The effect of heat treatments on Ni$_{43}$Mn$_{42}$Co$_4$Sn$_{11}$ meta-magnetic shape memory alloys for magnetic refrigeration

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Abstract

The inverse magnetocaloric effect (MCE) in bulk polycrystalline and melt-spun ribbons of the Ni$_{43}$Mn$_{42}$Co$_4$Sn$_{11}$ meta-magnetic shape memory alloy (MSMA) is investigated. The influence of several material properties on the MCE and relative cooling power (RCP) are discussed and the property combinations for optimum MCE and RCP identified for a given thermodynamic framework. These include a small slope of magnetic field vs. martensitic transformation temperature phase diagram, a narrow transformation range, low transformation thermal hysteresis and a large change in magnetization on martensitic transformation, which results in low levels of applied magnetic fields desired for repeated MCE on field cycling. The thermo-magnetic responses of the samples were measured before and after heat treatments. The heat-treated ribbons produced the most favorable MCE by exhibiting the highest magnetization change and smallest elastic energy storage through the transformation. This was attributed to the specific microstructural features, including grain size to thickness ratio and degree of L2$_1$ ordering. In addition, issues in the literature in determining RCP for MSMAs are discussed, and a new method to find RCP is proposed and implemented. Completely reversible magnetic-field-induced martensitic transformation cycles were used to investigate hysteresis losses relative to actual refrigeration cycles, whereby the RCP was calculated using the defined thermodynamic framework and indirectly measured entropy changes. The annealed ribbons exhibited the high RCP level of 242 J kg$^{-1}$C under the applied field of 7 T compared with a theoretical maximum of 343 J kg$^{-1}$C. Similar values of RCP in other MSMAs can be achievable if microstructural elastic energy storage and hysteresis loss are minimized during the transformation with the help of annealing treatments.

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1. Introduction

Over the last decade, there has been increased interest in the thermal behavior of Heusler-type meta-magnetic shape memory alloys (MSMAs) because of their potential for demonstrating a giant magnetocaloric effect (MCE). These materials offer a viable solution for environmentally friendly refrigeration, as their magnetic response may be tailored to provide relative cooling powers (RCP) comparable to those of expensive rare-earth-containing MCE materials. Giant isothermal entropy, or adiabatic temperature, changes associated with MCE have been measured for a variety of MSMAs such as Ni–Mn–X (X = In, Sn, Sb) \cite{1,2}.
MSMAs exhibit a change in magnetic order near a first-order structural phase (martensitic) transformation [3,4]. Often, the material changes from low temperature martensite, which exhibits small magnetic susceptibility, to a ferromagnetic (FM) austenite, resulting in the so-called inverse MCE, with the application of a magnetic field when the material is in its martensitic state. Conventional MCE is characterized by the cooling of a sample during the unloading of a magnetic field, while in common MSMAs, cooling occurs on the field loading on martensite and thereby stabilizing austenite.

MSMAs can be modified using simple heat treatments and conventional fabrication methods to control lattice parameters, atomic ordering and microstructure, resulting in various Curie temperatures, martensitic transformation (MT) temperatures, transformation hysteresis and magnetic responses across MT, affecting refrigeration performance parameters [5–12]. Heat treatments were reported to change atomic ordering, resulting in large changes in magnetic response [13–15] due to variations in Mn-Mn spacing and magnetic spin interactions [16]. Wu et al. [9] showed that the magnetic responses in Ni$_{50}$Mn$_{35}$Sn$_{15}$ ribbons differed between samples solutionized at 1273 K for 15 min and those solutionized for 4 h. The increase in magnetization resulting from the shorter annealing treatment was attributed to Mn ordering corresponding to an increase in the L$_2$$_1$ order parameter. However, an increase in magnetization difference across MT has been reported for increasing B2 disorder (decreasing L$_2$$_1$ order) [17] in NiMnIn systems. Clearly, the type of ternary addition in Ni–Mn systems plays a major role in the influence of atomic ordering on the magnetic response of these materials.

Most studies aimed at quantifying the MCE in MSMAs have focused on entropy changes related to magnetization increases across MT [1–10,13–18]. However, most of them have not properly identified other key parameters that should play a role in dictating how well MSMAs would perform as refrigerants or explained how manipulating the material’s microstructure will affect refrigeration cycles, as is attempted in the present work. The key performance parameters studied here include the entropy change across MT, the RCP, calculated using a simplified method developed specifically for MSMAs, and the magnetic fields required to induce and complete the MT. Furthermore, a clear distinction between the proper analysis that should be conducted to quantify the MCE in MSMAs and that which is typically conducted using archaic conventional methods for non-SMAs without significant hysteresis [19] has been made. Improper analysis poses problems in analyzing MSMAs, especially when determining the RCP.

The RCP is useful for comparing MSMA refrigerants and conventional MCE materials, when used properly. The RCP is a metric used for quantifying the maximum thermal energy that can be transferred between hot and cold reservoirs under application of a given external magnetic field [19]. Since some conventional MCE materials are capable of producing nearly reversible refrigeration cycles around their Curie point [20], the comparable RCP values in MSMAs can only be determined accurately when proper operating temperatures are defined and the thermodynamic irreversibility from transformation hysteresis is determined and subtracted from the apparent RCP values.

Thus, in the present work, a thermodynamic cycle for the inverse MCE in MSMA is defined and used to show how the RCP is quantified using simple magneto-thermal experimental loading paths. In addition, the influence of the types of experimental protocols [21] on reported RCP values is investigated, and it is shown how these affect the RCP measurements for MSMAs, which arises from the effect of the transformation hysteresis on these measurements.

Furthermore, the influence of the microstructural changes on MCE and RCP in Ni$_{43}$Mn$_{42}$Co$_{4}$Sn$_{11}$ was studied in bulk and melt-spun ribbon samples after heat treatments near the reported order–disorder transition (920 K) [9]. A homogeneous microstructure was achieved in solution heat-treated (SHT) ribbon samples, which resulted in low thermal hysteresis, small transformation ranges and large magnetization changes across MT. These material characteristics were further improved with secondary heat treatments, which in turn enhanced the refrigeration performance parameters. The peak entropy change values reported here for the present composition are greater than those reported for NiMnCoIn alloys in the literature [13].

The RCP for selected heat treatment cases was determined using the thermodynamic framework developed here, where the entropy change vs. temperature ($\Delta S - T$) diagrams were used to aid understanding. The applied fields below and above those capable of inducing a complete isothermal MT were determined, thus permitting the thermodynamic irreversibility to be subtracted easily from the apparent RCP values. The influence of microstructural factors and structural transformation characteristics, such as the transformation range and thermal hysteresis, on the refrigeration performance parameters is discussed in detail.

2. Determination of performance parameters for the inverse MCE in MSMAs

In general, the focus of MCE studies on MSMAs has been to determine magnetic field-induced temperature change or indirectly measured entropy change. However, these are not the only parameters that define the performance of MSMA refrigerants. Other important performance and critical materials parameters include the RCP, which is a fundamental property indicative of how much useful work can theoretically be performed by the refrigerant within some operating temperature range, the magnetic field required to induce, or complete, MT at a given temperature, MT characteristics such as transformation range and hysteresis and, ultimately, the sample microstructure that governs some of the aforementioned parameters.
To illustrate the importance of each of these parameters, a simple MCE refrigeration cycle is outlined in Fig. 1.

2.1. Example Brayton cycle for MCE in MSMAs

Fig. 1 demonstrates the idealized entropy vs. temperature ($S$–$T$) diagrams around a first-order thermoelastic martensitic transformation on cooling and subsequent heating, with (blue curve) and without (green curve) an applied magnetic field $H$. The $S$–$T$ curve shifts to lower temperatures on application of the field. The field reduces the transformation temperatures of the MSMA and stabilizes the austenite where the austenite is FM, and the magnetic ordering of martensite is defined by short-range frustrated anti-ferromagnetism [22,23]. For the sake of simplicity and ease of understanding the thermodynamic cycle, these idealized responses neglect the contribution of magnetic entropy to the total entropy in austenite and martensite phase regions, and thus the conventional MCE behavior of martensite and austenite phases. In addition, the diagrams assume that the difference between the martensite start $M_s$ and martensite finish $M_f$ temperatures is equivalent to the difference between the austenite finish $A_f$ and austenite start $A_s$ temperatures. The difference between start and finish temperatures is commonly known as the transformation range and, for the rest of the paper, the average of the transformation ranges (for forward and reverse MT) is defined as $\Delta T_{elas} = [(A_f - A_s) + (M_s - M_f)]/2$. The transformation range is controlled by microstructurally stored elastic energy, and therefore the transformation range is denoted by the subscript “elas”.

