Magnetic properties, martensitic and magneto-structural transformations of ferromagnetic Ni-Mn-Sn-Cu shape memory alloys

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Abstract: The influence of Cu doping on structural and magnetic properties of $\text{Ni}_{50-x}\text{Mn}_{36}\text{Sn}_{14-y}\text{Cu}_{x,y}$ ($x=0, 1, 2$ and $y=1$ at. %) ribbons has been investigated. The crystalline structures of the alloys were resolved by X-ray diffraction (XRD). It is found that the addition of Cu for Ni stabilizes austenite phase, whereas, replacing small amount of Cu for Sn stabilizes modulated martensite phase. Differential scanning calorimetry measurements have proved the characteristic transformation temperatures. The transformation temperatures generally rise as increasing the Cu content. Therefore, the magneto structural transition, analysed by vibrating sample magnetometry, is tuned by appropriate Cu doping in the alloys. Likewise, both martensitic and austenitic states exhibit ferromagnetic behaviour.

Keywords: Martensitic transformation, magnetic properties, phase transitions, Cu additions, Heusler alloys.

Introduction

Heusler alloys of Ni-Mn-Sn have gained substantial consideration owing to their useful properties and potential applications as smart materials in view of an environmental friendship. Moreover, these alloys exhibit very interesting shape-memory effect (SMAs). The reversible phase transformation can be considered as the main characteristic of SMAs, that is, it follows a first-order phase transition (FOPT) from a cubic austenite phase with high symmetry to a martensite phase with lower symmetry. By this means, applying external magnetic field or variable temperature result in a martensitic transition (MT). whence the gorgeous functional properties, like the shape memory effect, magnetoresistance response (MR) [1] and the inverse magnetocaloric effect (IMCE) [2]. The significance of magnetic field usage in these alloys offers a new generation of potential actuators and sensors which can be used in high frequency applications [3].

Generally, the magnetic properties of martensite depend on the coexistence of antiferromagnetic and ferromagnetic connections, although the austenite shows ferromagnetic correlations only. Afterward, a huge change in magnetization in the process of martensitic transition is due to a difference in Zeeman energy between the austenite and martensite phases, then a field induced reverse martensitic transformation (FIRMT) happens [4].

A large entropy change is therefore, due to unexpected magnetization change of these alloys at martensitic transition. Consequently, they show a good magnetocaloric effect (MCE). This later, derives from the magnetization jump produced by the variation of magnetic anisotropy upon the martensitic structure transition.

Generally, it is known that changing chemical composition and multiple doping in Heusler alloys disturb directly the MT temperature and magneto-structural properties of the alloys. Mostly, the topic discussed in this paper <<polycrystalline ternary full Heusler alloys heat treated>> have focused on the doping element on the off-stoichiometric Ni-Mn-Sn shape memory alloy to develop quaternary systems, such as Ni-Mn-Sn-Co [5], Ni-Mn-Sn-Cu [6], Ni-

Mn-Sn-Pd [7]. As motivation, we want to produce such alloys to improve their physical properties and promote their application in the future i.e., adding of fourth element atoms may tailor the microstructure and the magnetic response, the transition temperature and the degree of hysteresis associated with the martensitic transition. Thus, the main objective is to enhance the magnetic properties of alloys. Cu, for instance, has been shown to have a substantial effect on the properties of the Ni-Mn-Sn alloy. It has been revealed that the substitution of Ni by Cu in $\text{Ni}_{46-x}\text{Cu}_y\text{Mn}_{43}\text{Sn}_{11}$ [8] results in a shift of the martensitic transition to a lower temperature while the transition shifts to higher temperature when Cu replaces Sn in $\text{Ni}_{16}\text{Mn}_{12}\text{Sn}_{4-x}\text{Cu}_x$ [9]. Strain modulated ferromagnetic resonance (SMFMR) [10] is a unique technique which allows determination of magnetoelastic properties of magnetic shape memory ribbons. The use of this technique let us to determine the magnetoelastic properties of the ribbons.

