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Abstract

Microparticles of Ni$_{45.7}$Mn$_{36.6}$In$_{13.5}$Co$_{4.2}$ have been prepared by means of different grinding methods (hand-grinding, cryo-milling, planetary ball-milling) followed by annealing treatments in order to recover the original martensitic transition and magnetic properties. A rapid reduction of particle size down to the micrometres has been obtained after few hours of milling, as it results from morphological analyses. Milling temperature, time, and medium strongly impact on the degree of induced stresses and particles aggregation, significantly changing the morphology, crystal structure and magnetic properties. It was found that both magnetic and magneto-structural phase transitions can be recovered by high-temperature annealing treatments ($T>1000$ K). Time and temperature of the treatment have been optimized in relation to the disorder introduced by the milling process, which depends on its energy and duration. In general, our results show the strong dependence of the magneto-structural properties of the NiMnInCo compound on microstructural
features, atomic order and chemical homogeneity, that imposes a careful selection and improvement of the preparation route.

Keywords: Metamagnetic transition; Shape memory alloys; Ball-milling; Particle size effect; Magnetic behaviour; Magneto-structural correlations.

1. Introduction

Ni-Mn-based Heusler compounds have attracted a lot of attention, both theoretically and experimentally, for their unique magneto-structural martensitic transformation and the resulting richness in multifunctional properties [1, 2]. These multi-functionalities include magnetic shape memory effect (MSME) [3], giant magnetoresistance [4], and large magnetocaloric effect (MCE) [5, 6, 7]. Their highly-tunable multiferroicity makes these intermetallic compounds promising for energy-efficient technologies, as energy-harvesting devices, sensors/actuators, and magnetic refrigeration systems [8, 9, 10].

The off-stoichiometric Ni-Mn-(In, Sn, Sb, Ga) compounds and their Co-doped compositions [Error! Bookmark not defined., 11] are interesting for the metamagnetic martensitic transformation between a weak-magnetic martensite and a ferromagnetic austenite [12]. This enables a large inverse MCE, exploitable in solid-state magnetic refrigeration technology [13, 14], and magnetic-field-induced reversible martensitic transformation, for fast magnetic actuation and large work output [Error! Bookmark not defined., 15]. However, some drawbacks of the bulk, as the poor mechanical integrity, the irreversible hysteresis losses at the martensitic transformation, and the internal constraints imposed by the grain-boundaries, obstacle their actual and efficient use in repeated thermo-magnetic cycles [16]. To overcome these limitations, micro and nanostructured shapes have been investigated.

Ni-Mn-(In, Sn, Ga) compounds were produced in a variety of shapes and sizes using different fabrication methods: thin films by epitaxial growth [17, 18], micron and sub-micron particles by ball-milling techniques [19, 20, 21], ribbons by melt-extraction or melt-spinning methods [Error! Bookmark not defined., 22, 23, 24], foam structures by spark plasma sintering [25]. This miniaturization has permitted to gain a better understanding of the role of grain structure on the twinning stress and incompatibilities [Error! Bookmark not defined.], to reduce the thermal hysteresis, improve the phase homogeneity [Error! Bookmark not defined.], enhance the magnetocaloric capacity [Error! Bookmark not defined.], and manufacture Heusler compounds with Additive Manufacturing (AM) technologies [26, 27, 28]. Up to now, the studies on the 3D printed Ni-Mn-Ga magnetic shape memory materials, with binder jet or extrusion-based printing [Error! Bookmark not defined., Error! Bookmark not defined., Error! Bookmark not defined.], have highlighted the advantages of creating new complex geometries, with increased mechanical strength and flexibility. Although state-of-the-art additive manufacturing techniques typically use spherical powders that are produced using an atomization process, there is a growing
interest in using irregular shaped powders, obtainable through cheaper methods easily exploitable for different classes of materials [29, 30, 31, 32]. A further opportunity is the realization of smart composites, by embedding powders in a polymer matrix [Error! Bookmark not defined., Error! Bookmark not defined., Error! Bookmark not defined., 33], which represent potential solutions for applications in actuators, micro-pumps, energy-harvesting and magnetocaloric systems.