As shown in Fig. 1, the MSMA initially begins the depicted Brayton cycle [24] at $M_f$ (point 1 in the figure), or the hot reservoir of the cycle $T_{hot}$. The schematics under the $S$–$T$ plot in Fig. 1 represent microstructures of the material at specified points or regions in the $S$–$T$ diagram. Upon the field application $H_{comp}^{end}$, sufficient to induce a complete adiabatic reverse MT at $M_f$ ($A \rightarrow M$ : Martensite $\rightarrow$ Austenite), the sample exhibits endothermic behavior and cools to $T_{cold}$ (point 3) if insulated from external heat sources. This temperature change is shown in the figure by the line $T_{hot} \rightarrow T_{cold}$ (region 2) and is directly related to the transformation entropy change. Next, the sample is exposed to the refrigerated volume and allowed to absorb energy, thus heating the sample composed of field-induced austenite (see $T_{cold} \rightarrow T_{refrigerator}$, point 4 in the figure). The sample is then removed from the refrigerated volume, and the field is released under insulated conditions, warming up the sample because of the forward MT ($A \rightarrow M$), which is an exothermic process ($T_{refrigerator} \rightarrow T_{end}$, region 5). At this point (point 6 in the figure), the sample is exposed to ambient temperature and releases heat from the temperature $T_{end}$ to $T_{hot}$, returning the sample to a temperature $\leq M_f$, which allows the process to be repeated. As shown on the abscissa in Fig. 1, the operating temperatures that define the Brayton cycle.
cycle are $T_{\text{hot}} = M_f$ and $T_{\text{cold}} = T_{\text{hot}} - \Delta T_{\text{ad}}$, where $T_{\text{cold}}$ is the temperature that is achieved as a result of adiabatic magnetization of the sample, and $\Delta T_{\text{ad}}$ is the adiabatic temperature change on the field change (is $\Delta T_{\text{ad}}^{\text{max}}$ if the transformation is complete [25]).

As discussed in Ref. [19], the maximum work that can be performed by a magnetic refrigerant (RCP) has been defined in the past for non-SMA materials as the integral of the entropy change $\Delta S$ across the operating temperature range, or $\int_{T_{\text{cold}}}^{T_{\text{hot}}} \Delta S \, dT$, where $T_{\text{hot}}$ and $T_{\text{cold}}$ correspond to the operating temperature limits. However, using the Brayton cycle in Fig. 1, the maximum amount of work that can be performed by the MSMA is represented by the hatched region. Clearly, the Brayton cycle offers less work than the material is theoretically capable of performing, and the cycle is limited (bound) by the martensitic transformation temperatures.

MSMAs should theoretically be able to perform more work than that specified by the Brayton cycle in Fig. 1. This is illustrated in Fig. 2 for a given applied magnetic field capable of inducing a complete adiabatic structural transformation, $H_{\text{ad}}$. The theoretical maximum work, the RCP, that a MSMA can perform is independent of thermodynamic cycles and is defined as the area of the shaded region in the $\Delta S$ vs. $T$ plot in Fig. 2b. However, it is limited by the transformation temperatures. Fig. 2b is constructed based on the ideal $S$–$T$ diagrams shown in Fig. 2a: at a given temperature, $\Delta S = S^\text{Austenite at } H = H_{\text{comp}}^\text{ad} - S^\text{Martensite at } H = 0$, where $S^\text{Martensite at } H = 0$ is the entropy of martensite at $H = 0$, which fully transforms to austenite under $H = H_{\text{comp}}^\text{ad}$, and $S^\text{Austenite at } H = H_{\text{comp}}^\text{ad}$ is the entropy of the austenite under $H = H_{\text{comp}}^\text{ad}$, which transforms back to martensite under $H = 0$. The temperatures limiting the shaded region were extended down from Fig. 2a, and areas of thermal transformation hysteresis, i.e. two-phase regions, were not considered to contribute to reversible work on field cycling.

It is clear from Fig. 2b that the transformation temperatures and $\Delta S$ dictate the size of the shaded region that is used to determine the useful work, or RCP. Upon closer inspection of Fig. 2b, the elastic transformation ranges $(A_f^{H=H_{\text{comp}}^\text{ad}} - A_s^{H=H_{\text{comp}}^\text{ad}}$ and $M_f^{H=0} - M_s^{H=0})$ also contribute to the shaded region by amount $\Delta S \cdot \Delta T_{\text{class}}$, but these operating temperatures can only be accessed if special thermodynamic processes are used that allow martensite to form at the start of each cycle. In addition, it can be seen that, within the operating temperature range of $M_f^{H=0}$ and $A_f^{H=H_{\text{comp}}^\text{ad}}$, the maximum entropy change of the MSMA can be achieved, and thus is capable of contributing to the RCP by the amount $\Delta S \cdot \Delta T_{\text{ad}}^{\text{max}}$. For the Brayton cycle above, only part of this value was captured, and it is believed that special thermodynamic cycles, possibly involving mechanical stress or regenerative cycles, can be used to access the entire theoretical values.

The example cycle in Fig. 1 and depiction of RCP in Fig. 2 clearly indicate the importance of studying the critical materials parameters mentioned above. It is shown in Fig. 2 that a large RCP can be achieved if samples exhibit large adiabatic temperature changes, have large entropy changes across transformation, and have broad elastic transformation ranges. However, it will be shown later that decreasing the transformation ranges with annealing treatments affects the difference between $M_f^{H=0}$ and $A_f^{H=H_{\text{comp}}^\text{ad}}$ in Fig. 2, and thus presents the possibility of increasing the size of the shaded region and RCP. In addition, small elastic transformation ranges decrease $H_{\text{comp}}^\text{ad}$ and improve refrigeration performance. The following sections define how to calculate each performance parameter.

### 2.2. Calculating the magnetic field-induced entropy change

The first performance parameter that should be defined is the entropy change across MT. Traditionally, this value is measured indirectly using an integral form of the Maxwell relation linking experimental magnetic responses to entropy changes. This method has been used to quantify second-order magnetic entropy changes for most non-SMA MCE materials [19], and has been adopted by the SMA community to quantify entropy changes across the first-order MT. However, owing to the singular behavior of a first-order phase transformation, using derivatives to calculate entropy changes from the differential form of

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**Fig. 2.** (a) Entropy vs. temperature plot for a MSMA under zero and $H_{\text{comp}}^\text{ad}$ magnetic fields near the thermoelastic transformation. (b) Entropy change vs. temperature plot where the shaded region indicates RCP. The rectangular shaded region between $M_f^{H=0}$ and $A_f^{H=H_{\text{comp}}^\text{ad}}$ indicate the RCP in the temperature range where the total entropy change is reversible. The areas of the transformation hysteresis indicate the operating temperature ranges where the forward and reverse entropy changes during isothermal magnetization experiments are not the same, and are therefore cyclically irreversible.
the Maxwell relation may result in large discrepancies [20]. Maxwell relations are derived from a single energy potential, but SMAs have free energy equivalence in two phases, namely martensite and austenite, and thus require the equivalence of two free energy potentials. This manifests as the Clausius–Clapeyron (CC) relation, which looks very similar to the Maxwell relation. These two relations are often used interchangeably, but this is not valid.

Here, the magnetic field-induced entropy changes are calculated from the experimental isothermal magnetization responses following two experimental schemes, namely, the continuous and discontinuous heating protocols [21,25], using the traditional integral form of the CC relation in Eq. (1) and determine how each protocol affects the constructed $\Delta S - T$ diagram like that shown in Fig. 2. Entropy changes determined from the continuous heating scheme (whereby the sample temperature is increased a constant amount between the isothermal magnetization measurements) are denoted as the effective entropy changes, $\Delta S_{\text{eff}}$, and those predicted from the discontinuous heating (whereby the sample is cooled between each magnetization measurement below $M_f$ [25]) are simply denoted as the entropy change, $\Delta S$. To populate the $\Delta S - T$ diagram, like that shown in Fig. 2b, the magnetostatic energy density or area under $M$ vs. $H$ curves (Fig. 3) was found at discrete temperatures, and then $\Delta S$ was calculated using

$$\Delta S(T_K, 0 \rightarrow H) = \frac{1}{\Delta T_k} \left[ \int_0^H M_{T_k+1}dH - \int_0^H M_{T_k}dH \right]$$

(1)

where $T_{k+1}$ and $T_k$ are test temperatures, $T_{k+1} > T_k$, $\Delta T_k = (T_{k+1} - T_k)$ and $T_k = (T_{k+1} + T_k)/2$. According to Eq. (1), the entropy change caused by the field-induced transformation can be quantified by finding the difference in the magnetostatic energy density between two different magnetic responses at different temperatures (with small temperature increments), divided by the temperature increment [19]. A schematic representation of how to determine $\Delta S$ is shown in Fig. 3.

Fig. 3 depicts the isothermal magnetic response ($M-H$) of a MSMA during field-induced $M \rightarrow A$ transformation at five different temperatures, $T_1$, $M_f$, $A_s$, $T_2$ and $T_3$. Here, $T_1 < M_f < A_s < T_2 < T_3$ and, as the sample resides at hotter temperatures, the FM austenite phase is more stable, thus requiring less magnetic field to transform the sample from martensite to austenite, as indicated by $H_{\text{req}}$. The entropy change is then quantified by finding the area (hatched regions) between two reverse MT $M-H$ curves and dividing by the temperature increment responsible for the change (see area ‘A’). Area ‘A’ in Fig. 3 is related to a single point in Fig. 2b below the $M_f$ temperature. Clearly, if the magnetic field is not ramped to a level high enough to induce complete transformation, the total transformation entropy cannot be determined easily.