In the present paper, we have prepared a series of $\text{Mn}_{50-x}\text{Cu}_{x,y}\text{Ni}_{36}\text{Sn}_{14-y}$ ($x = 0, 1, 2$ and $y=1$) quaternary alloys with Cu substitution for Ni sites and Sn sites. Our aim is to figure out the impact of non-magnetic Cu addition on phase transformation characteristics, and magnetic structure which help us to appreciate the phase transformation profoundly and design new Ni-Mn-Sn alloys with excellent magnetic properties by doping. In addition, the magnetoelastic and magnetostriction properties of Ni-Mn-Sn and Ni-Mn-Sn-Cu Heusler alloys was studied. Numerous properties including shape memory effect and temperature dependence of magnetism have been examined as well.

2. Experimental procedure

Nominal compositions with atomic percentage (at. %) of $\text{Ni}_{50-x}\text{Mn}_{36}\text{Sn}_{14}\text{Cu}_x$ ($x = 0, 1$, and 2) and $\text{Ni}_{50}\text{Mn}_{36}\text{Sn}_{13}\text{Cu}_1$ alloys was elaborated by the non-consumable Buhler MAM-1 arc melting under argon atmosphere using high-purity elements ($> 99.98\%$). An additional 2 wt.% of manganese was added to fulfil losses related to its evaporation during fabrication progression. Each ingot was melted five times to guarantee an initial homogeneity and found

into a water-cooled copper mold to obtain a massive alloy with a round shape. The obtained ingot was sealed into a quartz cylinder under a vacuum of 10^{-4} Torr and were evicted, at room temperature, into a rotating copper wheel, with 40 ms^{-1} surface velocity. Melt spinning was achieved under Argon air and ribbons alloys were obtained. The microstructure, morphology and experimental structure of the alloys were examined by a scanning electron microscope using a Zeiss DSM 960A functioned at 30 kV, attached with an energy dispersive spectrometry (EDX) device (Carl Zeiss, Oberkochen, Germany). The X-ray diffraction (XRD) studies were made to verify the crystallographic structure of the spun-ribbons, at room temperature, on a Panalytical Empyrean diffractometer in a $(\theta-\theta)$ Bragg-Brentano geometry, by means of a radiation font of Cu-K α (with wave length of $\lambda = 1.5406 \text{ \AA}$). The refinement of crystalline structures are made by means of Maud software, which is founded on Rietveld method [11]. Crystal Structures of the austenite to martensite were attained by differential scanning calorimetry (DSC) in a DSC822 Mettler-Toledo calorimeter. Thereby, thermal cycling experiments, were achieved under argon atmosphere, thru a cooling and heating rate of 10 K/min. Thermomagnetic measurements were done by means of a vibrating sample magnetometer (VSM-Versa Lab, QD). Zero-field-cooling (ZFC), field-cooling (FC) and field-heating (FH) protocols, in a temperature range from 0 K up to 400 K and an applied magnetic field up to 5 Tesla. From SMFMR technique, we investigated the magnetoelastic properties of $\text{Ni}_{50}\text{Mn}_{36}\text{Sn}_{14}$ and $\text{Ni}_{48}\text{Mn}_{36}\text{Sn}_{14}\text{Cu}_2$ samples at room temperature. We used conventional X band EPR spectrometer with magnetic field variation (frequency 100 kHz, amplitude 10^{-1} - 100 Oe) equipped with the additional system for the strain modulation (frequency 48 kHz, amplitude 10^{-6} - 10^{-5}).