In the case of giant-magnetocaloric Ni-Mn-In-Co compounds, the investigation of materials of smaller size has not been extensively carried out. Some studies are reported on ribbons [34], thin films [35] and particles prepared by mechanical grinding and ball-milling [36, 37, 38]. However, the fulfillment of reliable preparation routes for micro-structured Ni-Mn-In-Co materials still deserves a careful investigation of the effect of morphology, microstructure and plastic deformation on their magnetic, structural and functional properties [Error! Bookmark not defined., Error! Bookmark not defined., Error! Bookmark not defined., 33].

In this work, we study the magnetic and magneto-structural properties of Ni-Mn-In-Co microparticles obtained by hand-grinding, cryo-milling and planetary ball-milling processes. Thermo-magnetic, structural, and morphological techniques are used to characterize the different powders. Suitable annealing treatments have been developed, depending on the type of deformation process, in order to recover the magneto-structural and magnetic transitions. Our results highlight the critical role of the thermo-mechanical and microstructural history of the compound, in particular the size and disorder effects, in preventing the recovery of the original martensitic and ferromagnetic properties.

2. Experimental methods

A bulk polycrystalline compound of 250 g, with nominal composition \( Ni_{45.7}Mn_{36.6}In_{13.5}Co_{4.2} \), was prepared from industrial grade powdered elements, following the route in Ref.[Error! Bookmark not defined.].

The bulk was crushed in an agate mortar to achieve micro-meter sized powders, which were sieved with different meshes to select particle size of 250 µm, 125 µm, 89 µm, and 66 µm. The finest hand-grinded (HG) particles (≤ 66 µm) were then subjected to two different ball-milling methods.

The cryo-milling (CM) process was carried out in a Retsch Shaker Cryo-mill, using a stainless-steel jar with a ball of 20 mm diameter and a ball-to-powder weight ratio of 12:1. The process was run in Ar atmosphere with a shaking frequency rotational speed of 400 rpm, in cycles of 5 min milling and 2.5 min rest up. The system was cooled with liquid nitrogen vapour for the entire milling duration. The HG powders were also Planetary ball-milled (PBM), in a Fritsch Pulverisette 7, using Zirconia jars, with 5 mm sized Zirconia balls, and a ball-to-powder weight ratio of 10:1. Isopropanol was added as the liquid milling medium to maintain the particles dispersed and avoid overheating. The process was run at the rotational speed of 400 rpm, in cycles of 15 min milling and 7 min rest up.
The milled powders were then annealed in a resistance furnace, inside an INOX tube filled with Ar. The parameters of utilized heat-treatments (temperature, time and cooling-rate) are summarized in Table 1. Two different cooling-rates were used after the annealing: water quenching (WQ) and slow-cooling (SC, characteristic time of 35 min).

For the bulk sample, compressive stress-strain measurements were performed at 297 and 230 K using an Instron 5967 30 kN universal testing machine to analyse the mechanical behaviour of this compound under compressive stress in the austenitic and martensitic phases, respectively. The specimens were prepared in shape of rectangular blocks, with flat parallel surfaces, and cross-sectional area of 2.5 x 2.5 mm² with a height of 5 mm. The strain was monitored via a strain gauge attached to compression platens directly next to the sample, while the stress was recorded via a 30 kN load cell.

The structure of the powders at room temperature was determined by X-ray diffraction (XRD) measurements using a STOE STADI P in transmission geometry with Mo Kα₁ radiation.

Table 1: Milling and annealing parameters of $Ni_{45.7}Mn_{36.9}Fe_{13.3}Co_{4.2}$ investigated samples (temperature, time and cooling rate: water quenching or slow cooling).