Fig. 3 also demonstrates the magnetic responses of MSMAs when their initial microstructural state is mixed, i.e. containing both martensite and austenite phases, shown by the curves labeled $T_2$ and $T_3$. It can be seen from the $M-H$ curves labeled $T_2$ and $T_3$ that, when the material is at a temperature in the two-phase region, small temperature changes may result in predicted entropy changes (shaded regions) at magnetic fields smaller than $H_{\text{req}}$ (see area B for small fields), which should not be confused with transformation entropy change.

The continuous heating protocol used to find magnetization curves like that in Fig. 3 is defined by heating the sample through small increments after loading and unloading the magnetic field. Thus, some of the austenite that forms on field loading may still be present in the microstructure after field unloading, especially if the temperature is $> M_f^{H=0}$. Owing to the mixed microstructure, the $M-H$ area measured from the differences in magnetostatic energy density is larger in regions of small applied field similar to those labeled $T_2$ and $T_3$ in Fig. 3 and yields incorrect values for entropy change related to the magnetic field-induced phase change. Therefore, the continuous heating protocol over-predicts entropy changes and RCP, as discussed in subsequent sections.

In the discontinuous heating protocol, in contrast, an extra step is added to cool the sample below $M_f$ after the field is ramped [25]. Ultimately, this results in magnetic responses like those shown by $T_1$, $M_f$ and $A_s$ in Fig. 3, and little to no entropy contribution is captured at magnetic fields smaller than that required to transform the MSMA below $A_s$. The entropy change captured from the discontinuous heating protocol is nearly representative of the transformation entropy change comparable to that measured with differential scanning calorimetry (DSC) as discussed in Section 5.

2.3. Calculating the RCP of MSMAs

Once the $\Delta S - T$ diagrams are constructed for a given material, the RCP is calculated as the area of the shaded region in Fig. 2b. The RCP is dependent not only on magnetic field, but also on the martensitic transformation temperatures and its maximum is defined here as

$$\text{RCP}^{\text{max}}(H,T) = \Delta S \cdot \Delta T_{\text{ad}}^{\text{max}} + \Delta S \cdot \Delta T_{\text{elas}}^{\text{max}} \cdot \frac{S_{\text{eff}}}{2} \left( \Delta T_{\text{ad}}^{\text{max}} + \Delta T_{\text{elas}}^{\text{max}} \right)$$

(2)
where \( \Delta T_{ad}^{\text{max}} \) is the maximum adiabatic temperature change. \( \Delta T_{elas} \) is the average of the forward and reverse elastic transformation ranges mentioned earlier, and \( S_{irr} \cdot (\Delta T_{ad}^{\text{max}} + \Delta T_{elas}) \) is the thermodynamic loss on the forward and reverse phase front motion associated with the transformation hysteresis. It is important to include this entropy production to avoid violating the second law of thermodynamics as defined by the Clausius inequality [2,26].

Compared with the conventional method of calculating RCP, or \( \frac{T}{J_{ref}} \Delta S dT \) from Ref. [19], the present authors have added terms to include work obtained within the elastic transformation ranges, losses due to transformation hysteresis, and have set limitations on \( T_{hot} \) and \( T_{cold} \) to correspond to the MT temperatures. Note that the adiabatic temperature change can be approximated using the traditional method [2,19], i.e. \(-\Delta T_{ad} \approx T_0 \Delta S/C_p \), where \( T_0 \) is the equilibrium MT temperature [27], and \( C_p \) is the isobaric heat capacity, assumed to be independent of magnetic field and equivalent in both austenite and martensite.

The third term in Eq. (2) approximates the cooling power losses from the entropy production during the transformation process. The entropy production from the transformation hysteresis is approximated as the hysteresis loss defined in Ref. [28] divided by the temperature of the isothermal magnetization tests [2] as

\[
S_{irr} = \frac{\xi(H) \cdot \Delta S_{irr} \cdot \Delta T_{hys}}{T}
\]  

where if \( \xi(H) = 1 \), approximates entropy production for a complete transformation cycle. For magnetic fields that induce only partial transformation, the percentage transformation \( \xi(H) \) is \( 0 < \xi(H) < 1 \). In Eq. (3), \( S_{irr} \) can be roughly determined by multiplying the transformation entropy from DSC, \( \Delta S_{irr} \), by the thermal hysteresis of transformation \( \Delta T_{hys} \), under zero magnetic field and dividing by the temperature of the isothermal field-induced transformation. Only half the \( S_{irr} \) is considered in Eq. (2) because, in the refrigeration cycle like that shown in Fig. 1, the transformation front propagates only once during the cooling step \( (T_{hot} \rightarrow T_{cold}) \), but \( S_{irr} \) takes into account both forward and reverse phase front motion. Upon releasing the magnetic field outside the refrigerated volume, the other half of frictional dissipation associated with the complete transformation is produced. This second half does not affect how much the sample will cool on field ramping but, as shown in Fig. 2b, the hysteresis does limit the operating temperatures and thus reduces RCP. Lastly, it is important to note that the approximation of entropy production from the MT is assumed to be independent of rate. This, however, is not true in general, and suggests that a more accurate model must be developed in future studies to account for the rate dependence of entropy production.

2.4. Calculating critical magnetic fields for MCE in MSMAs

The final two performance parameters that are essential to quantify the MCE of MSMAs are the magnetic fields required to induce and complete transformation, \( H_{req} \) and \( H_{comp} \), respectively. These parameters are dependent on the cycle in which the MSMA is to be analyzed. Their magnitude is dependent on the MT temperatures. Defining thermal hysteresis as \( \Delta T_{hys} = [(A_f + A_r) - (M_r + M_f)]/2 \), the magnetic field required to induce the transformation when \( T_{hot} = M_f \) is defined as

\[
H_{req} = (A_f - M_f) \cdot \frac{dH^A}{dT}
\]

(4)

where \( dH^A/dT \) is the austenite start temperature’s sensitivity to external magnetic field. The field required to induce a complete structural transformation under isothermal conditions is defined as

\[
H_{comp}^{iso} = (\Delta T_{hys} + \Delta T_{elas}) \cdot \frac{dH^A}{dT}
\]

\[
= \Delta T_{comp} \cdot \frac{dH^A}{dT}
\]

(5)

where \( (\Delta T_{hys} + \Delta T_{elas}) = \Delta T_{comp} \), which reduces to \( A_f - M_f \) (i.e. the difference between the \( A_f \) and \( T_{hot} \) temperatures when \( T_{hot} = M_f \)), and \( dH^A/dT \) is the austenite finish temperature’s sensitivity to the applied field. However, for the process described in Fig. 1, the magnetic field is increased and decreased under adiabatic conditions. This implies that the latent heat of the transformation will affect the field required to complete transformation. \( H_{comp} \) is then defined as

\[
H_{comp} = (\Delta T_{comp} + \Delta T_{ad}) \cdot \frac{dH^A}{dT}
\]

(6)

where \( \Delta T_{ad} \) is the field-dependent temperature change.

Fig. 4 depicts the magnetic responses of a MSMA at different states in Fig. 1. The magnetic response at \( M_f \) shows the magnetic field \( H_{req} \) needed to start the transformation. If the sample is to transform under isothermal conditions, the field required to complete the transformation would be defined by the same magnetization curve, and is labeled \( H_{comp}^{iso} \). However, the sample is insulated while the field is applied, and an endothermic reaction occurs, as shown in Fig. 1, thus the magnetic response is shifted to the right, while the sample cools and ultimately requires \( H_{comp} \) to complete the transformation. From Figs. 1 and 4, it can be deduced that \( T_{hot} = M_f \) and \( T_{cold} \geq A_f \cdot \frac{dH^A}{dT} \).

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When considering that the latent heat of transformation affects the required magnetic field to complete transforma-
tion, a MSMA will require the least amount of magnetic field to transform when $\Delta T_{\text{hys}}$ and $\Delta T_{\text{elas}}$ are the smallest and the $A_f$ field sensitivity is the highest, as shown by Eqs. (5) and (6). These imply that MSMAs with small $H_{\text{comp}}$ will have large RCP, because $S_{\text{irr}}$ will be small, and the temperature range $M_f^{H=0} \rightarrow A_f^{H=H_{\text{comp}}}$ in Fig. 2b will increase at the expense of the elastic transformation ranges, thus increasing the area of the shaded region. Unfortunately, large adiabatic temperature changes, although seeming to be desired at first, increase the required magnetic field to complete transformation. This emphasizes the need to determine heat treatments and processing techniques that yield optimum meta-magnetic behavior for inverse MCE refrigeration.