3. Results and discussion

3.1. Structure and microstructure

Fig.1 shows the x-ray diffraction patterns of $\text{Ni}_{50-x}\text{Mn}_{36}\text{Sn}_{14}\text{Cu}_x$ alloys ($x=0,1$ and 2) and $\text{Ni}_{50}\text{Mn}_{36}\text{Sn}_{13}\text{Cu}_1$ measured at room temperature. The structure of the samples was of nearly the similar pattern except for small differences in the peak intensities and angles. All the diffraction patterns were successfully recognized with the austenite structure. This is owing to the existence of (111) and (311) superlattice diffraction peaks which confirms the high order of $L2_1$ structure. Therefore, the XRD pattern corresponding to the melt-spun ribbons disclose a high symmetry $L2_1$ structure austenite phase. The lattice parameter a is 0.598 nm, 0.583 nm and 0.578 nm for $x=0, 1$, and 2 alloys, respectively and space group $Fm-3m$. The value of a is declined when the Cu content is decreased. This effect could be assigned to the replacement of larger atomic radius Ni (0.162 nm) by the smaller atomic radius of Cu (0.157 nm) [12]. The high/low degree of order might be attributed to the high/low vacancy concentration [13] .

Regarding to the occupation of crystallographic sites in these types of alloys; for stoichiometric Ni_2MnSn Heusler alloys Ni, Mn, Ni, and Sn occupy $(0, 0, 0)$, $(0.25, 0.25, 0.25)$, $(0.5, 0.5, 0.5)$, and $(0.75, 0.75, 0.75)$ sites, respectively [14]. Whereas, in off-stoichiometric $\text{Ni}_2\text{Mn}_{1+x}\text{Sn}_{1-x}$ some Sn sites might be occupied by the excess of Mn atoms. Thus, Mn atoms can have Mn atoms as adjacent neighbours along the $[110]$ directions. Then Mn-Mn interatomic distance, become smaller than that in the stoichiometric compound [2]. Figure 2 shows the XRD patterns of $\text{Ni}_{50}\text{Mn}_{36}\text{Sn}_{13}\text{Cu}_1$ alloy measured at room temperature. The diffractogram demonstrates a modulated martensitic phase, which is confirmed to be five-layered monoclinic $10M$, with cell parameter: $a= 0.448$ nm, $b= 0.563$ nm, $c= 2.928$ nm and $\beta= 92,28^\circ$. The Rietveld analysis is the most pertinent analysis for indexing and recognizing these types of diffractograms. These latter are carried out and indexed using Maud software [11]. It is important to note that the theoretical curves fit properly with the experimental ones excepting for the highest of certain peaks. This minor mismatch in the altitude of peaks is conceivably due to the anisotropy and

texture effect [15].for that, the degree of B2 and L21 ordering in the alloys was assessed using these relations [16]:

$$(I_{200}/I_{220})_{\text{exp}} = S_{\text{B2}}^2 (I_{200}/I_{220})_{\text{th.}} \quad (1)$$

$$(I_{111}/I_{220})_{\text{exp}} = [S_{\text{L21}} (3 - S_{\text{B2}}/2)]^2 (I_{111}/I_{220})_{\text{th.}} \quad (2)$$

where the $I(hkl)$ refer to the Bragg peak's intensity, Miller indices (hkl) and the suffixes 'exp' represent experimentally obtained intensity values and 'th' represent theoretically simulated ones, respectively. S_{B2} and S_{L21} correspond to the degree of B2 and L21 ordering, respectively. S_{B2} and S_{L21} determined for each alloy are listed in Table 1. It can be noticed that however high L21 ordering until 85% is achieved, atomic disorder of 15–18% exists in the alloys. This behaviour was seen by R.Modak et al [17].

The morphology of the fracture cross section and free surface of the attained ribbons are presented in Fig.4. The micrographs shows that the samples were entirely crystalline, the ribbon flakes (10-15 μm of width) have a similar morphology. Small equiaxed grains were found in fig.1(a)-(c) to be crystallized in a thin layer from the wheel side. In fact, this layer is one that illustrates the main differences in microstructure between the four compositions. Then, the wheel surface of the last one (fig.1(d)) clearly present the lamellar microstructure of the martensite. Heusler alloys produced by melt spinning shows a typical columnar structure in the fracture cross section (fig.1(a'')-(d'')). This is a sign of the quick crystallization and fast kinetics progress of the samples. The chemical structure of the obtained ribbons was checked by Energy dispersive X-ray spectroscopy (EDX) which is frequently coupled with SEM; these results are listed in Table 2. All of the ribbons had a chemical composition near to the respective composition for each of them. Ribbons are flimsy and easy to cleave in such direction.