<table>
<thead>
<tr>
<th>Grinding method</th>
<th>Sample Name</th>
<th>Milling duration (h)</th>
<th>Annealing temperature (K)</th>
<th>Annealing time (h)</th>
<th>Cooling rate</th>
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</thead>
<tbody>
<tr>
<td>Hand-grinding (HG)</td>
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<td>-</td>
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<td>-</td>
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<tr>
<td></td>
<td>HG4h773SC</td>
<td>773</td>
<td>4</td>
<td>SC</td>
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<td>HG4h973SC</td>
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<td>4</td>
<td>SC</td>
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<tr>
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<td>HG4h1100WQ</td>
<td>1100</td>
<td>4</td>
<td>WQ</td>
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<tr>
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<td>24</td>
<td>WQ</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2CM2h1030WQ</td>
<td>1030</td>
<td>24</td>
<td>WQ</td>
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</table>
Temperature-dependent XRD measurements were carried out in a custom-built setup in transmission geometry with Mo Kα₁ radiation and Mythen2 R 1K Detector (Dectris Ltd.). The sample was mixed with NIST 640d standard silicon powders for correcting geometric errors and glued on a graphite foil. The temperature was controlled by means of a closed cycle He-cryo-furnace. The X-ray diffractograms were analysed by the Le Bail refinement, by using Jana2006 software [39].

The morphological-compositional and microstructural analyses of the bulk and powder samples were carried out in a Field Emission Scanning Electron Microscope (SEM) FESEM-FIB Zeiss Auriga Compact, equipped with an INCA Energy Dispersive X-ray (EDX) Spectroscopy system. Compositional analysis on selected areas of the samples was carried out with high electron beam acceleration voltage (20 kV). SEM images obtained with acceleration voltage of 20 kV (HV-SEM) were analysed with ImageJ software to determine the particle and grain size and obtain the size distribution histograms. Low-voltage (5 kV) LV-SEM micrographs were collected with two different detectors of secondary electrons, the Everhart-Thornley detector (ET-SE) and the In-Lens detector, to study and compare the microstructural/morphological contrast and highlight the peculiar features of the particles after the annealing treatments.
The magnetic and magneto-structural phase transitions were studied with low-field (0.1 mT) a.c. (500 Hz) magnetic susceptibility measurements, in the 80-450 K temperature range on heating.

The temperature-dependent magnetization curves were measured with an extraction magnetometer (MAGLAB SYSTEM2000 by Oxford Instruments) under 1 T magnetic field.

3. Results and Discussion

3.1. Hand-grinding and ball-milling

The thermomagnetic response of the $\text{Ni}_{45.7\pm0.5}\text{Mn}_{36.9\pm0.3}\text{In}_{13.2\pm0.2}\text{Co}_{4.2\pm0.3}$ bulk sample is characterized by a large positive susceptibility change on heating between 275-292 K (Fig. 1). This is related to the magneto-structural reverse martensitic transformation, occurring from the low-temperature, weakly-magnetic martensitic phase, to the high-temperature ferromagnetic austenite. On further heating up, a sharp drop at around 393 K points out the occurrence of the ferro-to-paramagnetic transition of the austenite (austenite Curie transition). The effect of the hand-grinding (HG) process on the phase changes is highlighted by the thermomagnetic response reported in Fig. 1, from which a broadening is evident of both the martensitic transformation and the austenite Curie transition. This behaviour is strongly emphasized for the ball-milled powders, for which a complete disappearance of the magnetic phase changes occurs. By way of example, the pretty much flat thermomagnetic response of powders cryo-milled for 2 h (2CM) and planetary ball-milled for 3 h (3PBM), is also shown in Fig. 1.

After the HG process, at room temperature the powders display a tetragonal non-modulated martensitic structure (Fig. 2), with only few and low-intensity reflections of the cubic austenite.

After 2 h of cryo-milling, the diffraction peaks of the tetragonal martensite phase broaden without changing their angular positions, while those of the cubic phase are not detectable. By increasing the milling time to 3 h, the peak width of the tetragonal phase further increases. This fact is likely due to the accumulation of internal strains and defects caused by the milling process. The same effect occurs by treating the powder for 3 hours in the planetary ball-milling (3PBM).
Figure 1: Low-field ac susceptibility measurement as a function of temperature for $\text{Ni}_{45.5}\text{Mn}_{35}\text{Sb}_{11.5}\text{Co}_{8.5}$ bulk sample (Bulk), hand-grinded powders (HG), cryo-milled particles for 2 h (2CM) and 3h-planetary ball-milled ones (3PBM).

Figure 2: Room-temperature X-ray diffraction patterns of hand-grinded (HG), 2h-cryo-milled (2CM), 3h-cryo-milled (3CM), 3h-planetary ball-milled (3PBM) powders of $\text{Ni}_{45.5}\text{Mn}_{35}\text{Sb}_{11.5}\text{Co}_{8.5}$. The vertical dashed lines indicate the position of the tetragonal martensite (M) and cubic austenite (A) reflections of the HG powder.