Using Eqs. (4)-(6), the percentage of transforming volume is defined (when $T_{\text{hot}} = M_f$) as

$$\zeta(H) = \frac{H - H_{\text{req}}}{H_{\text{comp}} - H_{\text{req}}} \times 100 \quad \text{where } H_{\text{req}} < H < H_{\text{comp}}$$ (7)

where $H$ is constrained between the minimum field required to induce transformation and the field required to attain complete transformation. For $H < H_{\text{req}}$ and $H > H_{\text{comp}}$, $\zeta(H)$ obviously equals 0 and 1, respectively, when considering only the reverse transformation. The fraction of transformation can then be used to determine RCP, and $S_{\text{irr}}$ under any given field or transformed volume fraction.

The thermodynamic framework discussed above suggests that the entropy and magnetization changes across MT are not the only parameters required to quantify the MCE performance in MSMAs. The hot and cold temperature reservoirs used to determine RCP are limited by the transformation temperatures. $T_{\text{hot}}$ must be less than or equal to $M_f$ in order for the refrigeration cycle to be repeatable through fully reversible complete transformation [25]. Alternatively, $T_{\text{hot}}$ could be a temperature between $M_s$ and $M_f$ to use only partial phase transformation for refrigeration. In order to use the elastic transformation ranges for better RCP levels, special thermodynamic cycles need to be implemented to capture the entire useful work regime, like that shown by the path from point 6 to point 1 in Fig. 1. Therefore, processing and fabrication methods that affect the sample microstructure and the transformation characteristics can be used to improve the performance parameters for MSMAs so that they may be used as refrigerants at maximum capacity. The following demonstrates how simple heat treatments can change the refrigeration performance parameters of MSMAs by modifying the microstructure, and how the reported values for entropy change in the literature across MT can be misleading in evaluating the real refrigeration capacity of these alloys.

3. Experimental procedures

Bulk polycrystalline Ni$_{43}$Mn$_{42}$Co$_4$Sn$_{11}$ (at.%) alloys were prepared using vacuum induction melting. Some induction melted samples were then homogenized in argon at 1173 K (above the reported L2$_1$ ordering temperature [9]) for 24 h and quenched in ice water. The melt-spun ribbon samples were prepared by re-induction melting the bulk samples. Once melted, the alloy was ejected onto a copper wheel rotating with a surface velocity of 30 m s$^{-1}$. The melt-spun ribbons were heat treated in an argon atmosphere at 1173 K for 2 h and then quenched in ice water. Secondary heat treatments were then conducted on the SHT ribbons. They were conducted for 1 h at 673 K, 773 K and 873 K, and the ribbons were either rapidly quenched (RQ) in water or furnace cooled (FC). All these heat treatments were conducted below the reported B2/L2$_1$ order temperature [9].

Microstructural analysis of the samples was conducted using optical microscopy and a Cameca SX-50 electron probe microanalyzer. Compositional analysis was performed using wavelength dispersive spectrometry (WDS). Thermo-magnetic measurements were carried out using a Quantum Design SQUID-VSM magnetometer at a heating-cooling rate of 5 K min$^{-1}$ under constant magnetic fields. These measurements were used in determining MT temperatures and transformation hysteresis. All thermomagnetic measurements began with zero field heating to 400 K, whereby the field was ramped to a constant level after stabilizing at 400 K. The temperature was then reduced to 10 K, stabilized, and ramped back up to 400 K. For qualitative comparison of the effect of the secondary heat treatments, the change in magnetization across MT, $\Delta M$, was determined from the difference of the magnetization levels at $A_f$ and $A_s$ from the thermomagnetization curves 0.05 T or $H_{\text{req}}$ (defined in Eq. (4)).

Isothermal $M$–$H$ data were obtained using experimental schemes referred to as continuous and discontinuous heating protocols [21], as described in Section 2. The discontinuous heating scheme was carried out as follows.

1. The samples were cooled to a temperature $< M_f$ under zero magnetic field, resulting in a fully martensitic state.
2. The samples were then heated under zero magnetic field to a temperature just below the austenite start temperature, without overshooting the target temperature.
3. Holding the temperature constant, the magnetic field was ramped from zero to 7 T and then back down to zero at a rate of 25 Oe s$^{-1}$; meanwhile, the magnetization was measured.
4. The temperature was then decreased to $< M_f$.
5. Next, the temperature was increased to the previous temperature plus 3 K (without overshoot), and then step 3 was repeated.
6. Step 4 and 5 were repeated until the test temperature was very close to the austenite finish temperature.

The continuous heating protocol was conducted as follows.

1. The samples were cooled to a temperature $< M_f$ under zero magnetic field.
2. They were then heated under zero magnetic field to a temperature just below the austenite start temperature, without overshoot.
3. Holding temperature constant, the magnetic field was ramped from zero to 7 T and then back down to zero at a rate of 25 Oe s\(^{-1}\), meanwhile, the magnetization was measured.
4. The temperature was increased by 3 K without overshoot, and then step 3 was repeated.
5. Step 4 was repeated until the test temperature was very close to the austenite finish temperature.

Once the isothermal magnetization responses had been measured at small temperature intervals, the forward (\(A \rightarrow M\)) and reverse (\(M \rightarrow A\)) paths were separated so that Eq. (1) could be applied to construct a diagram like that in Fig. 2b. Only the reverse transformation was considered here, because the \(M \rightarrow A\) transformation was associated with the endothermic response responsible for the cooling, as shown in Fig. 1. In these experiments, since the applied field was ramped at 25 Oe s\(^{-1}\), the magnetic responses were considered as isothermal, because this rate is sufficiently low to prevent temperature changes from the latent heat of the transformation. Eventually, Eq. (1) yielded \(\Delta S_{\text{ad}}\) (the entropy change from the continuous heating protocol) and \(\Delta S\) (from the discontinuous heating protocol) over a range of temperatures from the isothermal magnetization curves, which then allowed RCP to be calculated using Eq. (2). Isothermal magnetization measurements also provided information for finding the critical fields \(H_{\text{iso}}^{\text{comp}}, H_{\text{comp}}^{\text{iso}}, H_{\text{req}}^{\text{comp}}\), and \(H_{\text{req}}\) using Eqs. (4)–(6).

Thermo-magnetic MT temperatures measured under 0.05 T were then compared with the MT temperatures measured by DSC. For DSC analysis, the temperature was ramped at 2 K min\(^{-1}\). In order to determine \(\Delta T_{\text{max}}^{\text{ad}}\) in Eq. (2), approximate heat capacity measurements were conducted using a Quantum Design Physical Property Measurement System (PPMS) from 10 K to 250 K by a pulsed-relaxation method employing the continuous heating scheme.

4. Results

This section presents the results obtained from the experiments described in Section 3. Here, the basis for selecting the most favorable ribbons for further MCE study is presented. Most importantly, \(\Delta T_{\text{elas}}, \Delta T_{\text{hys}}, \Delta T_{\text{comp}}, \Delta T_{\text{ad}}, H_{\text{comp}}^{\text{ad}}, H_{\text{comp}}, H_{\text{req}}, dH/dT\) and the RCP, defined using Eqs. (2)–(6), were determined for all samples studied in this work.

4.1 Magnetic and martensitic transformation characteristics

Magnetic characterization of the Ni\(_{43}\)Mn\(_{42}\)Co\(_4\)Sn\(_{11}\) samples was performed, and the results are compared in Fig. 5a. The figure shows the thermo-magnetization curves of the solutionized bulk, and as-spun and solutionized ribbon samples under 0.05 T. The as-cast bulk specimen did not exhibit a notable meta-magnetic phase transition, thus the results are not shown here. The austenite phase of the bulk sample is FM for a narrow temperature interval on heating until its Curie temperature \(T_c\) is reached. The \(T_c\) of the austenite was found to be \(\sim 365\) K. The martensite exhibits a small magnetic susceptibility, which in past studies was attributed to short-range frustrated antiferromagnetic interactions by neutron polarization measurements [22,23]. The frustrated antiferromagnetic response is shown by the low magnitude of magnetization values from 4.2 K to 160 K. Around 200 K, the sample started transforming to highly magnetic austenite during the reverse transformation. Both as-spun and solutionized ribbons exhibited good meta-magnetic shape memory characteristics, with a sharp transition between the austenite and martensite. The changes in magnetization across MT (\(\Delta M\)), transformation ranges (\(\Delta T_{\text{elas}}\)), temperature hysteresis (\(\Delta T_{\text{hys}}\)) and their sum (\(\Delta T_{\text{comp}}\)) were extracted from Fig. 5a, as defined by the schematic in Fig. 5b, and tabulated in Table 1. The data indicate that the solutionized bulk sample exhibits the smallest thermal hysteresis, but the ribbon samples exhibit the smallest transformation range.

To find out whether the aforementioned performance parameters, such as \(H_{\text{iso}}^{\text{comp}}\) and \(H_{\text{req}}\), are dependent on sample microstructure, they need to be determined using the equations in Section 2 and the data in Table 1. In addition, the CC slopes (the slope of the critical field for the transformation vs. temperature phase diagram) should be found using the thermo-magnetization results like those seen in Fig. 5c for the solutionized ribbon samples. The corresponding phase diagrams are shown for the solutionized bulk and ribbon samples in Fig. 5d. These results will later be used to discuss the effect of microstructure on the performance parameters summarized in Section 2.

