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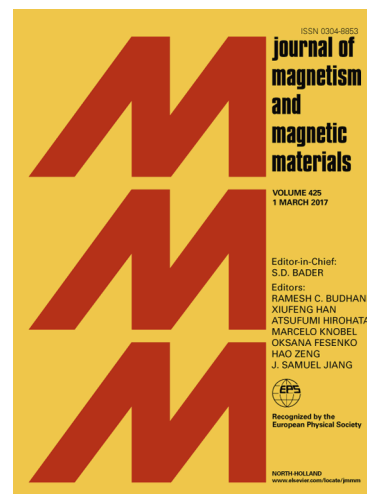
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**Enhanced magnetocaloric effect tuning efficiency in Ni-Mn-Sn alloy ribbons.**A. Quintana-Nedelcos,<sup>1</sup> J. L. Sánchez Llamazares,<sup>2</sup> G. Daniel-Perez,<sup>3</sup><sup>1</sup>*Department of Materials Science and Engineering, University of Sheffield, Sheffield S1 3JD, United Kingdom*<sup>2</sup>*Instituto Potosino de Investigación Científica y Tecnológica A.C., Camino a la Presa San José 2055, Col. Lomas 4ª, San Luis Potosí, S.L.P. 78216, Mexico*<sup>3</sup>*Instituto Tecnológico Superior de Irapuato (ITESI), 36821 Irapuato, Guanajuato, Mexico.*

**Abstract.** The present work was undertaken to investigate the effect of microstructure on the magnetic entropy change of Ni<sub>50</sub>Mn<sub>37</sub>Sn<sub>13</sub> ribbon alloys. Unchanged sample composition and cell parameter of austenite allowed us to study strictly the correlation between the average grain size and the total magnetic field induced entropy change ( $\Delta S_T$ ). We found that a size-dependent martensitic transformation tuning results in a wide temperature range tailoring (> 40 K) of the magnetic entropy change with a reasonably small variation on the peak value of the total field induced entropy change. The peak values varied from 6.0 Jkg<sup>-1</sup>K<sup>-1</sup> to 7.7 Jkg<sup>-1</sup>K<sup>-1</sup> for applied fields up to 2 T. Different tuning efficiencies obtained by diverse MCE tailoring approaches are compared to highlight the advantages of the herein proposed mechanism.

**Keywords:** Ni-Mn-Sn melt-spun ribbons; magnetocaloric effect; martensitic transformation; tuning efficiency.

## I. INTRODUCTION

Ferromagnetic shape memory alloys (FSMA) have been extensively investigated in the last twenty years [1]. These materials show a structural martensitic transition (MT) from a higher temperature parent phase (austenite; AST) to the lower temperature phase (martensite; MST) accompanied by a significant abrupt magnetization jump. One of the most studied FSMA are those of the Ni–Mn–Ga system [1][2]. However, later important efforts have been carried out to find Ga-free Heusler alloys. These have been mainly focused on Ni-Mn-X system alloys, with X=Sn, In, Sb [3][4][5][6][7]. These alloys have several attractive multifunctional properties such as: inverse giant magnetocaloric-effects (MCE) [8][9][10], large magnetoresistance change [11][12], magnetic field-induced reverse martensitic transformation [13][14][15][16], magnetic superelasticity [9][17], exchange bias effect [18][19][20], and kinetic arrest of martensitic transformation [15][20][21].

Regarding potential magnetic-cooling applications, a table-like MCE for ideal Ericsson refrigeration cycles is one of the most desired features. A suitable approach to obtain a table-like MCE consists on fabricating composite materials made of constituents with tuned transition temperatures (TT) and similar total magnetic field induced magnetic entropy change ( $\Delta S_T$ ) [22][23][24][25]. As a case in point, in soft magnetic  $\text{Fe}_{91-x}\text{Mo}_8\text{Cu}_1\text{B}_x$  ( $x = 15, 17, 20$ ) amorphous alloys, the shift in Curie temperature ( $T_C$ ) was reported as approximately 85 K without altering the  $\Delta S_T$  peak value ( $\Delta S_T^{\max}$ ) [23]. In Gd-Co amorphous ribbons with Gd/Co ratios from 71:29 to 62:38,  $T_C$  increases from 166K to 193K when  $\Delta S_T^{\max}$  slightly decreases from  $-3.1 \text{ Jkg}^{-1}\text{K}^{-1}$  to  $-2.8 \text{ Jkg}^{-1}\text{K}^{-1}$  [25]. In  $\text{Mn}_{2-x}\text{Cr}_x\text{Sb}$  ( $0.06 \leq x \leq 0.12$ ), in which the MCE is given by an antiferro to ferri-magnetic first-order phase transition (FOPT), with the increases on Cr content the transition temperature shifts from 232K to 333K and  $\Delta S_T^{\max}$  decreases from  $7.5 \text{ Jkg}^{-1}\text{K}^{-1}$  to  $5.5 \text{ Jkg}^{-1}\text{K}^{-1}$  [24].