3.2. Thermal analysis

Shape-memory alloys (SMAs) are a unique family of metals that undergo a solid-to-solid transformation and can exhibit large recoverable strains introduced at low temperature, simply

by heating the material through a transformation temperature. To study the thermal stability of alloys and to be able to follow the transitions of phases carried out, one must resort to the XRD results. One knows that thermal hysteresis is a typical characteristic for the martensitic transition due to the first-order nature of the transition [18]. Hence, in order to notice the martensite-austenite transition, the DSC scans of $\text{Ni}_{50-x}\text{Mn}_{36}\text{Sn}_{14}\text{Cu}_x$ ($x = 0, 1$ and 2) ribbons should be performed by heating from room temperature at a critical temperature of A_s . Whereas the DSC scan of $\text{Ni}_{50}\text{Mn}_{36}\text{Sn}_{13}\text{Cu}_1$ alloy might be performed by cooling from room temperature, starting from a critical temperature of M_s . The corresponding DSC results are given in Fig.3. The high temperature causes the atoms to arrange themselves into the most compact and regular pattern possible resulting in a rigid cubic arrangement. These Heusler alloys display a first-order structural transformation, for which M_s increases with increasing Cu content. We can notice here that M_s increases bit by bit by substituting Ni by Cu from 194.09 to 228.31 K. Nevertheless, replacing Sn by 1at% of Cu notices an abrupt increase in M_s from 194.09 to reach a value of 325.02 K. One visibly notices that the M_s for $\text{Ni}_{50-x}\text{Mn}_{36}\text{Sn}_{14}\text{Cu}_x$ ($x=0,1$ and 2) is below room temperature. However, the M_s for $\text{Ni}_{50}\text{Mn}_{36}\text{Sn}_{14-x}\text{Cu}_x$ ($x=1$) is in above room temperature. These behaviours can be recognized, distinctly, from XRD studies. Other interesting features extracted from the calorimetric measurements are following thermodynamic parameters. The difference between the temperatures of the peak positions represent the width of the hysteresis ΔT . The nonappearance of second thermal process disclose us the homogeneity of the as spun-ribbons.

The entropy change can be calculated as of the baseline calorimetry data by the following relationship:

$$\Delta S = \int_{T_i}^{T_f} \frac{1}{T} \left(\frac{dQ}{dt} \right) \left(\frac{dT}{dt} \right)^{-1} dT \quad (3)$$

The integrals were numerically performed from M_s on cooling and from A_f on heating to a given temperature T within the transformation interval after choosing an appropriate base line. Q is the heat exchange determined through the transformation process. It is considered as the area of the DSC peak and can be similarly defined as the enthalpy change (ΔH) at the temperature that denotes martensitic transformation (T_0), the Gibbs energies of martensitic phase are equivalent to the parent phase [16].

Thus, the thermodynamic equilibrium condition is:

$$\Delta G = 0 = \Delta H - T_0 \Delta S \quad (4)$$

we can deduce that:

$$T_0 = \Delta H / \Delta S \quad (5)$$

Whence:

$$T_0 = \frac{1}{2} (M_s + A_f) \quad (6)$$

Thus, all the thermodynamics parameters and characteristic temperatures (ΔH , ΔS , A_s , A_f , M_s and M_f) are collected in Table 3.

To further describe this alloy, the average number of valence electrons by atom (e/a) parameter was introduced. One must know that (e/a) has a strong impact on the transformation temperatures for Ni-Mn-Sn Heusler alloys [19].