4.2 Microstructure

Since \(\Delta M, \Delta T_{\text{elas}}\) and \(\Delta T_{\text{hys}}\) are quite different in the bulk and ribbon samples, WDS analysis was conducted to check for compositional differences. Table 2 contains the average content (in at\(\%\)) for each component measured over eight different locations and their standard deviations for the solutionized samples. Clearly, the composition was relatively homogeneous throughout the samples, as indicated by the low standard deviations, and therefore, the observed differences in the transformation characteristics must be largely due to factors other than compositional inhomogeneity. The bulk sample, however, was found to contain \(\sim 0.5\) at\(\%\) more Co than the solutionized ribbon. It has been reported that a small substitution of Co for either Mn or Ni reduces the MT temperatures and increases the \(T_c\) of austenite [1,29], which is consistent with the magnetic responses of the present samples.

Fig. 6 shows the SEM images of the SHT bulk and ribbon samples. The average grain size of the solutionized ribbons is \(\sim 15\) \(\mu\)m. The ribbons are \(\sim 50\) \(\mu\)m thick.
Solutionized bulk samples have an average grain diameter of 140 μm. The differences in grain size and specimen thickness, and thus grain size to thickness ratio, are believed to be some of the main reasons for the observed differences in MT characteristics between the bulk and ribbon samples. This will be discussed further in the subsequent sections.

4.3. Secondary heat treatments

Differing from the samples in the bulk form, the ribbons exhibit a large $\Delta M$ with the application of very low magnetic fields. In addition, the ribbons show the smallest $\Delta T_{\text{hys}}$ that is desired for efficient refrigeration performance per Eqs. (4)–(6). In contrast, the solutionized bulk sample exhibits the smallest $\Delta T_{\text{hys}}$. Since the refrigeration performance parameters can be improved by decreasing $\Delta T_{\text{hys}}$, the solutionized Ni$_{43}$Mn$_{42}$Co$_{4}$Sn$_{11}$ ribbons were exposed to secondary heat treatments in attempts to further reduce their $\Delta T_{\text{hys}}$, as can typically be done for NiMnIn alloys [17].

In Ref. [17], it was shown that $\Delta T_{\text{hys}}$ is related to L2$_1$ ordering, and therefore secondary heat treatments were conducted at temperatures (673 K, 773 K, 873 K) below the reported B2/L2$_1$ ordering temperature for 1 h to promote L2$_1$ ordering as observed in NiMnIn alloys. At each temperature, ribbons were RQ or FC. Characteristic features of the MT after secondary heat treatments are determined directly from the experiments or calculated using the equations in Section 2 and tabulated in Table 3.
The critical field vs. temperature phase diagrams for the completion of the martensite to austenite transformation in the secondary heat-treated ribbons are shown in Fig. 7a, which are extracted from the thermo-magnetization curves. Later, these phase diagrams will be used to find the $H_{\text{iso}}^{\text{comp}}$ parameter.

As shown in Table 3, secondary heat treatments resulted in slight changes in transformation temperatures, thermal hysteresis and magnetic field sensitivity of $A_s$ and $A_f$, but on average, the $\Delta M$ across MT remained approximately the same and therefore was not included in the table. The RQ samples exhibited an increase in transformation temperatures, whereas the FC samples showed a decrease in transformation temperatures compared with the SHT ribbons. This suggests that slight changes in atomic ordering were dependent on the cooling rate of the secondary heat-treated ribbons.

The product of the slopes of the CC lines in Fig. 7a and the $\Delta T_{\text{comp}}$ tabulated in Table 3 yielded $H_{\text{iso}}^{\text{comp}}$, following Eq. (5), which is also tabulated in Table 3. The solutionized ribbon that was heat treated at 673 K for 1 h and then RQ was found to exhibit the smallest $H_{\text{iso}}^{\text{comp}}$ of 6.9 T, whereas the solutionized ribbon sample originally had a $H_{\text{iso}}^{\text{comp}}$ of 7.6 T.

4.4. Meta-magnetic response of heat-treated ribbons

Fig. 7b shows the 7 T thermo-magnetization curves of the Ni$_{43}$Mn$_{42}$Co$_4$Sn$_{11}$ as-spun, solutionized (SHT), and solutionized plus 673 K 1 h RQ ribbons (SHT+673K(RQ)). The 0.05 T thermo-magnetization curve for the SHT+673K(RQ) sample is shown in the inset. The inset shows that the 7 T field does not lead to a large change in the magnetization of austenite, and the large applied field reduces $\Delta M$ across MT, as the magnetization of martensite increased more than that of the austenite. This is attributed to the short-range antiferromagnetic interactions of martensite [22,23,30], making magnetic saturation of martensite difficult. Large fields decrease the MT temperatures, as expected. The CC slopes, $dH^{\text{iso}}/dT$
and \( dH^f/dT \), for the SHT+673K(RQ) ribbons were determined as \(-0.16\) T K\(^{-1}\) and \(-0.25\) T K\(^{-1}\), respectively, from thermo-magnetization curves.

To verify the validity of Eqs. (4) and (5), the isothermal magnetic response of the \( \text{Ni}_{43}\text{Mn}_{42}\text{Co}_{4}\text{Sn}_{11} \) SHT+673K(RQ) ribbons was measured under applied magnetic fields up to 7 T at a temperature (=190 K) much below \( M_f \), at \( M_f (=210\) K), and at a temperature \( > A_f (=245\) K), using martensite as the initial phase in the former two cases. The response is shown in Fig. 7c. The magnetization values at low temperatures are small. Small magnetic hysteresis is observed at \( T = 190\) K, since the field is not sufficient to induce a large structural transformation, and the sample is composed mainly of short-range frustrated antiferromagnetic martensite. The small hysteresis may be attributed to a low concentration of magnetic domains rotating at low applied fields or a small volume fraction of phase transformation. The response near \( M_f \) shows magnetic hysteresis on unloading the field, indicating that structural transformation has taken place. At temperatures \( > A_f \), no magnetic hysteresis is observed, indicating that the field does not induce a transformation from austenite to another phase, and austenite is purely FM.

More importantly, the isothermal magnetization curves in Fig. 7c verify the validity of Eqs. (4) and (5) for the SHT+673K(RQ) ribbons. In Table 3, \( H^\text{iso}_{\text{comp}} \) and \( H_{\text{req}} \) were predicted to be 6.9 T and 3.1 T, respectively, using the thermo-magnetization results. As can be seen from the isothermal magnetization curve at \( T = M_f \) in Fig. 7c, these magnetic fields reasonably match those experimentally observed in the figure for the \( M \rightarrow A \) transformation.

4.5. Entropy of transformation, heat capacity and RCP

The latent heat and heat capacity were determined for the SHT ribbon samples using DSC and the PPMS mentioned in Section 3. As shown in Fig. 8a, \( \Delta S_{\text{fr}} \) was found to be 18 J kg K\(^{-1}\) from the area of the endothermic peak \( (\Delta S_{\text{fr}} = \int (C_p/T)dT) \). In addition, the transformation temperatures match those obtained from 0.05 T thermo-magnetic measurements for the SHT ribbons.

The CC relation can also be used to find \( \Delta S_{\text{fr}} \). The CC relation is defined as [31]

\[
\Delta S_{\text{fr}} = \Delta M^{M \rightarrow A} dH^f/dT 
\]

(8)

where \( \Delta M^{M \rightarrow A} \) is the magnetization change across MT. To further verify that the \( \Delta S_{\text{fr}} \) was \( \sim 18\) J kg K\(^{-1}\), the above equation was used, where \( \Delta M \) was found, from magnetic data like that shown in Fig. 7c, at \( T = M_f \), to be 84.1 emu g\(^{-1}\) and \( dH^f/dT \) was found to be \(-0.22\) T K\(^{-1}\) from thermo-magnetic measurements. The CC relation predicted the transformation entropy of 18.6 J kg K\(^{-1}\), which is in good agreement with the DSC measurements. This indicates that either Eq. (8) or the experimental results shown in Fig. 8 can be used to determine \( \Delta S_{\text{fr}} \).
In Fig. 8b, the heat capacity data are shown. The data provide an accurate measure of the heat capacity bracketing the hysteresis region, although the first-order transition region itself is not reproduced by the pulse-relaxation technique. These values are used to determine the adiabatic temperature change near $T_0$, as required in Eq. (2) to calculate the RCP. At higher temperatures, the heat approach the classical $3Nk_B$ per mole, as expected, plus a small electronic term. Using $\Delta S_p$ of 18 J kg K$^{-1}$ and a $C_p$ of 434 J kg K$^{-1}$ at 190 K (near $M_f$), and a $T_0$ of 224 K from Table 3, $\Delta T_{\text{ad}}^{\text{max}}$ is calculated to be 9.3 K. This implies that, if $T_{\text{hot}}$ is considered to be equal to $M_f$ = 198 K as in Fig. 1, $T_{\text{cold}}$ would be 188.6 K (i.e. $T_{\text{hot}} - \Delta T_{\text{ad}}$). The RCP contribution within the temperature range permitting the complete field-induced entropy change ($A_{\text{comp}}^{M_f = M_f}$ to $M_f^{H = 0}$) is defined as $\Delta S_p \cdot \Delta T_{\text{ad}}^{\text{max}} - (S_{\text{orr}} \cdot \Delta T_{\text{el}}^{\text{max}})/2$. Here $S_{\text{orr}}$ equals 1.9 J kg K$^{-1}$ when $T = M_f$ in Eq. (3). This leads to the RCP of 159 J kg$^{-1}$ for the SHT ribbons in this temperature range. However, when considering the entropy changes in the elastic regions of transformation, the total reversible RCP is calculated as $\Delta S_p \cdot \Delta T_{\text{ad}}^{\text{max}} + \Delta S_p \cdot \Delta T_{\text{el}}^{\text{max}} - S_{\text{orr}}$ ($\Delta T_{\text{el}}^{\text{max}} + \Delta T_{\text{el}}^{\text{max}})/2$ (Eq. (2)). For the SHT ribbons, this total reversible RCP is 389 J kg$^{-1}$.