By combining the structural and magnetic results of the as-milled powders, it appears that the longer and/or more energetic are the milling processes, the larger is the stabilization at high temperature of a stress-induced tetragonal martensite phase.

Looking at the particles’ morphology, the SEM micrographs show that with respect to the starting HG powders, characterized by a particle size distribution centred at $60 \pm 20 \mu m$ (Fig. 3(a)), the 2CM powders have a significant smaller average size shifted to $27 \pm 6$ (Fig. 3(b)). On increasing the milling time, the 3CM particles present a different morphology, and a further size reduction with a distribution centred at $15 \pm 11 \mu m$ and a more irregular shape and rougher surface, due to the tendency for the smaller pieces to be cold-welded (Fig. 3(c)).

In order to avoid such cold-welding effect and the consequent particle agglomeration, we have chosen to carry out a wet milling process by utilizing the planetary ball mill with a solvent in the jars. The 3PBM particles processed with isopropanol result in a homogeneous flaky shape, with flat surface of average size lower than 10 $\mu m$ and typical thickness of 1-2 $\mu m$ (Fig. 3(d)). Moreover, these particles are well dispersed and slide on each other, rather than be cold-welded.
In summary, the preparation of Ni-Mn-In-Co microparticles with different grinding processes (hand-grinding, cryo-milling, planetary ball-milling) pointed out the rapid reduction of particle size down to the micrometres by few hours of energetic milling and the strong effect of the mechanically induced plastic deformations and defects on structural, microstructural and magnetic properties of particles which turned out to be irreversibly changed in comparison to the bulk. Moreover, CM and PBM processes resulted in different powders due to the phase of the material (austenite/martensite) that is involved in the milling: indeed, in the CM process the larger amount of the material is kept at low temperature, reasonably in the martensite phase, whereas the PBM process certainly involves the austenite phase. All these results highlight the important role that the bulk mechanical properties of Ni-Mn-In-Co play on the outcomes of milling processes.

![Figure 3](image_url)

**Figure 3**: SEM images of the \(\text{Ni}_{45.7}\text{Mn}_{36.9}\text{In}_{12.2}\text{Co}_{4.2}\) (a) HG, (b) 2CM, (c) 3CM, and (d) 3PBM particles, with corresponding particle size distributions in the insets.

For this reason, we have performed a mechanical characterization of bulk Ni-Mn-In-Co sample, by measuring compressive stress-strain curves at two different temperatures, corresponding to the martensite phase (230 K) and to the austenite phase (297 K) (Supplementary Material, Fig. S1). Results at low and high temperatures demonstrate in general a brittle behaviour of the Ni-Mn-In-Co bulk, likely due to the formation of a high density of dislocations under compressive stress. However, the stress-strain behaviour is significantly different at the two temperatures. At 230 K,
after an initial elastic deformation up to a relatively low critical stress (about 75 MPa), the material
tends to accommodate the increase of stress with the onset of detwinning, i.e., the martensitic
variants reorientation up to a maximum stress before fracture of about 150 MPa. At 297 K, instead,
the bulk fragment shows an elastic deformation of the austenite up a slightly larger critical stress
and a subsequent stress-induced martensitic transformation. The so-obtained martensite phase
undergoes only a partial detwinning and it shows a much larger maximum stress before fracture
(550 MPa) with respect to the martensite at the lower temperature. As a general comment, the poor
compressive strength and high embrittlement of the bulk can reasonably justify the rapid size
reduction observed during the HG process and the high structural worsening after few hours (2-3 h)
of ball-milling. On the morphological side, the different shape and size distribution of obtained
particles for the CM and wet-PBM processes can be related to the different mechanical behaviour of
bulk Ni-Mn-In-Co at the different process temperature.

3.2. Annealing treatments

The powders obtained by HG, CM and wet-PBM processes were subjected to suitable annealing
treatments in order to recover the original bulk behaviour, in terms of magneto-thermal properties
and transition temperatures.