Even though in Ni-Mn-X (X=Sn, In, Sb) FSMA significant efforts have been effectively implemented to tune the MT through the change of the Mn/X ratio [4][5][6], the partial atomic substitution of one (or more) of the three main elements of the alloy [26][27][28][29][30] and the introduction of elements of small atomic radius into interstitial sites [31][32]). However, these methods have failed in keeping reasonable unchanged the  $\Delta S_T^{\max}$ . Table 1 shows the peak value of the total field induced magnetic entropy change ( $\Delta S_T^{\max}$ ) together with the corresponding

order-disorder MT temperature reported for different Ni-Mn-Sn bulk samples. The considerable effect of the different MT tuning mechanisms on the  $\Delta S_T^{max}$  is clearly observed.

**Table 1.** Reported transition temperature and  $\Delta S_T^{max}$  values related to their transition path for some Ni-Mn-Sn bulk alloys.

Alloy composition	Transition path	Trans. temp. (K)	$\Delta S_T^{max}$ (Jkg <sup>-1</sup> K <sup>-1</sup> )	Ref.
Ni <sub>43</sub> Mn <sub>45</sub> Sn <sub>11</sub> B <sub>x</sub>			$\mu_o\Delta H_{max} = 1$ T	[31]
x=0	MST → AST	200*	10.4	
x=1	MST → AST	215*	13.0	
x=3	MST → AST	242*	6.5	
x=5	MST → AST	275*	2.2	
Ni <sub>43</sub> Mn <sub>46-x</sub> Cu <sub>x</sub> Sn <sub>11</sub>			$\mu_o\Delta H_{max} = 1$ T	[26]
x=1	MST → AST	226**	14.1	
x=2	MST → AST	255**	18.0	
x=3	MST → AST	260**	15.8	
Ni <sub>50</sub> Mn <sub>50-x</sub> Sn <sub>x</sub>				
x=13	AST → MST	307*	18; $\mu_o\Delta H_{max} = 5$ T	[8]
x=15	AST → MST	192*	15; $\mu_o\Delta H_{max} = 5$ T	[8]
x=16	MST → AST	220***	2.0; $\mu_o\Delta H_{max} = 8$ T	[33]
Ni <sub>50-x</sub> Mn <sub>39+x</sub> Sn <sub>11</sub>			$\mu_o\Delta H_{max} = 1$ T	[34]
x=5	AST → MST	270*	6.8	
x=6	AST → MST	245*	10.1	
x=7	AST → MST	200*	10.1	

\*M<sub>s</sub>, \*\*A<sub>f</sub>, \*\*\*temperature of  $\Delta S_T^{max}$

Evidence indicates that the tuning mechanisms do not only strongly influence the MT shift, they also affect considerable the  $\Delta S_T^{max}$  magnitudes. The latter could be due to uncontrolled variables that may directly influence the thermo-magnetic response of the material. For instance, the high dispersion obtained in average grain sizes  $\langle d \rangle$  in Ni-Mn-Sn bulk samples ( $50 \mu\text{m} \leq \langle d \rangle \leq 300 \mu\text{m}$ ) does not allow to study the effect of this parameter on the thermo-magnetic features of these materials [3][35][36].

On the other hand, it has been established that the melt spinning technique is an effective process to obtain single phase alloy ribbons in the Ni<sub>50</sub>Mn<sub>50-x</sub>Sn<sub>x</sub> system [16][37][38] with a considerably refined microstructure [4][36]. The technique reasonably reproduces the MCE properties of the bulk alloys while reducing the characteristic martensitic starting ( $M_s$ ) and austenitic starting ( $A_s$ ) transformation temperatures. For example, for Ni<sub>50</sub>Mn<sub>37</sub>Sn<sub>13</sub> bulk samples,  $\Delta S_T^{max}$  has been reported as  $\sim 8 \text{ Jkg}^{-1}\text{K}^{-1}$  (at  $\mu_o\Delta H_{max} = 2$  T) [8] with  $M_s$  near room temperature (RT), 290 K [36] and 307 K [8][35]; while  $\Delta S_T^{max} = 10 \text{ Jkg}^{-1}\text{K}^{-1}$  ( $\mu_o\Delta H_{max} = 2$  T) [39] and  $M_s =$

218 K [37] for alloy ribbons of similar composition. Further studies in Ni-Mn-Sn ribbons [40][41] and thin films [42][43] have confirmed the magneto-structural transition dependence on  $\langle d \rangle$ .