In the SHT+673K(RQ) ribbon samples, the entropy change across transformation was calculated using the CC equation (Eq. (8)) as explained for the SHT sample above. The $\Delta M$ was measured at $T = (A_f + A_s)/2$ to be 79 emu g$^{-1}$, and the CC slope ($dH/dT$) to be $-0.25$ T K$^{-1}$. Eq. (8) then results in $\Delta S_p$ of 19.7 J kg K$^{-1}$. Assuming the heat capacity does not significantly change after the secondary heat treatments, $\Delta T_{\text{ad}}^{\text{max}}$ is found to be 10.4 K, and thus the $H_{\text{comp}}$ (from Eq. (6)) then equals 9.5 T for the SHT+673K(RQ) ribbon, which is slightly lower than that of the SHT ribbons. The RCP contribution within the temperature range permitting the complete field-induced entropy change ($A_{\text{comp}}^{M_f = M_f}$ to $M_f^{H = 0}$) is calculated to be 196 J kg$^{-1}$, with $S_{\text{orr}}$ being equal to 1.5 J kg K$^{-1}$ when $T = M_f$ in Eq. (3). Including the entropy changes in the elastic regions of transformation, the total reversible RCP is calculated to be 385 J kg$^{-1}$ for the SHT+673K(RQ) ribbon.

Comparing the SHT ribbons with those exposed to secondary heat treatments, it was found that the transformation entropy change increases as a result of these heat treatments, $H_{\text{comp}}^{s}$ decreases for the RQ samples, and $A_{\text{comp}}^{M_f = M_f}$ to $M_f^{H = 0}$ (temperature region where the complete reversible entropy change can be achieved) grows at the expense of the elastic transformation regions $A_{\text{el}}^{M_f = M_f}$ to $M_f^{H = 0}$ and $M_f^{H = 0} - M_f^{H = 0}$. These findings suggest that the material can easily be tailored for a given cycle with simple heat treatments to permit not only a certain cooling capacity under a given field, but also that the field levels required to achieve refrigeration and their operating temperatures can be modified.

5. Analysis and discussion

So far, this work has presented an accurate characterization framework describing the magnetic refrigeration performance in MSMAs. An example Brayton refrigeration cycle was used to show how important materials property parameters will affect the refrigeration performance of a solid-state refrigerant exhibiting a first-order phase transformation and latent heat. The parameters affecting the refrigeration performance in this work have been identified as the entropy change across the MT, the magnetic fields required to initiate and complete the MT both adiabatically and isothermally, and the RCP. Each parameter was described and discussed in detail. Finally, a NiCo MnSn SMA alloy composition was selected to demonstrate how simple heat treatments can influence these refrigeration performance parameters explained in Section 2. The following sections discuss what heat treatments change in the microstructures and how these changes influence the MT characteristics and performance parameters in the same alloy composition.

5.1. Effect of fabrication method on martensitic and magnetic transformation characteristics

As shown in Table 1, the responses of the SHT samples in Fig. 5a under 0.05 T vary significantly owing to the fabrication technique. After the SHT, no second phases were observed in the backscattered electron images in Fig. 6 or from the WDS analysis. This indicates that second
phases are not the cause of the differences in $\Delta T_{\text{elas}}$ between the SHT bulk and ribbon samples like that reported for NiMnCoIn alloys [13]. Instead, the present authors believe that other stress non-uniformities developing during the reversible martensitic transformation, such as those caused by a large degree of grain constraints, affect the transformation range. In conventional SMAs, elastic energy storage has been linked to grain size to thickness ratio [32,33] during superelastic loading and, thus, thermally or magnetically induced martensitic transformation ranges should also be affected by this microstructural parameter as discussed below.

5.2. Effect of grain size constraint on elastic energy storage during martensitic transformation

In conventional SMAs, Wert et al. [32,33] showed that the ratio of grain size ($GS$) to specimen thickness ($t$) is inversely proportional to the elastic energy storage, or $\Delta T_{\text{elas}}$. The larger transformation range was an indication of the difficulty for transformation phase front motion, which required further undercooling or superheating (or higher stress levels in the case of superelasticity), and resulted in more nucleation events and higher stored elastic energy in CuZnSn and CuZnAl alloys [32,33]. For example, superelastic loading on CuZnSn [32] alloys showed a transformation stress range of $<4.7$ MPa with a $GS/t$ ratio of 2.5. However, the same composition transformed under the stress range of 7.4 MPa with a $GS/t$ ratio of 0.55 [32]. The larger transformation stress ranges indicate more elastic energy stored during transformation, owing to small $GS/t$ ratios. Similarly, the $GS/t$ ratio affects the amount of stored elastic energy in the Ni$_{43}$Mn$_{42}$Co$_4$Sn$_{11}$ and the corresponding percent elastic energy storage of $E_{\text{elas}}$.

Table 4 shows average grain sizes for the SHT samples and their corresponding $GS/t$ ratios. The solutionized ribbon exhibits $\sim$1.7 times larger $GS/t$ than the solutionized bulk sample, and thus less elastic energy is stored in the microstructure on transformation, owing to the relaxation of the strain energy on the free surface. Moreover, less driving force is required to complete the transformation, hence the smaller $\Delta T_{\text{elas}}$ and $\Delta T_{\text{comp}}$ in the ribbon samples, as shown in Table 1.

The reduction in $\Delta T_{\text{elas}}$ will, in turn, decrease the second term in Eq. (2). Decreasing this term may seem undesirable, since it would reduce the reversible RCP levels, but minimizing $\Delta T_{\text{elas}}$ should also drop $\Delta T_{\text{comp}}$ and $H_{\text{comp}}$. A reduction in $H_{\text{comp}}$ is desired to make the field requirements for magnetic refrigeration more practical. In addition, in order to take advantage of reversible RCP in the temperature ranges $M_s$-$M_f$ and $A_T$-$A_s$, one needs special refrigeration cycles to access the energy in those regions, which may bring about practical challenges.

Therefore, minimizing stored elastic energy within the SMA microstructure is beneficial to magnetic refrigeration applications, and it should be consistently analyzed to compare SMA performance in different compositions and microstructures. A relative measure of the elastic energy stored in the MSMA across MT has been shown in Ref. [28] to be the ratio of the elastic free energy to the latent heat of the MT. Using this framework, the ratio can be determined as $E_{\text{elas}}/\Delta H_{fr} = \Delta T_{\text{elas}}/(2M_s)$ where $\Delta H_{fr}$ is the latent heat of the MT. $E_{\text{elas}}$ is dependent on the $GS/t$ ratio and, therefore, these values are listed in Table 4. Here, $\Delta T_{\text{elas}}$ was determined as explained earlier, and $M_s$ was determined as shown in Fig. 5b. The difference in the $GS/t$ ratio for the samples is a result of the fabrication method, and the ribbon samples demonstrated more favorable parameters for MCE, such as small $\Delta T_{\text{elas}}$ (Table 3) and large $\Delta M$ (Table 1), because they would require less energy for the cyclic response, as outlined in Fig. 1.

5.3. Effect of solution heat treatment on martensitic and magnetic transformation characteristics

In addition to $\Delta T_{\text{elas}}$, the role of transformation hysteresis $\Delta T_{\text{hys}}$ on the refrigeration performance parameters was investigated in the Ni$_{43}$Mn$_{42}$Co$_4$Sn$_{11}$ samples. As shown in Eqs. (4)-(6), thermal hysteresis is directly related to the magnetic fields required to induce and complete the transformation. Also, it can be seen in Fig. 2b that decreasing $\Delta T_{\text{hys}}$ will result in a wider temperature range that will allow a fully reversible field-induced transformation, $A_f^{H=H_{\text{comp}}} \rightarrow M_s^{H=0}$. Increasing the shaded area in Fig. 2b ultimately increases the achievable thermal work produced by the SMA. Heat treatments provide a means for changing $\Delta T_{\text{hys}}$, because they influence the atomic order in SMAs.