3.2.1. Post-annealed hand-grinded (HG) powders

The HG powders of different particle size (250 µm, 125 µm, 89 µm and 66 µm), selected by sieve,
were subjected to the same heat-treatment at 773 K for 4 h followed by slow cooling
(HG4h773SC). This particular heat treatment has been chosen on the base of results on hand-
grinded Ni-Mn-Ga/Ni-Mn-Cu-Ga particles [Error! Bookmark not defined.].

As it can be noticed from low-field susceptibility measurements reported in Fig. 4(a), with respect
to the starting bulk, the martensitic transformation temperature in the case of HG powders is shifted
to a higher temperature and the transition is considerably broadened. In contrast, the austenite Curie
transition temperature is independent on the particle size and, with respect to the bulk, is decreased
Figure 4: (a) low-field susceptibility response upon heating for several batches of HG powders, characterized by different particle size, selected by sieving, and subjected to the same thermal treatment at 773 K for 4 h, in comparison to the curve of the bulk, showing the reverse martensitic transformation ($T_{\text{rev}}$) and the Curie transition of the austenite ($T_C$). (b) Corresponding high-field (1 T) magnetization measurements in the temperature range of the martensitic transformation.

![Figure 4](image_url)

Figure 5: X-ray diffraction patterns at 340 K and at 20 K for the HG powders with particle size below 66 µm subjected to the thermal treatment for 4 h at 773 K.

![Figure 5](image_url)

by only 4 K. The same behaviour is evident from the temperature dependence of magnetization curves at 1 T, reported in Fig. 4(b). The M(T) curves show a lower saturation magnetization of the austenite with respect to the bulk, especially for particles with a size below 100 µm, and a larger increase of magnetization at low temperatures. On decreasing the particle size, the forward martensitic transformation ($T_{\text{fwd}}$) broadens, while the reverse branch and $M_s$ temperature remain nearly coincident, thus leading to an increase of thermal hysteresis.

Looking at the temperature-dependent XRD patterns of the HG4h773SC particles with dimensions below 66 µm (Fig. 5), it can be noticed the formation of a monoclinic-distorted 7M modulated martensite below 280 K and the retaining of low-intensity reflections from the austenite even down to 20 K. The latter ones show a large peak width at both high (340 K) and low (20 K) temperatures, thus revealing the presence of a certain amount of unrelaxed stress after the applied thermal treatment. With respect to the M(T) curves (Fig. 4(b)), the residual austenitic traces and the remaining lattice stress can account for the retained magnetization at low T and the large thermal hysteresis of the martensitic transformation.
The broadening to lower temperatures of the martensitic transition, leading to an increase of the hysteresis width, and the concomitant increase of retained austenite fraction on decreasing the particle size, denote the primary role of the characteristic length-scales governing the nucleation and growth processes of the martensite inside the parent phase. The observed behaviour of the hysteresis resembles that reported for Cu-based shape memory alloys and low-carbon steels, subjected to the grain-size refinement below 100 µm. In fact, the grain-size reduction and the higher contribution from the grain-boundaries (i.e., regions of non-thermodynamic equilibrium and usually source of chemical inhomogeneity) can reasonably account for a more difficult accommodation of the elastic strain energy at the phase interfaces. This phenomenon is substantially in contrast with what observed for Ni-Mn-Ga and Ni-Mn-Cu-Ga particles, for which the thermal hysteresis associated with the coupled magneto-structural transformation is lowered by decreasing the particle size.

In order to further reduce the internal defects in the smaller HG powders (d < 66 µm), annealing treatments for 4 h at higher temperatures, i.e. 973 K and 1100 K, above the B2 transition temperature (T_{B2} ≈ 900 K), have been tested. The M(T) measurements performed at 1T (Fig. 6(b)) point out an increase of the austenite magnetization and a decrease of the martensitic transformation temperature closer to the bulk’s one on increasing the annealing temperature. However, the thermal hysteresis remains significantly larger than the bulk’s one and the retained magnetization at low temperatures presents a non-monotonic behaviour with the annealing temperature. Interestingly, by decreasing the annealing time from 4 to 2 h, for heat treatments above 1023 K, the forward transformation sharpness and the magnetization change are improved (Fig. 6(b)). A rapid water quenching increases the martensitic transformation temperature and, in the case of annealing temperatures above the L2₁/B2 transition, decreases the Curie temperature (Fig. 6(a) and 6(b)). This phenomenon, also studied in bulk samples, can be related to the concentration of vacancies and the change of degree of order.