Electron configurations of the outer shells of different elements is extracted to compute the valence electron concentrations per atom. The e/a ratio is considered to affect the martensite start temperature, M_s , because of the linear relationship between them; M_s declines with declining e/a value [20]. Thereby, the two values of e/a and M_s must follow the rule and increase monotonously [21]. Since the outer atom of Cu contains fewer electrons than Ni or Sn, the substitution of Ni by Cu atoms ensures a reduction in the value of e/a .

Hence, the value of the starting temperature of martensite diminishes. Recurring to this present work, for $Ni_{50}Mn_{36}Sn_{14}$, $Ni_{49}Mn_{36}Sn_{14}Cu_1$, $Ni_{48}Mn_{36}Sn_{14}Cu_2$ and $Ni_{50}Mn_{36}Sn_{13}Cu_1$, the

obtained value of e/a are 8.08, 7.99, 7.90 and 8.05 respectively. it would be renowned that e/a ratio decreases with gradual Cu-doping, whether by substitution of Cu for Ni or for Sn. Analogous findings were create to prove the dependence of e/a on M_s and % of Cu-content [12,20].

Obviously, the modest rule between e/a and the % of Cu-content does not fit the finding showed by B.Gao et al [23]. This can be accredited to the amount of valence electrons for Cu.

Then, the electron configuration of Cu can be $3d^{10}4s^1$ in some ways. We can choose only the 4s electron, i.e. 1 electron, as the valence electron of Cu [22], while other authors measured equally 3d and 4s electrons, i.e. [22,23].

3.3. Magnetic properties

In order to accustomed the transition temperatures and the magnetic state of the alloys, the magnetization temperature dependence, $M(T)$, of the ribbons studied in this paper, has been measured in zero-field-cooled (ZFC), field-cooled (FC), and field-heated (FH) methods. First of all, samples were first cooled down to 100 K in zero field; then applying magnetic field to the sample and the magnetization was measured on heating with the field fixed, hence the obtention of ZFC magnetization curve. The FC (cooling) magnetization was measured while cooling the sample to 100 K with the similar field, at that point the FH (heating) magnetization was reached while heating the sample to 400 K below unmoved field. The temperature dependence of magnetization for all samples recorded 50 Oe and 50 KOe are revealed in Fig.5 and 6, respectively. Through the process of magnetic transition, both FC and ZFC curves exhibits an irreversible behaviour due to an obvious hysteresis lead to forward and inverse MT. The martensitic transformation requires an overheating to transform martensite to austenite and an undercooling to transform austenite to martensite. This behaviour was presented in such a thermal hysteresis in the Field-Cooling _Field Heating sequence. Moreover, under the

ferromagnetic transition temperature, a deviation between the ZFC and FC curves can be accredited to the coexisting of antiferromagnetic (AFM) coupling in the melt-spun ribbons[9]. It is worth noting that the martensitic transition is a first-order transition. This is represented by thermal hysteresis, which is an emblematic characteristic for the martensitic to austenite transition [18]. The gap detected in the thermal hysteresis of ZFC and FC around 200-220 K (Fig. 5) recommend for us the position of the martensitic start transformation. Similarly, we can understand that the magnetization of the alloys has a minor growth with Cu addition. Likewise, Kun Zhang et al [9] have stated the same behaviour. Through a supplementary rise of the temperature, the magnetization decreased rapidly for $x=0,1$ and 2 alloys. The Curie temperature demonstrate a second-order characteristics transition (no thermal hysteresis happens around T_C) from the ferromagnetic to the paramagnetic state.

For $\text{Ni}_{50}\text{Mn}_{36}\text{Sn}_{13}\text{Cu}_1$, it seems that the martensitic transformation has not thoroughly accomplished. It would be observed that the martensitic transformation temperature will be detected at higher than the Curie temperature and beyond the measurement temperature range, by introducing additional amount of Cu. The martensitic transition can be observed at temperatures above and below the Curie temperature [26]. Curie temperature undergoes a slight change to low temperature under the effect of Cu addition; $T_C= 307, 306, 298$ and 294K for $x=0, 1, 2$ and $y=1$ respectively. The martensitic transformation temperatures measured from the $M(T)$ curves are a little bit lower, compared to the results extracted from the DSC measurements (Table3). One can see that $M_s=190\text{ K}, 198\text{ K}, 227,5\text{ K}$ and $324,25\text{ K}$ for $x=0, 1, 2$ and $y=1$ respectively. Those divergences might be linked to the experimental conditions/effects such as the application of a magnetic field, or/and the error in measurement from instruments.