The present work has been carried out to continue and expand previous results reported in [41], in which the authors demonstrated that for  $\text{Ni}_{50}\text{Mn}_{37}\text{Sn}_{13}$  ribbons with decreased  $\langle d \rangle$ , the multivariant MT temperature shifts downward due to the stabilization of the AST phase. The experiment was carefully designed to study the viability of tuning the MT in  $\text{Ni}_{50}\text{Mn}_{37}\text{Sn}_{13}$  ribbons by controlling solely its microstructural features (i.e. average grain size) while keeping unaffected structural and compositional parameters. In turn, undesired variables contribution to the MT tuning is minimized. For instance, existing phase (single highly-ordered  $L2_1$ -type AST cubic structure), stress relaxation (fair constant lattice parameter  $a = 5.970 \pm 0.005 \text{ \AA}$ ) and chemical deviation (average valence electron concentration per atom  $e/a = 8.12 \pm 0.01$ ) parameters show to have a negligible impact on the MT shift in our experiment. As such, it was proven that the decrease in  $M_S$  from 258 K to 212 K (i.e., 46 K) can be strictly ascribed to the austenite stabilization due to the reduction in the grain size [41]. As present contribution is built on [41] outcomes, herein proposal aims to evaluate the  $\Delta S_T^{\text{max}}$  tuning efficiency by means of the MT dependence on  $\langle d \rangle$ .

## II. EXPERIMENTAL PROCEDURE

Alloy ribbons with  $1.4 \mu\text{m} \leq \langle d \rangle \leq 7.3 \mu\text{m}$  obtained by varying wheel speed (ranging from 50  $\text{ms}^{-1}$  to 15  $\text{ms}^{-1}$ ) were prepared from bulk ingots of  $\text{Ni}_{50}\text{Mn}_{37}\text{Sn}_{13}$  nominal composition. They were annealed in closed quartz ampoules at 1123 K (850 °C) for 10 min under high vacuum to improve atomic ordering. Microstructural characterization was done in a Phillips model XL-30 scanning electron microscope (SEM). Structural analysis by phase transition studies were carried out by differential scanning calorimeter (DSC) using a TA Instruments model Q200. Additional information on ribbons fabrication and characterization can be found elsewhere [41].

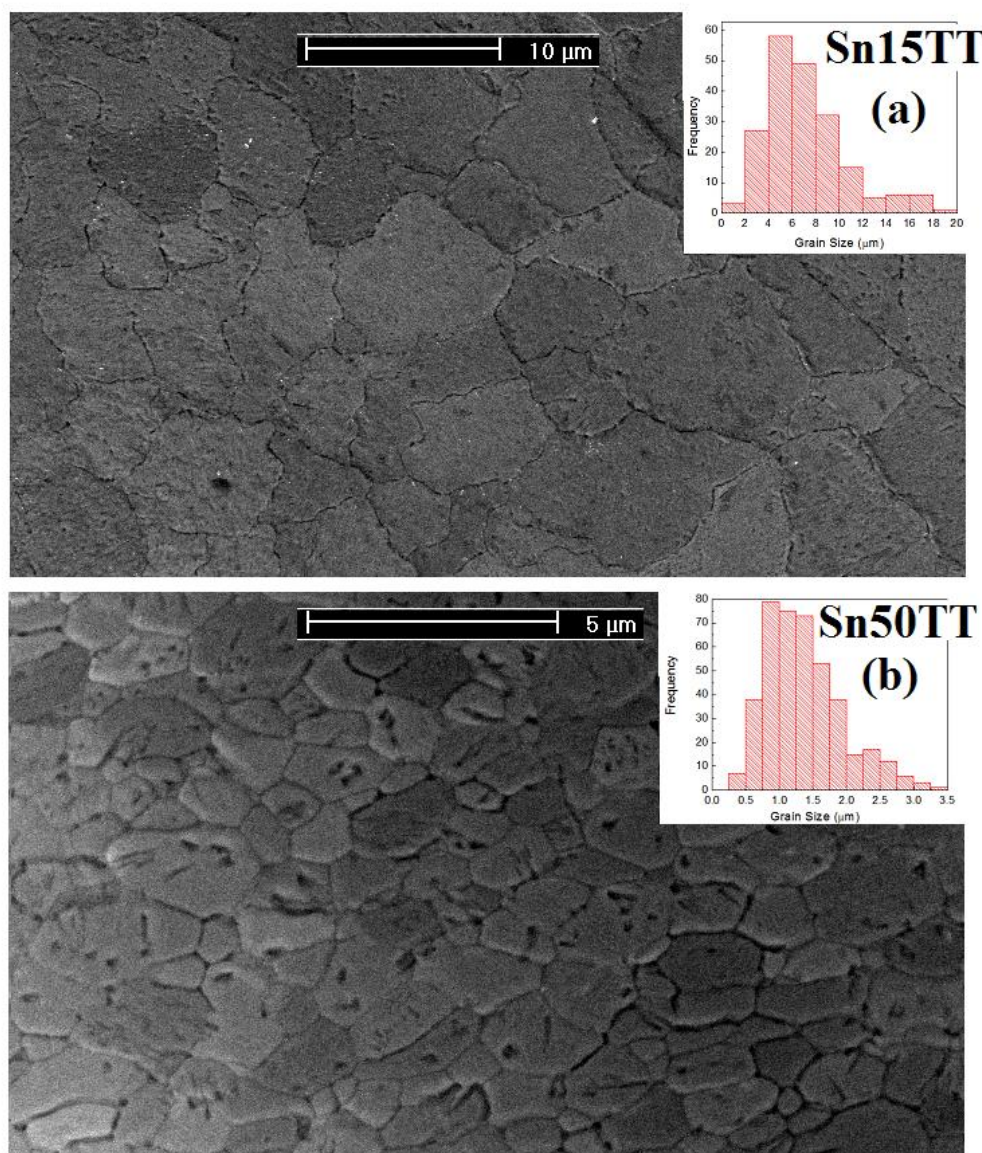
Magnetization measurements were performed using the vibrating sample magnetometer option of a physical properties measurement system (Quantum Design PPMS® EverCool-I, 9 Tesla). The magnetic field  $H$  was applied along the ribbon axis (i.e., the rolling direction) to minimize demagnetizing field effects. The magnetization as a function of temperature  $\sigma(T)$  curves were