Figure 6: (a) Low-field susceptibility measurements on heating for bulk sample and hand-grinded powders after several annealing treatments. The vertical dashed lines are guides for the eyes indicating the Curie transition and the reverse martensitic transformation.
of the bulk sample. (b) Temperature-dependent magnetization measurements at 1 T for hand-grinded powders annealed for 4 h or 2 h at three different temperatures (773, 973, 1100 K) and slowly cooled down in comparison with the bulk (dashed curve).

3.2.2. Post-annealed ball-milled powders

On the basis of the results reported in previous paragraph, the powders obtained from CM and PBM processes were subjected to annealing at high temperatures, above the $L_2_1/B2$ transition temperature, followed by rapid cooling.

In particular, for the 2CM powders, the martensitic transition is restored by selecting annealing treatments at above 1000 K (Fig. 7(a)). The powder annealed for 24 h at 1030 K and water quenched shows the recovery of the reverse martensitic transition between 275 and 300 K. However, the Curie temperature (Fig. 7(a)) and the magnetization of austenite (Fig. S3, Supplementary Material) are lower than those of the HG4h1100SC powders. By increasing the annealing temperature to 1100 K, a monotonic increase of both martensitic transformation and Curie transition temperatures is observed with the annealing time (from 1 h to 24 h). The short heat treatments (1 h and 4 h) at 1100 K can only promote a partial recovery of the martensitic transformation, which occurs at very low temperature, and it is partially arrested, resulting in a small magnetization change and a large hysteresis width (Fig. 7(b)). The increase of annealing time up to 24 h shifts the magneto-structural transformation to temperatures even higher than those of HG4h1100WQ powders and reduces the thermal hysteresis and magnetization retained at low temperatures.

Figure 7: (a) susceptibility response of the 2h-cryomilled powders subjected to different heat treatments (b) high-field (1 T) magnetization measurements for the 2h-cryomilled powders annealed at the fixed temperature of 1100 K for 1, 4 and 24 h, in comparison to the behaviour of the hand-grinded HG4h1100WQ powders (dashed line).
The micrographs of 2CM particles heat-treated at 973 K, which do not recover the martensitic transformation (Fig. 7(a)), highlight the presence of an inhomogeneous and rough microstructure (Figs. 8(a,b)), due to the heterogeneous nucleation of multiple nanoscale grains.

A long heat treatment at 1030 K allows the recrystallization phenomenon, hence the formation of new grains of few microns (inset), while preserving the separation between particles and almost their original shape (Supplementary Material, Fig. S4(a)). By further increasing the annealing temperature to 1100 K, the powders start to agglomerate (Supplementary Material, Figs. S4(b) and S4(c)). After 4 h of heat treatment the particles show the formation of an underneath bamboo-grain structure thanks to the higher atomic mobility (Fig. 8(c)). However, this is still characterized by overlying microstructural and phase inhomogeneity. In fact, it can be distinguished between the smooth regions recovering the martensitic phase with the peculiar lamella-like contrast and a composition, $\text{Ni}_{46.6}\text{Mn}_{35.6}\text{In}_{13.6}\text{Co}_{4.2}$, close to the expected one, and the residual portions of the surface with granular or grid-like morphology, richer in Mn (Fig. 8(d)). Interestingly, these microstructural discontinuities completely disappear with long-time (24h) and high-temperature (1100 K) thermal treatments, as visible by the enlargement of only homogeneous and smooth bamboo grains, showing the martensitic twin variants propagating throughout the cross-section and across the neighbouring grains (Fig. 8(e)). Furthermore, also a better phase homogeneity and composition ($\text{Ni}_{45.6\pm0.5}\text{Mn}_{37.1\pm0.6}\text{In}_{13.1\pm0.3}\text{Co}_{4.2\pm0.3}$) closer to that of the bulk are attained (Fig. 8(f)). Accordingly, the recovery of the expected magneto-structural behaviour after the heat treatments (Fig. 7) is strongly connected to the removal of compositional-morphological inhomogeneity on the particle surface (Figs. 8(c,d)), which demonstrate the pivotal role of the overall phase homogeneity on the martensitic phase formation.
Figure 8: LV-SEM micrographs of the 2CM powders annealed (a,b) for 24 h at 973 K (ET-SE detector), (c,d) for 4 h at 1100 K (In-Lens detector) and (e,f) for 24 h at 1100 K. The right-hand figures highlight the peculiar microstructural features.