The atomic order and thermal hysteresis in SMAs are linked by the compatibility between austenite and martensite phases [34]. Some ordered Heusler alloy compositions may exhibit good compatibility between the transforming phases and therefore, produce small thermal hysteresis [17]. In addition, atomic order influences the Mn–Mn distances for Mn-containing Heusler alloys and this significantly affects the magnetic response of the MSMA [9]. In the present materials, $\Delta M$ increases after the SHT, as shown in Fig. 5a, which indicates that there may have been a slight change in atomic order. This increase in $\Delta M$ coincides with the information reported in Ref. [9]. In addition, $\Delta T_{\text{hys}}$ and $\Delta T_{\text{elas}}$ are smaller in the SHT ribbons compared...
with the as-spun ones. Clearly, a decrease in $\Delta T_{hys}$ is observed after SHT with an apparent grain growth and homogenization of the as-spun ribbons. Since the SHT has such a large effect on the transformation characteristics, the Ni$_{43}$Mn$_{42}$Co$_{4}$Sn$_{11}$ alloy could potentially exhibit even smaller $H_{\text{comp}}$ and larger RCP, if tailored properly with secondary heat treatments, as in NiMnIn systems [17].

5.4. Effect of secondary heat treatments

In attempts to further change the atomic order in Ni$_{43}$Mn$_{42}$Co$_{4}$Sn$_{11}$, secondary annealing treatments were conducted in 100 K increments followed by two different cooling procedures. As a result, small but notable changes in the magnetic response and MT characteristics were recorded, as presented in Table 3. The differences between the samples with different cooling procedures may be explained by point defect concentration within the crystal lattice. After RQ, point defects, such as vacancies, result in slightly higher lattice strain, thus martensite is stabilized, and MT temperatures increase [35].

To check whether atomic order was influenced by secondary heat treatments, thermal hysteresis and $A_s$ field sensitivity were plotted in Fig. 9 against the parameter $(T_c - T_0)/T_c$ [17,36], or the ratio between the difference in the austenite Curie temperature and the MT temperatures and the austenite Curie temperature (see Table 3).

This parameter has been shown to be related to the L$_2$ order in NiMnIn and NiMnSn alloys [17,36] whereby, as $(T_c - T_0)/T_c$ increases, the L$_2$ order also increases. Interestingly, the trends observed from the secondary heat treatments in Ni$_{43}$Mn$_{42}$Co$_{4}$Sn$_{11}$ match the trends observed in other MSMAs, only their changes are on a much smaller scale owing to the high L$_2$ stability [37].

As shown in Fig. 9b, the FC samples tend to order toward L$_2$ more than the RQ samples, and the RQ process seems to retain more disorder. In Fig. 9c, the L$_2$ ordering also results in larger temperature hysteresis, which is linked to the changing lattice coherency between austenite and martensite phases. Clearly, in the present NiMnCoSn alloy composition, atomic disorder improves lattice coherence between martensite and austenite phases.

Fig. 10a and b shows the transformation range as a function of the parameter $(T_c - T_0)/T_c$ and heat treatment temperatures for the RQ and FC cases. It can be seen that the FC procedure results in broader temperature ranges. It is observed that the lowest temperature heat treatment corresponds to the smallest transformation range, even smaller than the solutionized ribbon. The results in Fig. 10 indicate that the cooling process greatly affects the transformation range. Since FC and RQ procedures result in the same $(T_c - T_0)/T_c$ parameter with different $\Delta T_{elast}$, the evolved microstructure must be responsible for this difference. Since FC samples were held at an elevated temperature
for a longer period of time, it is possible that some phase decomposition may have occurred [38], but on a scale small enough not to be observed with BSE imaging (<1 µm). In the FC samples, the transformation may have been “pinned” by the presence of anti-phase boundaries, as observed in Ni<sub>2</sub>Mn(Ga<sub>0.5</sub>Al<sub>0.5</sub>) alloys [39–41]. Further studies, however, are needed to verify the existence of these anti-phase boundaries in NiMnCoSn alloys.

Nevertheless, the parameters measured from the SHT+673K(RQ) sample indicate that thermal hysteresis had further decreased compared with that of the SHT ribbon, the 4<sub>s</sub> field sensitivity remained about the same, and the transformation range had also decreased. Therefore, since the SHT+673K(RQ) ribbons showed the largest ΔM and smallest ΔT<sub>comp</sub>, they were selected for further MCE study and are compared with the SHT samples.

5.5. Calculated performance parameters for magnetic refrigeration

The main goal of the following section is to discuss the influence of experimental protocol and MT characteristics on the ΔS–T curves as in Fig. 2. As mentioned earlier, RCP can be directly calculated using Eq. (2), and integrating the ΔS–T diagram is not needed when considering the latent heat of a first-order transition. However, since much of the SMA community has published results that include the ΔS–T diagrams, correctly interpreting these results is important. These diagrams can still serve as an indication of how well a SMA would perform as a refrigerant, as long as the experimental protocol is declared, the MT temperatures are given, and the alloy’s heat capacity is known. Below, the ΔS–T diagrams are compared for two experimental protocols on the same sample. Furthermore, the ΔS–T diagrams are presented for the SHT+673K(RQ) and SHT samples, to show how improving the sample microstructure (and MT characteristics) affects these diagrams.

Fig. 11 displays the ΔS<sub>eff</sub> values (discussed in Section 3) deduced for the Ni<sub>43</sub>Mn<sub>42</sub>Co<sub>4</sub>Sn<sub>11</sub> SHT ribbon using the continuous heating protocol for which all the values were calculated from the reverse (M→A) transformation magnetization curves such as those in Fig. 7c, and using Eq. (1). A schematic of the ΔS–T diagram using the same thermodynamic assumptions in Fig. 2b has also been drawn over the data to indicate how the ΔS–T diagram should look to calculate the maximum theoretical thermal work (RCP). This ΔS–T schematic shows the maximum theoretical reversible entropy change expected from this sample as a result of the reverse martensitic transformation assuming that the applied field is not limited to 7 T, but is sufficient to complete the adiabatic transformation. Clearly, there are a few discrepancies between the theoretical and measured curves. At first glance, the most obvious discrepancy is that Eq. (1) combined with the continuous heating protocol over-predicts the transformation entropy change, ΔS<sub>eff</sub>, i.e. the maximum ΔS<sub>eff</sub> value in the figure. ΔS<sub>eff</sub> values were generated for different field changes between 0 and 7 T. The maximum ΔS<sub>eff</sub> value (ΔS<sub>eff</sub>) obtained for the SHT ribbons was 28 J kg K<sup>−1</sup> at 219 K for 4 T, 5 T, 6 T and 7 T in the continuous heating scheme. This entropy change is comparable with other reports on Ni<sub>43</sub>Mn<sub>43</sub>Co<sub>4</sub>Sn<sub>14</sub> (15.3 J kg K<sup>−1</sup>, 5 T) [13], Ni<sub>43</sub>Mn<sub>43</sub>Co<sub>4</sub>Sn<sub>11</sub> (33 J kg K<sup>−1</sup>, 5 T) [29], Ni<sub>50</sub>Mn<sub>34</sub>Sn<sub>16</sub> (20 J kg K<sup>−1</sup>, 5 T) [42] and Ni<sub>45</sub>Co<sub>3</sub>Mn<sub>37.5</sub>In<sub>12.5</sub> (30 J kg K<sup>−1</sup>, 7 T) [43]. However, ΔS<sub>eff</sub> is larger than ΔS<sub>eff</sub> calculated from Eq. (8), indicating that a
discrepancy is present from the experimental scheme. This could also mean that the transformation entropy change increases with applied field, but this is not the case, as shown by the discontinuous heating protocol discussed next. For smaller applied fields, the $\Delta S_{\text{eff}}$ values in Ni$_{43}$Mn$_{42}$Co$_{4}$Sn$_{11}$ SHT ribbons are larger than those typically reported. For example, under 2 T and 3 T, solutionized ribbons seem to produce 14.6 J kg$^{-1}$ and 20.8 J kg$^{-1}$, respectively, whereas Ni$_{60}$Mn$_{35.5}$In$_{14.5}$ (10 J kg$^{-1}$, 1.8 T) [9] and Ni$_{50}$Mn$_{37}$Si$_{13}$ (13 J kg$^{-1}$, 3 T) [14] alloys produce smaller entropy changes under similar fields. This may be due to the fact that the continuous heating scheme permits an initially mixed microstructural state to be analyzed with Eq. (1).