Fig.5 and 6 also reflect the existence of the phase transformation. One can note that the martensite is more stable through applying an external magnetic field. It takes more energy from the austenite to martensite. And that makes martensitic transformation temperature shift

to higher temperature. This is related to the ferromagnetic state of the martensitic phase [27]. Thereupon, hysteresis loops at 50 K of all the Heusler ribbons are shown in Fig. 7. Hysteresis loops measured at 50 K, emphasize the ferromagnetic ordering of all the Heusler ribbons. From small hysteresis loops, we may perceive the magnetically soft character of austenitic phase, correlated to its highly symmetric cubic structure and low magneto-crystalline anisotropy [28]. This result is in accordance with XRD and refinement results (L21 cubic structure). As expected, austenite phase is magnetically softer than martensite ($\text{Ni}_{50}\text{Mn}_{36}\text{Sn}_{13}\text{Cu}_1$), shows high saturation magnetization at low fields and fast approach to saturation. This behaviour was also seen by L. González-Legarreta et al [27]. The small hysteresis loops are characteristic of soft magnetic materials. It is acknowledged that hysteresis loop of the austenite phase saturated more quickly than that of the martensite [13].

Figure 8 gives the temperature dependence of electrical resistance measured at 0 T and 5 T for $\text{Ni}_{50}\text{Mn}_{36}\text{Sn}_{13}\text{Cu}_1$ alloy from 0 to 350 K. For this martensitic phase, the electrical resistance declines slightly as the temperature increases, showing a semiconductor-like behaviour (electrical conductivity value between that of a metal and an insulator). The martensitic transformation brings a sharp jump of electrical resistance, which has also been shown in Ni-Mn-Sn and Ni-Mn-In Heusler alloys[27-29]. It is conveyed that the resistivity of martensite is higher than that of austenite in the Ni-Mn based Heusler alloys [31]. In the vicinity of 325 K, the resistivity drops brusquely, corresponding to the reverse MT. The first order nature transition is confirmed by the existence of thermal hysteresis between heating and cooling processes around MT temperature. So, the diminishing of resistivity values is due to the transformation from martensitic frictions to austenitic in the alloy. The resistivity dependence of magnetic field (up to 9 T) at different temperatures for $\text{Ni}_{50}\text{Mn}_{36}\text{Sn}_{13}\text{Cu}_1$ is plotted in Fig. 9. The resistivity returns to its initial value of 0, when, the magnetic field is decreased from 9 T to 0 T.

Furthermore, as an incomplete martensite has been transformed to austenite by heating, thus, the residual martensite transforms to austenite by magnetic field.