determined following field-cooling (FC), and field-heating (FH) regimens under an applied magnetic field of 5 mT. The heating/cooling rate was  $1.0 \text{ Kmin}^{-1}$ . Magnetization isotherms were measured through the MST-to-AST phase transition up to 5 T. The total field-induced magnetic entropy change  $\Delta S_T(T)$  curves were obtained from a set of  $M(\mu_0 H)$  isotherms by applying the Maxwell relation (equation 1). A fixed thermal protocol, referred in [44] as BnF, was used to reach each measuring temperature  $T_{\text{measur}}$ .

$$\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial M}{\partial T}\right)_B \rightarrow \Delta S_T = \int_0^B \left(\frac{\partial M}{\partial T}\right)_B dB \quad (\text{equation 1})$$

### III. EXPERIMENTAL RESULTS AND DISCUSSION

Figures 1a and 1b show SEM images of the free-surface microstructure of the ribbons obtained at copper linear speeds of 15 and 50  $\text{ms}^{-1}$ , respectively. More than 200 measurements of the free surface were used to estimate the average grain diameter,  $\langle d \rangle = 7.3 \pm 3.4 \text{ }\mu\text{m}$  and  $1.4 \pm 0.6 \text{ }\mu\text{m}$  for the Sn15TT and Sn50TT ribbons, respectively. The inset images show histograms of the measured grain diameters as determined from SEM images.

