On account of an attractive field change of 5 T, the magnetic entropy change values $ΔS_M$, for the Mn$_{50}$Ni$_{36}$Co$_x$Sn$_8$, Mn$_{50}$Ni$_{43}$Co$_7$Sn$_8$, and Mn$_{50}$Ni$_{34}$Co$_8$Sn$_8$ ribbons are 14.1, 18.6, and 16.0 J kg$^{-1}$ K$^{-1}$, respectively. Subsequently, contrasted with the Mn–Ni–Sn ternary alloys, the addition of Co permits a solid magnetostructural coupling over a wide temperature range with enhanced magnetocaloric properties in Mn$_{50}$Ni$_{42-x}$Co$_x$Sn$_8$ combinations. Wang et al. [82] revealed that the 2 at% Co-doping to the Ni$_{50}$Mn$_{30}$Sn$_{10}$ combination enhances the martensitic transformation temperatures about 25 K; in any case, it does not create any impact on the gem structure of the martensite. They noticed that the distinction in magnetization between martensite and austenite through the magnetotropic transformation increases strikingly. In this way, the magnetic transition temperature for martensite increments from 320 to 342 K with an expansion of 2 at% Co. Instead of the examinations on the MCE in Ni–Co–Mn–Sn alloys, electrical and thermal transports were scarcely investigated. Chen et al. [83] examined the thermo-control and resistivity regards in zero magnetic fields for Ni$_{47}$Co$_3$Mn$_{32}$Sn$_{10}$ tests. It’s found that the electrical transport is metallic, anyway by virtue of the paramagnetic and ferromagnetic austenite stages, a distinction in inclination occurs toward the start of the ferromagnetic change. Chen et al. [84] observed the martensitic transformation in Ti-doped Ni$_{43}$Ti$_x$Co$_{3}$Mn$_{32}$Sn$_{7}$. It’s confirmed that MT decreases and the mechanical properties are obviously improved by adding an appropriate amount of Ti. The experimental results confirm that the compressive strength and compressive strain of Ni$_{42.5}$Ti$_{0.5}$Co$_7$Mn$_{43}$Sn$_7$ alloy reach a maximum value of 1760 MPa and 23%, respectively [84]. Although the addition of Ti may improve the ductility to some extent, the substitution of Ti for Ni does not change the brittle nature of NiCoMnSn alloy.

### 3.3 Characteristics and properties of Ni–Co–Mn–Sb alloys

As effectively noticed, a few investigations have likewise reported the magnetic properties of the Ni–Mn–Sb alloys [62, 63]. In order to create new and better materials having a place with this series and to test the impact of structural variation on ECM, late examinations have explored the fractional substitution of Co for Ni in the non-stoichiometric Ni–Mn–Sb alloy [85–93]. Nayak et al. [85] reported the effect of Co on the structural, attractive, and magnetocaloric impact of Ni$_{50-x}$Co$_x$Mn$_{33}$Sb$_{12}$ alloys with x = 0, 2, 3, 4, and 5. They noticed that the martensitic progress temperature is found to diminish monotonically with Co focus. The estimation of the entropy change in Ni$_{45}$Co$_5$Mn$_{38}$Sb$_{12}$ compound is 29 J kg$^{-1}$ K$^{-1}$ at room temperature, while this estimation comes to 34 J kg$^{-1}$ K$^{-1}$ at 262 K under a magnetic field of 5 T. Sahoo et al. [92] analyzed the magnetic properties of as spun ribbon with the annealed ribbon and the bulk alloy of Ni$_{46}$Co$_4$Mn$_{38}$Sb$_{12}$, and observed that MT of as-spin ribbon was higher than that of the bulk sample, while the magnetization of as-spin ribbon was lower. In Ni$_{46}$Co$_4$Mn$_{38}$Sb$_{12}$–Z$_x$ (Z = Si, Ga), the Si substitution for Sb balances out the austenite stage, whereas, the Ga substitution stabilizes the martensite phase. With x = 1 for Si, the change martensitic abatements to 254 K, and a large MCE of 70 J kg$^{-1}$ K$^{-1}$ are obtained [87]. The content outcomes in reference [86] uncovered the magnetocaloric and magnetotransport properties in Ge-doped Ni–Mn–Sb Heusler compounds. The most extreme $ΔS_M$ estimation of 39 J kg$^{-1}$ K$^{-1}$ was gotten in the warming mode at 273.5 K with a 50 kOe field change, while, a maximum estimation of 42 J kg$^{-1}$ K$^{-1}$ was obtained in cooling mode at 272.5 K in a similar field. Nayak et al. [88] analyzed the effect of weight on the magnetic properties and the magnetocaloric effect in Ni–Co–Mn–Sb Heusler combination.