The next notable discrepancy is that most of the constructed $\Delta S - T$ diagram is outside the temperature range required to find the reversible RCP. This is due to the fact that $H_{\text{req}}$ is relatively large (Table 3). In order to achieve a field-induced transformation under applied fields <7 T, the temperature of the SHT ribbon must reside near $A_{f}^{H=0}$. Comparing Fig. 2b with Fig. 11, it can be seen that most of the $\Delta S - T$ diagram has been found in the area of thermal hysteresis, $M_{s}^{H=0} \rightarrow A_{f}^{H=0}$. $M_{s}^{H=0}$ is labeled in Fig. 11 for clarity. This indicates that the SHT ribbon sample cannot be used as a refrigerant in the Brayton cycle depicted in Fig. 1 under the applied field of 7 T, because the entropy change will not be repeatable with field cycling. Lastly, a close comparison between Fig. 2b and Fig. 11 shows that $A_{f}^{H=0}$, represented on the $\Delta S - T$ diagram in Fig. 11, is under-predicted by ~6 K. In Table 3, $A_{f}^{H=0}$ is listed as 233 K, whereas in Fig. 11 it is shown to be 227.5 K. This discrepancy is a product of the continuous heating protocol.

Fig. 12 shows the $\Delta S$ curves from the discontinuous heating protocol for the SHT ribbons. Note that, previously, $\Delta S_{\text{eff}}$ was used to describe entropy changes from the continuous heating protocol. Here, $\Delta S$ from the field-induced transformation, over the entire temperature range, seemed to plateau at a value (18 J kg$^{-1}$), which nearly matches that measured in DSC. This indicates that the transformation entropy change is not largely a function of magnetic field, and entropy production from hysteresis is relatively small compared with the entropy change of the MT. In addition, a clear growth of the $\Delta S - T$ diagram to lower temperatures is observed as the fields become larger. This is due to the negative CC slope shown in Figs. 5d, 7a and 9a. In addition, the $A_{f}^{H=0}$ in Fig. 12 now agrees with the data in Table 3.

Again, a schematic of the $\Delta S - T$ diagram derived from Fig. 2b has been drawn over the data to indicate how the $\Delta S - T$ diagram should look to experimentally verify the calculated RCP from the first two terms of Eq. (2). Clearly, the magnitude of the entropy change is now consistent with the theoretical diagram, but a majority of measurements still reside outside the temperatures of interest, enclosed by the black trapezoid in Fig. 12. Again, this is due to the large $\Delta T_{\text{elas}}$, $\Delta T_{\text{hys}}$ and $H_{\text{iso}}^{\text{corr}}$ (or $H_{\text{ad}}^{\text{corr}}$) exhibited by the SHT ribbons. This can also be viewed as the inability to sufficiently decrease the transformation temperatures with the applied field of 7 T. Reducing $\Delta T_{\text{elas}}$ and $\Delta T_{\text{hys}}$ would effectively overlap theoretical $\Delta S - T$ and experimentally captured $\Delta S - T$ curves with small applied magnetic fields.

The RCP is determined from the data in Fig. 12 by the area of the overlapping theoretical and experimental $\Delta S - T$ curves (shaded area) with the hysteresis losses subtracted as defined in Eq. (3). The applied fields, in this case, will produce very small RCP values, as only a fraction of the theoretical curve overlaps the experimentally captured one up to 7 T. The maximum measured RCP value (overlapping of two curves) was found to be 74 J kg$^{-1}$ under the applied field of 7 T. However, the projected RCP of 389 J kg$^{-1}$ was found using Eq. (2).

Finally, the discontinuous heating protocol was performed for the SHT+673K(RQ) ribbons, and the $\Delta S - T$ diagram is shown in Fig. 13a. The theoretical $\Delta S - T$ curve from the thermodynamic framework in Fig. 2b has also been drawn over the data. $H_{\text{req}}$, $H_{\text{iso}}^{\text{corr}}$ and $H_{\text{ad}}^{\text{corr}}$ for the SHT+673K(RQ) ribbons were calculated to be 3.1 T, 6.9 T and 9.5 T, respectively, as shown in Table 3. The $\Delta S$ value saturates near 19.7 J kg$^{-1}$ as calculated from Eq. (8). It is important to note that the SHT+673K(RQ) ribbons show a $H_{\text{iso}}^{\text{corr}}$ of 6.9 T. According to Eq. (5) in Section 2, this means that an isothermal test at temperature $M_{f}$ will produce a complete field-induced structural transformation with the application of 6.9 T. This prediction is verified in Fig. 13a, because the 7 T $\Delta S - T$ curve shows an entropy change of ~19 J kg$^{-1}$ at temperature $M_{s}^{H=0}$ as indicated by point 1 in the figure.

Furthermore, the RCP for the SHT+673K(RQ) ribbons was calculated as the overlapping areas of the theoretical and experimental $\Delta S - T$ curves for each applied field level (shaded area) with hysteresis losses subtracted as defined in Eq. (3). Fig. 13b shows $\Delta S_{\text{comp}} / 2 - T$ diagrams, which were calculated using Eq. (3). Since the $\Delta S - T$ curves saturate at $\Delta S_{\text{comp}}$ measured by DSC, the diagram in Fig. 13a can be used at every temperature and field level to yield a value
most results in the literature calculate the RCP in the conventional way, which defines $T_{\text{hot}}$ and $T_{\text{cold}}$ arbitrarily at full width at half maximum of the $\Delta S - T$ curve [19]. These temperatures are often inside the thermal hysteresis range shown in Fig. 2b, and the values do not reflect reversible $\Delta S$ and RCP values. It has been shown here that, for the framework given in Fig. 2, the conventional way of calculating RCP is not correct for MSMAs.

$\text{Ni}_{43}\text{Mn}_{42}\text{Co}_{4}\text{Sn}_{11}$ SHT ribbons exhibit a RCP of 389 J kg$^{-1}$ and, from the isothermal tests, only 74 J kg$^{-1}$ was accessible experimentally under 7 T. The MCE performance of the solutionized ribbons was improved with secondary heat treatments, whereby a RCP of 385 J kg$^{-1}$ is achievable under an applied field of 9.5 T. The SHT ribbons allow for a slightly larger RCP using special thermodynamic cycles, because they also have a larger elastic temperature range. This, in turn, requires higher applied fields to transform the ribbon. The alloys in the literature, such as $\text{Ni}_{50}\text{Mn}_{37}\text{Sn}_{13}$ (39 J kg$^{-1}$, 1.8 T) [9] and $\text{NiMnIn}$ (130 J kg$^{-1}$, 3 T) [14], have been reported to exhibit smaller RCP under smaller fields, but neither their measurement protocol nor their heat capacity were reported.

6. Conclusions

In the present work, to demonstrate how MSMAs can be used as solid-state refrigerants in a refrigeration cycle, an example Brayton cycle was introduced and discussed in detail. From this cycle, the key material parameters, important for controlling MCE and refrigeration performance, such as the magnetic fields required to induce and complete the martensitic transformation, magnetization change across the transformation, transformation temperature range and thermal hysteresis, were identified. The performance parameter RCP was used to compare the refrigeration capability of MSMAs with different compositions and microstructures. It was shown that the conventional method of finding the RCP for non-SMAs is not a
valid approach for materials that exhibit a latent heat across a first-order transformation.

In attempt to validate the selection of the above materials parameters, a case study was conducted on a specific NiMnCoSn composition. The results indicated that these parameters can be optimized using simple heat treatments even in the compositions of MSMAs that show high L21 atomic stability. The grain size to thickness ratio was found to influence the size of the transformation range. Atomic ordering was shown to change the transformation thermal hysteresis. The best performance parameters were achieved in Ni43Mn42Co4Sn11 polycrystalline ribbons when they were homogenized at 1173 K and then annealed at 673 K for 1 h, followed by RQ in water. Furthermore, the cooling method after the secondary heat treatments was shown to affect the meta-magnetic response and ultimately control the transformation range and thermal hysteresis.

More precisely, the effects of secondary heat treatments on the aforementioned materials parameters were studied in Ni33Mn24Co12Sn11 melt-spun ribbons. Promoting atomic disorder decreased the thermal hysteresis. The elastic energy storage on martensitic transformation was reduced by increasing the grain size to thickness ratio, which reduced the transformation range from 25 K in the as-spun ribbons to only 10 K in the heat-treated ribbons. This effectively reduced the magnetic fields required to transform the materials and increased the operating temperature range of the refrigerant.

Finally, the relationships between the magneto-thermal loading protocol, sample microstructure and entropy change vs. temperature diagrams were discussed. It was shown that the continuous heating protocol over-predicts the entropy change on the phase transformation. In addition, the comparison between theoretical and experimental entropy change vs. temperature curves showed how the sample responses were improved by the optimization heat treatments. Ultimately, it was found that past reports on the MCE in MSMAs can still yield valuable information as long as the experimental protocol, martensitic transformation temperatures and heat capacity are also presented so that the RCP can be calculated accurately.

The key materials parameters proposed in the present work provide a powerful tool for analyzing MSMA refrigerants. The alloy composition and responses presented in this study indicate MSMAs can be used as solid state refrigerants. Moreover, further composition and microstructural optimization through thermal treatments can improve the transformation characteristics and thus the refrigeration performance parameters for them to compete with conventional rare-earth-based MCE materials such as Gd alloys.

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