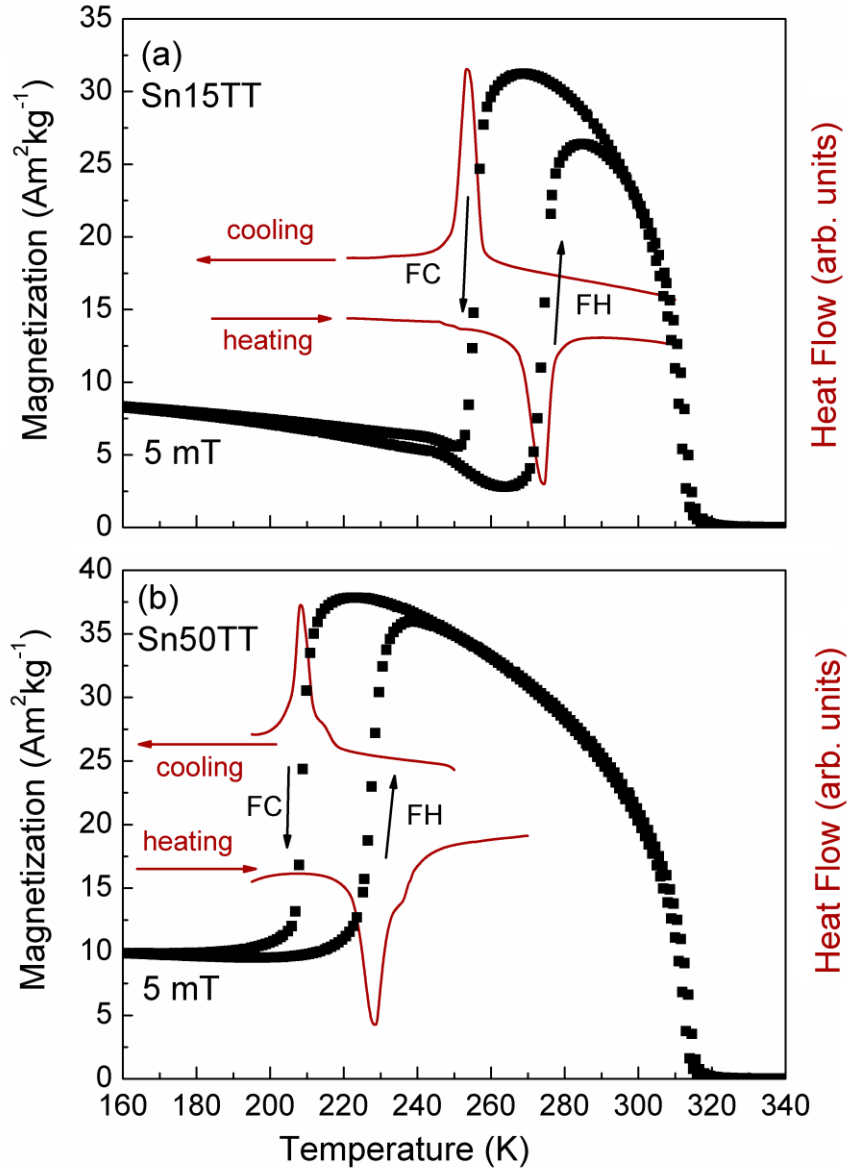


**Fig 1.** Typical SEM images showing the surface microstructure of ribbons on their free surface (i.e., non-contact side, NCS). Insets: Histogram of grain sizes measured from SEM micrographs.

Figures 2a and 2b show the DSC and low-field magnetization curves of the Sn15TT and Sn50TT samples, respectively. The thermal hysteresis of the magnetization curves indicates the first-order behaviour of the transition. On both sets of curves, the two well-distinct MST and AST ferromagnetic regions and the jump in magnetization associated to the structural phase transition are observed. The AST Curie temperature  $T_C^A$  is found to be 313 K for both samples. As revealed, the coupled magneto-structural transition shifts to lower temperatures with the decrease of  $\langle d \rangle$ . The latter was explained under a phenomenological model consideration in which the decrease in the average grain size stabilizes the austenitic parent phase [41]. The



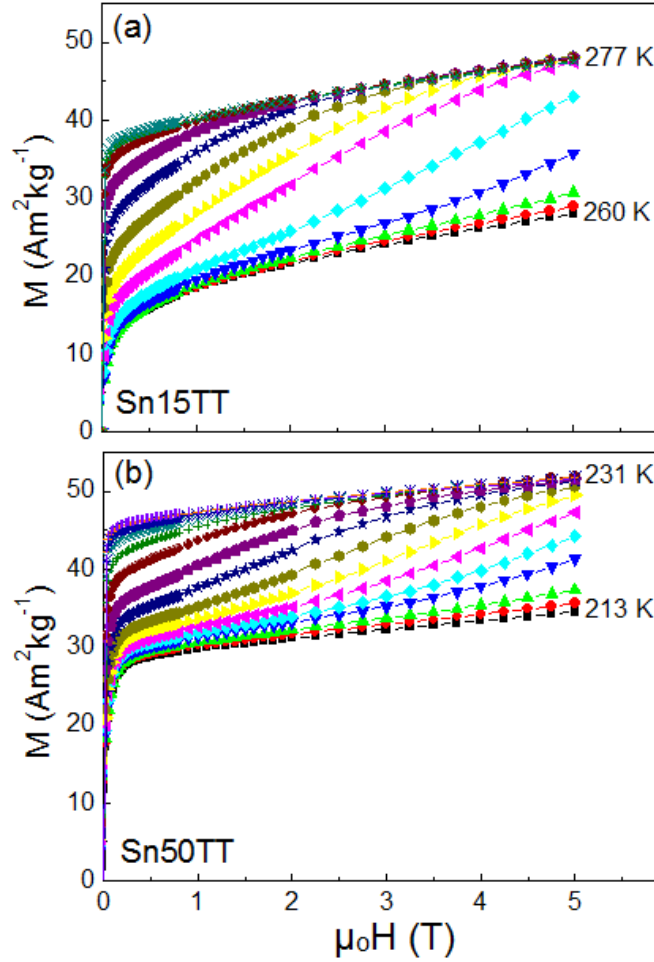
experiment was carefully designed to minimize the undesired contribution of changes in the elemental chemical composition and cell parameter of AST on the magneto-structural transition features. Experimental details on the procedure can be found elsewhere [41].



**Fig 2.** FC and FH temperature dependence of the magnetization  $M(T)$  at 5 mT and DSC curves of (a) Sn15TT and (b) Sn50TT ribbons.

Figures 3a and 3b show the magnetizing (FU)  $M(\mu_0 H)$  curves for the Sn15TT and Sn50TT alloy ribbons, respectively. In both samples,  $M(\mu_0 H)$  curves were computed across the reverse martensitic transformation (i.e.  $MST \rightarrow AST$ ) with a temperature step of 1.5 K between consecutive measuring temperatures ( $T_{\text{measur}}$ ) and an increasing applied field from 0 to  $\mu_0 H_{\text{max}} = 5T$ . To ensure that the sample reaches every  $T_{\text{measur}}$  following the same thermal and magnetic