The magnetoelastic constants of $\text{Ni}_{50}\text{Mn}_{36}\text{Sn}_{14}$ and $\text{Ni}_{48}\text{Mn}_{36}\text{Sn}_{14}\text{Cu}_2$ ribbons were taken from SMFMR studies and given in table 4. For uniaxial symmetry, the magnetoelastic tensor has five independent components (in Voigt notation): B_{11} , B_{12} , B_{13} , B_{33} , and B_{44} [32]. There are no shear strains in our system. Hence, $\varepsilon_{13} = \varepsilon_{23} = \varepsilon_{12} = 0$ (in Voigt notation $\varepsilon_4 = \varepsilon_5 = \varepsilon_6 = 0$), and the B_{44} magnetoelastic constant does not affect on the free energy change produced by the strains. If the magnetoelastic effect is linked mainly with the variation of the magneto crystalline anisotropy, we can assume that the volume magnetoelastic effect is relatively small. In such case $B_{12} = -(1/2) B_{11}$ and $B_{13} = -(1/2) B_{33}$, and the magnetoelastic energy in our system is associated with only two independent magnetoelastic constants (e.g. B_{11} and B_{33}). One can see that the room temperature magnetoelastic constants of the ribbons are relatively small of an order of 10^6 erg/cm^3 for the $\text{Ni}_{50}\text{Mn}_{36}\text{Sn}_{14}$ sample, and of an order of 10^5 erg/cm^3 for the $\text{Ni}_{48}\text{Mn}_{36}\text{Sn}_{14}\text{Cu}_2$ sample. The anisotropy of the magnetoelastic constants is negligible. Magnetostriction constants of $\text{Ni}_{50}\text{Mn}_{36}\text{Sn}_{14}$ and $\text{Ni}_{48}\text{Mn}_{36}\text{Sn}_{14}\text{Cu}_2$ ribbons $\lambda_s(B_{ij})$ are given in table 3, also and were calculated using the formula for saturation magnetostriction of an isotropic sample:

$$\lambda_s(B_{ij}) = -\frac{B_{ij}}{C_{11}-C_{12}} \quad (7)$$

We used the elastic constants for the Ni_2MnSn compound; elastic constant of $C_{11} = 161 \text{ GPa}$ and elastic constant of $C_{12} = 137 \text{ GPa}$ [33].

4. Conclusions

The martensitic transformation temperature, magnetic properties and shape memory characteristics can be meaningfully adjusted by Cu doping in $\text{Ni}_{50-x}\text{Mn}_{36}\text{Cu}_{x,y}\text{Sn}_{14-y}$ melt-spun ribbons. It was found that the martensitic transition behaviour and magnetic properties are sensitive to the Cu content, even in small quantities. XRD measurements demonstrate that the structure undergoes the existence of $L2_1$ austenitic state when $x=0, 1$ and 2 , and modulated

martensitic structure with Cu substitution on the Sn sites. The martensitic start temperature grows from 194 K to 228 K, by means of the increase of switch of Cu for Ni. besides, the Curie temperature T_C of the austenitic state decreases a little bit. In addition, Cu substitution for Sn convert significantly the martensitic transformation to high temperatures from 194 K to 325 K. From calorimetric and magnetic measurements, we can make sure that melt-spun ribbons studied in this work are a good ferromagnetic shape memory alloy. For the magnetic field or strain modulation, the magnetoelastic and magnetostriction effects in the as spun ribbons of $\text{Ni}_{50}\text{Mn}_{36}\text{Sn}_{14}$ and $\text{Ni}_{48}\text{Mn}_{36}\text{Sn}_{14}\text{Cu}_2$ Heusler alloys at room temperature, is comparatively weak.

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Figures captions:

Fig.1 X-ray diffraction patterns of $\text{Ni}_{50-x}\text{Mn}_{36}\text{Sn}_{14}\text{Cu}_x$ alloys ($x=0,1$ and 2) measured at room temperature.

Fig.2 X-ray diffraction patterns of $\text{Ni}_{50}\text{Mn}_{36}\text{Sn}_{13}\text{Cu}_1$ measured at room temperature.

Fig.3 DSC curves during the heating and cooling processes. The reverse martensitic transition (austenitic transition) upon heating start (As) and finish (Af) temperatures and martensitic transition upon cooling start (Ms) and finish (Mf) temperatures are indicated.

Fig4. SEM micrographs of the free surface (a-d) and the fracture cross section (a''-d'') of the attained ribbons: (a, a'') $\text{Ni}_{50}\text{Mn}_{36}\text{Sn}_{14}$, (b, b'') $\text{Ni}_{49}\text{Mn}_{36}\text{Sn}_{14}\text{Cu}_1$, (c, c'') $\text{Ni}_{48}\text{Mn}_{36}\text{Sn}_{14}\text{Cu}_2$ and (d, d'') $\text{Ni}_{50}\text{Mn}_{36}\text{Sn}_{13}\text{Cu}_1$.