Figure 9: Temperature-dependent magnetization curves at 1 T for the 3h-cryomilled (3CM) and 3h-planetary ball-milled (3PBM) powders annealed at 1100 K for 24 and 29 h in comparison with the HG4h1100WQ powders (dashed line).
By increasing the milling time, as in the 3CM and 3PBM powders, a higher annealing temperature and time has been necessary to retrieve the martensitic transformation. As visible in Fig. 9, only after annealing treatments at 1100 K for a minimum duration of 24 and 29 h (for 3PBM and 3CM respectively), a considerable magnetization jump between the two phases is obtained. However, the M(T) measurements (Fig. 9) reveal that the recovered martensitic behaviour for the 3PBM24h1100WQ powders is less complete than that of 2CM24h1030WQ, showing an increase of thermal hysteresis, accompanied by the rise of magnetization at low temperature. Moreover, by annealing at 1100 K for 24h, followed by water quenching, the recovery for the 3CM powders is more challenging than for the 3PBM under the same annealing conditions, as highlighted by the increase of broadening and the smaller magnetization change on the cooling branch. The transformation behaviour of the 3CM powders can be improved through the increase of annealing time to 29 h (Fig. 9).

As for the 2CM particles, the SEM analysis of the post-annealed 3CM and 3PBM particles has pointed out the occurrence of sintering phenomenon after long treatments at high temperature, but also a strong dependence of the microstructural evolution on the peculiar size and shape of the as-milled particles. In fact, for the 3CM particles, characterized by a rounder shape and a non-uniform size distribution after the milling process (Fig. 3(c)), the annealing treatment at 1100 K has caused the formation of complex and thick 3D structures (Fig. 10(a)), reaching several tens of microns thickness and up to hundreds of microns length by increasing the annealing time from 24 to 29 h (Fig. 10(b)).
Particularly, it emerges the development of foam-like architectures (inset of Fig. 10(b)), with different degree of porosity and multi-interacting micrometric grains, resembling the Ni-Mn-Ga 3D-printed micro-trusses reported in Refs. [Error! Bookmark not defined., Error! Bookmark not defined., Error! Bookmark not defined.]. On the other hand, the 3PBM particles, originally similar to flakes (Fig. 3(d)), have maintained their individual and elongated shape even during the annealing treatment at 1100 K for 24 h (Fig. 10(c)). Moreover, they have shown a grain-growth process (inset of Fig. 10(c)) responsible for the stabilization of only few and large recrystallized grains, spanning the whole particle cross-section. The increase of annealing time to 29 h has resulted in an enhancement of particles’ agglomeration and curvature until the achievement of microparticles, constituted by few roundish bamboo-grains with average size of 7 ± 3 µm (Fig. 10(d)).

Therefore, the preservation after milling of a small particle size while concomitantly restoring the magnetic and martensitic phase transitions turns out to be a complex issue. Nevertheless, the particle shape can have a fundamental role in determining the rate of the martensitic recovery and the aggregation and recrystallization processes occurring during the annealing. For instance, in elongated and thin flakes the grains can expand more easily throughout the particle cross-section giving rise to a better microstructural homogeneity and coherence [Error! Bookmark not defined.].
A summary of the achieved magnetic and magneto-structural results of all the powder batches heat-treated at 1100 K and water cooled is provided in Fig. 11: the Curie temperature ($T_C$), martensite start temperature ($M_s$), thermal hysteresis ($\Delta T_{hyst}$), and the retained magnetization at the martensite finish temperature, $M(M_f)$ are plotted against the annealing time.