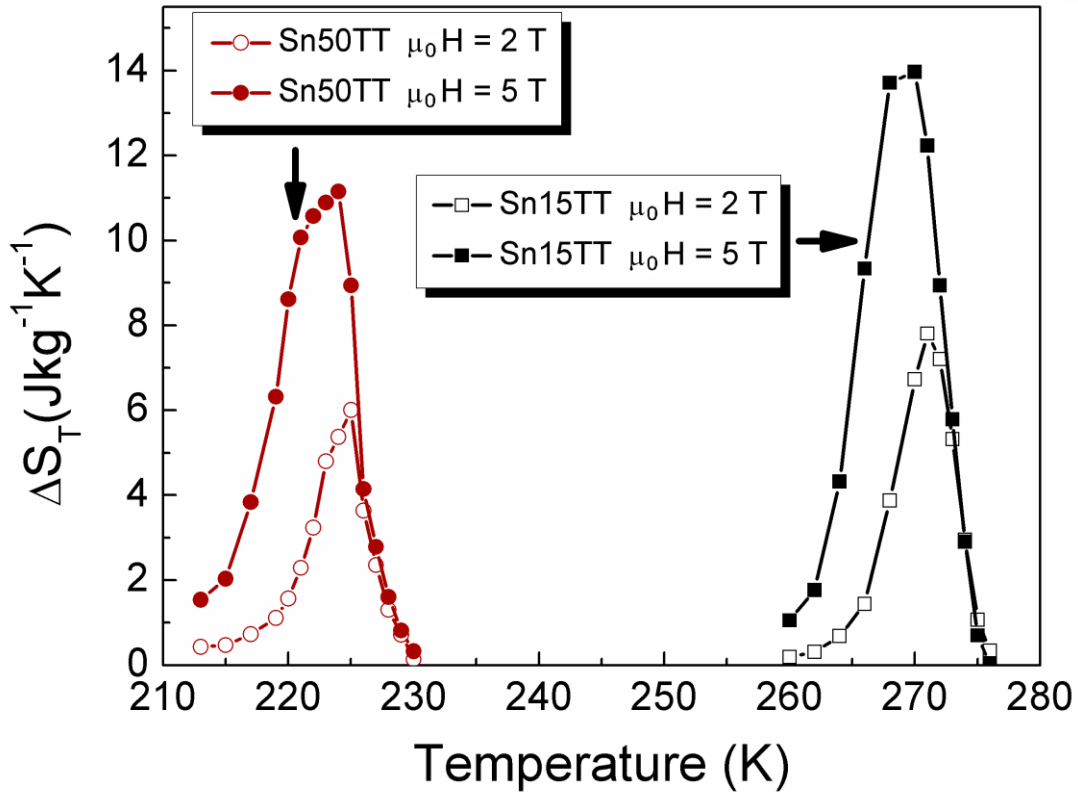
history, at zero magnetic field the sample was first warmed up to a completely AST-paramagnetic state at  $T = 400$  K, followed by a cooling to a MST-ferromagnetic phase at  $T = 180$  K, before heated up to the next  $T_{\text{measur}}$ . This thermal cycle is repeated after every  $M(\mu_0 H)$  measurement.  $\Delta S_T(T)$  curves obtained from these  $M(\mu_0 H)$  measurements are shown in Fig. 4.



**Fig 3.** Isothermal magnetization  $M(\mu_0 H)$  curves of (a) Sn15TT and (b) Sn50TT alloy ribbons for increasing field across the reverse martensitic transformation.

For sample Sn15TT (Sn50TT),  $\Delta S_T^{\text{max}}$  is found to be equal to  $7.7 \text{ Jkg}^{-1}\text{K}^{-1}$  ( $6.0 \text{ Jkg}^{-1}\text{K}^{-1}$ ) and  $14.0 \text{ Jkg}^{-1}\text{K}^{-1}$  ( $11.2 \text{ Jkg}^{-1}\text{K}^{-1}$ ) for  $\mu_0 \Delta H_{\text{max}} = 2$  T and 5 T, respectively. These magnitudes are comparable to others previously reported for alloys of similar composition. For instance,  $\Delta S_T^{\text{max}} = 6.1 \text{ Jkg}^{-1}\text{K}^{-1}$  [45] and  $10 \text{ Jkg}^{-1}\text{K}^{-1}$  [39] for alloy ribbons of  $\text{Ni}_{49.0}\text{Mn}_{37.4}\text{Sn}_{13.6}$  and  $\text{Ni}_{50}\text{Mn}_{37}\text{Sn}_{13}$ , respectively and  $\Delta S_T^{\text{max}} = 8 \text{ Jkg}^{-1}\text{K}^{-1}$  for  $\text{Ni}_{50}\text{Mn}_{37}\text{Sn}_{13}$  bulk alloys [8]. All of them calculated for an applied field change of 2 T. Moreover, a more important result than the calculated  $\Delta S_T^{\text{max}}$  magnitude of our samples is the relatively small variation of this physical quantity across the

temperature window herein studied. In our samples, a shift of  $\Delta A_s = 42$  K is obtained at a cost of  $1.7 \text{ Jkg}^{-1}\text{K}^{-1}$  (for  $\mu_0\Delta H_{max} = 2$  T) and  $3.0 \text{ Jkg}^{-1}\text{K}^{-1}$  (for  $\mu_0\Delta H_{max} = 5$  T) on  $\Delta S_T^{max}$ . The increase of  $\Delta S_T^{max}$  in samples with higher MT can be ascribed to the shorter temperature proximity of  $A_s$  to  $T_C^A$  [46]. It's worth noting that the irreversibly dissipated energy slightly rise from 7.1 % to 9.4 % while the thermal hysteresis of the transformation remains similar (within the measurement error) with the decrease of  $\langle d \rangle$  from  $7.3 \text{ }\mu\text{m}$  (Sn15TT) to  $1.4 \text{ }\mu\text{m}$  (Sn50TT). For further details of the effect of microstructure on transformation parameters see reference [41].