Fig.5 Temperature dependence of the magnetization of all the samples measured at 50 Oe

Fig.6 Temperature dependence of the magnetization of all the samples measured at 50 KOe. Transformation temperatures (M_s , M_f , A_s , A_f) are defined as the intersection of the extrapolation from the linear regions.

Fig.7 Hysteresis loops measured at 50K of $\text{Ni}_{50}\text{Mn}_{36}\text{Sn}_{14}$, $\text{Ni}_{50}\text{Mn}_{36}\text{Sn}_{14}\text{Cu}_1$, $\text{Ni}_{48}\text{Mn}_{36}\text{Sn}_{14}\text{Cu}_2$ and $\text{Ni}_{49}\text{Mn}_{36}\text{Sn}_{14}\text{Cu}_1$.

Fig.8 Temperature dependence of electrical resistance measured at 0 T and 5 T for $\text{Ni}_{50}\text{Mn}_{36}\text{Sn}_{13}\text{Cu}_1$ alloy.

Fig.9 Resistivity dependence of magnetic field (up to 9 T) at different temperatures for $\text{Ni}_{50}\text{Mn}_{36}\text{Sn}_{13}\text{Cu}_1$.

Table captions:**Table 1** Percentage of L21 and B2 order in austenite alloys.

Ribbons	Percentage of L21 order	Percentage of B2 order
Ni₅₀Mn₃₆Sn₁₄	88	87
Ni₄₉Mn₃₆Sn₁₄Cu₁	85	88
Ni₄₈Mn₃₆Sn₁₄Cu₂	86	87

Table 2 Composition of the melt-spun ribbons extracted from the energy dispersive X-ray spectroscopy (EDX).

X, Y (at. %)	Ni (at. %)	Mn (at. %)	Sn (at. %)	Cu (at. %)
X=0	50.82	35.75	13.43	0
X=1	49.43	36.06	13.38	1.13
X=2	48.03	36.20	13.50	2.27
Y=1	50.80	34.78	12.91	1.51

Table 3 The characteristic transformation temperatures (As, Af, Ms and Mf) the enthalpies and entropies obtained from DSC curves upon cooling and heating process.

Ribbons	Ms/K	Mf/K	As/K	Af/K	T₀/K	ΔH/ J. g⁻¹	ΔS/ J. g⁻¹. K⁻¹
Ni₅₀Mn₃₆Sn₁₄	194.09	183	198	212.2	203.17	(h) 1.573 (c) 1.516	(h) 0.0078 (c) 0.00758
Ni₄₉Mn₃₆Sn₁₄Cu₁	200.41	186.3	205.25	226.65	211.53	(h) 1.680 (c) 1.543	(h) 0.00794 (c) 0.00729
Ni₄₈Mn₃₆Sn₁₄Cu₂	228.31	213	230.54	245.7	237.005	(h) 2.597 (c) 2.489	(h) 0.00951 (c) 0.0105
Ni₅₀Mn₃₆Sn₁₃Cu₁	325.02	316	325.63	335	343.51	(h) 5.122 (c) 4.559	(h) 0.195 (c) 0.219

Table 4 Magnetoelastic and magnetostriction constants of $\text{Ni}_{50}\text{Mn}_{36}\text{Sn}_{14}$ and $\text{Ni}_{48}\text{Mn}_{36}\text{Sn}_{14}\text{Cu}_2$ Heusler alloys.

Sample	Magnetoelastic constant, B11, erg/cm ³	Magnetoelastic constant, B33, erg/cm ³	Magnetostriction constant, $\lambda_s(\text{B11})$	Magnetostriction constant, $\lambda_s(\text{B33})$
Ni₅₀Mn₃₆Sn₁₄	1.16 E+06	1.61 E+06	-4.03 E-06	-6.70 E-06
Ni₄₈Mn₃₆Sn₁₄Cu₂	3.23 E+05	3.90 E+05	-1.35 E-06	-1.62 E-06