The recovered martensite start temperature $M_s$ (Fig. 11(b)) increases with the annealing time, reaching at 24 h a much higher value for the 2CM powders as compared to the 3CM and 3PBM ones, which show temperatures closer to the value of HG4h1100WQ sample ($M_s = 283 \pm 2$ K). For the 2CM24h1100WQ powders, also $T_C$ (Fig. 11(a)) has a greater increase, till almost the value of HG powders ($T_C = 385 \pm 2$ K), with respect to the longer-milled particles, which, instead, maintain an almost constant value of $T_C$.

**Figure 11:** Dependence on the annealing time of (a) Curie transition temperature ($T_C$) of the austenite, (b) martensitic start temperature ($M_s$), (c) thermal hysteresis of the martensitic transition ($\Delta T_{hyst}$) and (d) the magnetization retained at the martensitic finish temperature ($M(M_f)$) for the 2CM (squares), 3CM (circles) and 3PBM (triangles) powders treated at 1100 K. The related features for the reference HG4h1100WQ sample are reported for comparison (stars).

Generally, it can be observed that a shift to higher temperatures of $M_s$ with the annealing time (Fig. 11(b)) can be correlated with a decrease of both thermal hysteresis $\Delta T_{hyst}$ (Fig. 11(c)) and retained
magnetization $M(M_f)$ (Fig. 11(d)), thus approximately recovering the expected martensitic features.

Therefore, albeit the Curie transition temperature is irreversibly reduced as compared to the original one, by properly tailoring the annealing conditions the martensitic transformation temperature and thermal hysteresis are feasibly recovered similarly to the coarser-grained HG counterpart.

As a general feature, by combining the microstructural and M(T) results, it emerges that the grain-growth process leads to the decrease of the thermal hysteresis and of the fractions of retained austenite at low temperature, thanks to the decrease of defects density and interfacial constraints at the microscale. On the other hand, the sintering between particles causes the enlargement of the transformation temperature range, likely due to the new phase interfaces generated by the multi-interactions between differently oriented grains and neck junctions and possibly by the enhancement of bending stress in roundish bamboo-grains [48].

4. Conclusions

In this work, we prepared micrometric powders of $Ni_{45.7}Mn_{36.6}In_{13.5}Co_{4.2}$ Heusler compound by hand-grinding, cryo-milling and planetary ball-milling methods. The lowest obtained mean particle size was 10 µm and 15 µm by wet planetary ball milling and cryo-milling, respectively. The analysis of CM milled particles has highlighted their tendency to react and cold-weld due to the high energy of the milling, thus hindering the achievement of smaller separated and still-crystalline particles. In this respect, the use of a liquid milling medium (i.e., isopropanol) during the PBM seems to be a more advantageous and effective method.

However, all the utilized milling processes cause a deterioration of the magnetic properties, a partial stabilization at high temperature of a tetragonal martensite phase and the complete suppression of the magneto-structural transition.

The martensitic transformation near room temperature, characterized by a large magnetization change, has been restored through the implementation of heat treatments at high temperatures, above the B2 transition (about 900 K). The temperature and duration of the treatment were tailored on the energy involved in the milling process.

Moreover, the particle shape can have a fundamental role in avoiding the aggregation of particles during the heat treatments.

It has to be noticed that an increase of thermal hysteresis and of the fraction of arrested austenite at low temperature was observed by decreasing the particles size, independently on the optimization of
the annealing treatment, preventing the full recovery of the structural and magnetic properties of the starting bulk.

Generally, we have observed a large sensitivity of Ni-Mn-In-Co metamagnetic and ferromagnetic properties to mechanical and thermal treatments due to the complex interplay between structural, microstructural, chemical, and magnetic degrees of freedom. Particularly, we observed two different kinetics for the recovery of the magneto-structural transition and of the magnetic order in the austenite. The recovery of the magneto-structural transition occurs with the recrystallization of the post-milled inhomogeneous and disordered state. Whereas the Curie transition is more sensitive to the overall degree of atomic order, and thus reflects the configurational disorder on Mn/In sites.

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References


Graphical abstract
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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:
Highlights

• Micro-meter sized NiMnInCo particles prepared by different milling techniques
• Suppression of magneto-structural transition in as-milled particles
• Recovery of bulk martensitic transition by high-temperature annealing treatments
• Important role of particle shape in determining the rate of martensitic recovery
• Two different kinetics for the recovery of magneto-structural and magnetic transition