**Fig 4.** Total field-induced magnetic entropy change as a function of temperature  $\Delta S_T(T)$  under an applied magnetic field change of 2 T and 5 T.

For comparative assessment, we can define the tuning efficiency ( $T_e = |\Delta TT / \Delta(\Delta S_T^{max})|$ ) as the TT shifted interval at the expense of a  $\Delta S_T^{max}$  variation of  $1 \text{ Jkg}^{-1}\text{K}^{-1}$ . For practical purposes, TT can be any of the characteristic transition temperatures of the magneto-structural transition (i.e., martensitic starting  $M_S$ , martensitic finishing  $M_f$ , austenitic starting  $A_S$ , austenitic finishing  $A_f$ , among others). For example, for interstitially doped  $\text{Ni}_{43}\text{Mn}_{45}\text{Sn}_{11}\text{B}_x$  bulk samples,  $M_S$  shifts from 200 K ( $x = 0$ ) to 245 K ( $x = 3$ ); while  $\Delta S_T^{max}$  decreases from  $10.4 \text{ Jkg}^{-1}\text{K}^{-1}$  to  $6.5 \text{ Jkg}^{-1}\text{K}^{-1}$

[31] at  $T_e = 11.5 \text{ J}^{-1}\text{kgK}^2$ . A comparison of estimated TT,  $\Delta S_T^{max}$ , and  $T_e$  for both ribbons studied in the present work (PW) and other research groups are listed in Table 2.

**Table 2.** Reported transition temperature (TT),  $\Delta S_T^{max}$  and,  $T_e$  values related to their transition path for some Ni-Mn-Sn system alloy ribbons. Dashed squares enclose the data used for the  $T_e$  calculation.

Alloy composition	Transition path	TT (K)	$\Delta S_T^{max}$ ( $\text{Jkg}^{-1}\text{K}^{-1}$ )	$T_e$ ( $\text{J}^{-1}\text{kgK}^2$ )	Ref.
Sn15TT	MST → AST	267***	$\mu_o\Delta H_{max} = 5 \text{ T}$ 14	24.7	PW
Sn50TT	MST → AST	225***	11		
Sn15TT	MST → AST	267***	$\mu_o\Delta H_{max} = 2 \text{ T}$ 7.7	14.0	PW
Sn50TT	MST → AST	225***	6.0		
Ni <sub>49.0</sub> Mn <sub>37.4</sub> Sn <sub>13.6</sub>	MST → AST	297.5**	$\mu_o\Delta H_{max} = 2 \text{ T}$ 6.1		[45]
Ni <sub>50.3</sub> Mn <sub>35.5</sub> Sn <sub>14.4</sub>	MST → AST	237***	$\mu_o\Delta H_{max} = 2 \text{ T}$ 4.1		[47]
Ni <sub>48</sub> Mn <sub>39.5</sub> Sn <sub>12.5-x</sub> Al <sub>x</sub>			$\mu_o\Delta H_{max} = 2 \text{ T}$		[18]
x=0	MST → AST	269**	7.8	9.0	
x=1	MST → AST	287**	5.7		
x=2	MST → AST	306**	4.8		
x=3	MST → AST	314**	2.8		
Ni <sub>44.1</sub> Mn <sub>44.2</sub> Sn <sub>11.7</sub>			$\mu_o\Delta H_{max} = 1 \text{ T}$		[38]
As-quenched	MST → AST	230****	~ 7	2.5	
TA <sup>a</sup> – A	MST → AST	235****	~ 32		
TA <sup>a</sup> – B	MST → AST	265****	~ 20		
Ni <sub>50-x</sub> Fe <sub>x</sub> Mn <sub>40</sub> Sn <sub>10</sub>			$\mu_o\Delta H_{max} = 5 \text{ T}$		[48]
x=2	MST → AST	377***	~ 2	10	
x=4	MST → AST	356***	~ 4		
x=6	MST → AST	309***	~ 7		
x=8	MST → AST	286***	~ 11		
Ni <sub>43</sub> Co <sub>7</sub> Mn <sub>39</sub> Sn <sub>11</sub> WS <sup>b</sup> =			$\mu_o\Delta H_{max} = 1 \text{ T}$		[40]
10 ms <sup>-1</sup>	MST → AST	278.05***	16.42	33.4	
WS <sup>b</sup> = 15 ms <sup>-1</sup>	MST → AST	296.85***	17.49		
WS <sup>b</sup> = 20 ms <sup>-1</sup>	MST → AST	296.85***	14.21		
WS <sup>b</sup> = 25 ms <sup>-1</sup>	MST → AST	302.75***	15.68		
WS <sup>b</sup> = 30 ms <sup>-1</sup>	MST → AST	266.05***	23.89		

\*minimum of the derivative of the M(T)-FH curve; \*\*  $A_f$ ; \*\*\*  $A_s$ ; \*\*\*\* temperature at which  $\Delta S_T^{max}$  is found; <sup>a</sup>Thermal Annealing; <sup>b</sup>Wheel Speed.