The temperature dependence of magnetization under various pressures (0–9 kPa) shows that MT moves to higher temperature with the expansion in the pressure, and the martensitic stage is overhauled under pressure, while the isothermal magnetic entropy change decreases with the extension in the pressure. The field dependence of resistivity ($ρ$(H)) in Ni$_{45}$Co$_5$Mn$_{38}$Sb$_{12}$ at different temperatures represents that the martensitic arrange which changes to parent stage couldn’t absolutely recover to its original state without an outer magnetic field. It is attested that the austenite phase would be able
to be stuck and the transformation couldn’t be totally reversible in the field dependence of resistivity, and heat capacity [94]. At the point, when reheated temperature/field cycling is connected in Ni₄₅Co₈Mn₁₈Sb₁₂, the resistivity on a very basic level increases and the magnetization decreases due to the microstructural deformation and lattice disorder [88]. Millan-Solsona et al. [95] examined the polycrystalline Ni–Mn–Sb–Co magnetic shape memory alloys which are known to exhibit a magnetocaloric effect. They have demonstrated that the entropy change values related to the elastocaloric effect. They have accounted that the energy stress, high stress output, high reaction recurrence, and new stress compare favorably to ΔS values detailed for non-magnetic shape memory alloys.

In summary, a large portion of the properties of the quaternary Ni–Co–Mn–Y (Y = In, Sn, Sb) Heusler-type MSMA₄, outflank those of the Ni–Mn–X (X = In, Sn, Sb) ternary systems.

- The Ni–Co–Mn–In alloy has great metamagnetic properties in which the large magnetization change is ~ 80 A m⁻² Kg⁻¹ during the martensitic progress. It reveals the largest change in magnetocaloric entropy among quaternary systems.
- The Ni–Co–Mn–Sn compound has a low thermal hysteresis about 10 K and a low magnetic hysteresis about 1.5 T.
- The Ni–Co–Mn–Sb compound demonstrates a high magnetoresistance more noteworthy 70%.

4 Conclusion

This paper is committed to a review of exploratory examinations on phase transitions magnetic and mechanical properties of Heusler Ni–Mn–X (X = In, Sn, Sb) and Ni–Co–Mn–Y (Y = In, Sn, Sb) shape memory alloys. Various studies believe that they have examined the multifunctional properties of these Heusler alloys. These materials have many multifunctional properties, for example, metamagnetic properties: correspondent (ferromagnetic-antiferromagnetic and martensitic advances), shape memory effect, exceptional magnetocaloric impact, and giant magnetoresistance. The idea of high recovery stress, high stress output, high reaction recurrence, and exact control make for an expansive point of view in scientific research and applications design. Be that as it may, the investigation of these alloys has burdens, for example, these alloys with poor mechanical properties normally crack under repeated stress cycles and the cooling life is reduced. The real utilization of magnetocaloric materials and elastocaloric materials requires good mechanical properties. Unfortunately, at present, the main disadvantage of existing MSMA₄ is its very fragile nature and poor mechanical properties. Therefore, it’s urgent to solve the brittleness problem. In addition, due to the coupling of the martensitic transformation and the ferromagnetic transition, the MSMA₄, has a lower operating temperature. However, very few studies have been conducted to increase the operating temperature of these MSMA₄, which is also one of the main requirements of the practical applications. The advancement of MSMA₄ is even at the research stage and the degree is limited. New applications, for example, in the fields of the actuator and the magnetic sensor must be studied. It is clear that the fundamental research in materials science and Heusler MSMA applications are still in the beginning.

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