The calculated tuning efficiency of  $14.0 \text{ J}^{-1}\text{kgK}^2$  (at  $\mu_o\Delta H_{max} = 2 \text{ T}$ ) and  $24.7 \text{ J}^{-1}\text{kgK}^2$  (at  $\mu_o\Delta H_{max} = 5 \text{ T}$ ) in our samples is higher than those computed for other series where different tuning mechanism were used: Sn/Al [18] ( $T_e = 9.0 \text{ J}^{-1}\text{kgK}^2$ ;  $\mu_o\Delta H_{max} = 2 \text{ T}$ ) and Ni/Fe [48] ( $T_e = 10 \text{ J}^{-1}\text{kgK}^2$ ;  $\mu_o\Delta H_{max} = 5 \text{ T}$ ) partial substitution; applied different thermal treatments on Ni<sub>44.1</sub>Mn<sub>44.2</sub>Sn<sub>11.7</sub> alloy ribbons ( $T_e = 2.5 \text{ J}^{-1}\text{kgK}^2$ ;  $\mu_o\Delta H_{max} = 1 \text{ T}$ ) [38]; and Ni<sub>43</sub>Mn<sub>45</sub>Sn<sub>11</sub>B<sub>x</sub> ( $T_e$

=  $11.5 \text{ J}^{-1}\text{kgK}^2$ ;  $\mu_o\Delta H_{max} = 1 \text{ T}$ ) interstitial doping [31]. Notice that  $T_e = 33.4 \text{ J}^{-1}\text{kgK}^2$  ( $\mu_o\Delta H_{max} = 1 \text{ T}$ ) for ribbon samples of  $\text{Ni}_{43}\text{Co}_7\text{Mn}_{39}\text{Sn}_{11}$  is considerably higher than our results. Similarly to our work, the MT was tuned through a variation of the wheel speed (WS) during the spinning process [40]. However, Ma et al, [40] obtained a non-monotonous dependence of TT on WS, which causes up-and-down unrelated values of  $\Delta S_T^{max}$  with TT (see arrows in table 2). Therefore, if for the  $T_e$  computing from  $A_s = 278 \text{ K}$  (WS =  $10 \text{ ms}^{-1}$ ) to  $A_s = 303 \text{ K}$  (WS =  $25 \text{ ms}^{-1}$ ) we use the maximum ( $17.5 \text{ Jkg}^{-1}\text{K}^{-1}$ ) and minimum ( $14.2 \text{ Jkg}^{-1}\text{K}^{-1}$ ) values reported within the temperature  $\Delta A_s$  interval of  $24.7 \text{ K}$  [40], the tuning efficiency results to be  $7.5 \text{ J}^{-1}\text{kgK}^2$ . This is an order of magnitude smaller than that calculated from the  $\Delta S_T^{max}$  values corresponding to the lower and higher  $A_s$  temperatures of the same interval (i.e.,  $T_e = 33.4 \text{ J}^{-1}\text{kgK}^2$ ). However, the up-and-down values of  $\Delta S_T^{max}$  should not necessary impact the tuning efficiency, provided that the peak values remain relatively close to each other.

#### IV. CONCLUSIONS.

In conclusion, in studying ribbons of  $\text{Ni}_{50}\text{Mn}_{37}\text{Sn}_{13}$  nominal composition and different grain sizes we found that with the decrease of  $\langle d \rangle$  from  $7.3 \mu\text{m}$  to  $1.4 \mu\text{m}$ , the MCE of the material was successfully tailored in a broad range of temperatures ( $\Delta A_s = 42 \text{ K}$  and  $\Delta M_s = 46 \text{ K}$ ) at a relatively small cost in terms of  $\Delta S_T^{max}$  peak value. Results confirm that the MT dependence on extrinsic properties of the material (for instance, average grain size) allows a better MCE tuning efficiency than other tailoring approaches that uses the MT dependence on intrinsic properties based on the chemical composition or structural features of the material. The latter has a significant added value as keeping nearly constant the MCE magnitude of the material is a key pre-condition in view of the potential application of these materials in magnetic refrigeration.

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**Highlights**

- We compare the MCE tuning efficiency of different tailoring approaches.
- Changing extrinsic properties allows a better MCE tuning efficiency.

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