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Cold working consequence on the magnetocaloric effect of $Ni_{50}Mn_{34}In_{16}$ Heusler alloy

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ABSTRACT

The negative effect of cold working on the magnetocaloric effect across the Curie transition of Mn-based Heusler alloys is highlighted. The results of manual crushing and subsequent heat treatment on the magnetic and magnetocaloric properties of a $Ni_{50}Mn_{34}In_{16}$ sample are reported. Plausible explanations of the degradation of the magnetocaloric effect by cold working are discussed, on the basis of magnetic and structural measurements performed on a reference sample. The study of the connection between microstructure and magnetic properties of these materials represents a key point for the improvement of Heusler-based magnetic refrigeration.

1. Introduction

Solid-state refrigeration, based on caloric effects of ferroic materials, represents a promising efficient and environmentally friendly alternative to replace the current technology [1,2]. Ni-Mn-based Heusler alloys are one of the most studied families of materials to be used as active refrigerants, due to the possibility to exploit and to tune, by varying the composition, various caloric effects: direct and inverse magnetocaloric (MCE), barocaloric (BCE) and elastocaloric effect (ECE) [3–6]. The most relevant effects appear in these alloys across their first-order magnetostructural transition between a low temperature martensitic phase and a cubic austenitic phase. The intrinsic irreversibility of this structural transition and the relevant volume discontinuity between the two phases reduce the reversible effect exploitable in applications and may give rise to structural fatigue issues because of thermomagnetic cycling across the transition [7,8]. A direct MCE is also present across the second-order Curie transition of the austenitic phase [9]. This MCE is characterized by values of adiabatic temperature change (ΔT_{ad}) and isothermal entropy change (Δs_T) lower than those observed at the structural transition but they are completely reversible. The values of Δs_T depend mainly on the saturation magnetization. Co-rich Heusler alloys show the largest values of saturation magnetization but their Curie temperatures are so high making these compositions useless for room-temperature refrigeration machines [10]. On the other hand, Ni_2MnZ (with Z = In, Sn, Sb) Heusler alloys show appropriate Curie temperatures and interesting values of magnetization thanks to the ferromagnetic interaction of Mn and Ni atoms [11]. The value of magnetization can be further increased by replacing a part of the Z element with Mn atoms until the austenitic phase turns out to be stable at room temperature [12,13]. In the case of the alloy with In ($Ni_2Mn_{1+x}In_{1-x}$) the upper limit of excess Mn atoms to maximize magnetization is about x = 0.4 [14]. The corresponding magnetization value is 6 μ_B/FU [9]. Although this value is lower than that of Gd (7.5 μ_B/FU), the absence of rare earths, the facile method of preparation and the tunability of the transition temperature make these alloys promising for applications.

In this work, the impact of cold working on the magnetocaloric (MC) properties of these alloys is evaluated. The possible alteration of their magnetic and MC properties can be of relevance for both technological and fundamental science aspects. Indeed, large

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values of ΔT_{ad} and Δs_T do not represent a sufficient discriminating condition for the effective use of a specific material in the design of marketable refrigeration machines. High thermal conductivity, good mechanical and chemical stability and a reproducible large-scale preparation process are required to ensure optimized and constant performances of suitable devices [15]. A degradation of MC properties provided by the application of mechanical stress has to be considered during the preparation of bulk materials and the following processing steps for the realization of complex high surface-area structures or smart composites for heat exchangers [2,16]. Alike, the cold working and further annealing processes may introduce relevant alterations of the properties featured by laboratory-scale samples, giving rise to inconsistent results for the same nominal composition. This effect can represent a possible explanation for the spread of values reported in literature concerning magnetic properties of nominally identical samples (see for example the case of $Ni_{50}Mn_{35}In_{15}$ described in several papers [6,9,13,17–20]).

Here we study the effect of manual crushing of a $Ni_{50}Mn_{34}In_{16}$ sample on its magnetic and MC features. This composition was selected because it represents the prototypical combination showing the largest saturation magnetization, a suitable Curie temperature and the cubic parent phase which is stable down to 2 K [9]. In this way, a possible martensitic transition induced by mechanical stresses, as observed by Singh et al. [21] in a $Ni_{45}Mn_{45}In_{10}$ sample and by Belesi et al. in a $Ni_{50}Mn_{25}Ga_{25}$ sample [22], is reasonably avoided. The magnetic, MC and structural properties of an as prepared sample were compared with those obtained: (a) after crushing the sample and (b) after a successive heat treatment.

2. Experimental methods

The sample was prepared by arc melting the stoichiometric amount of high-purity (99,99%) elements. First, two ingots of Ni-Mn and of Ni-In were melted. An excess of 5% Mn and In were added to compensate the evaporation of these two elements. Afterwards, the two ingots were melted together. The sample was flipped and re-melted three times for every side to improve homogeneity. Then it was annealed at 1173 K for 72 h in Ar atmosphere and quenched in cold water. The final composition of the sample ($Ni_{49.1}Mn_{33.9}In_{17}$) was determined through energy dispersive spectroscopy (EDS) microanalysis on a Philips 515 scanning electron microscope.

A part of the ingot was manually crushed in an agate mortar. Half of the powder and some fragments of the bulk sample were annealed for 24 h at 773 K in Ar atmosphere [21].

Magnetization measurements of the bulk and powder samples were performed as a function of temperature and magnetic field with a superconducting quantum interference device (SQUID) MPMS-XL magnetometer (Quantum Design).

The magnetocaloric characterization of the alloy was performed with indirect and direct methods. The isothermal entropy change was calculated as a function of temperature and magnetic field change from magnetization data. Direct measurements of the adiabatic temperature change were performed on a fragment of the sample through a dedicated experimental setup based on a resistive temperature sensor [23].

Powder X-rays diffraction data were collected at room temperature for the untreated and annealed powder sample with a X'PERT PRO PANalytical diffractometer equipped with a Cu Kα radiation. Neutron diffraction experiments were performed at room temperature, with the PEARL diffractometer at TU Delft [24], on fragments of the bulk sample, untreated powder and annealed powder. The ⟨533⟩ reflection of the Ge monochromator was used ($\lambda = 1.67$ Å). X-rays and neutron data were refined with JANA2006 software.

3. Results and discussion

The temperature dependence of the magnetization under a magnetic field of 2 T, measured on a single fragment of the sample (mass = 5.53 mg), is reported in Fig. 1 with the red triangles. The sample undergoes a magnetic transition at 319 K between the ferromagnetic and the paramagnetic state. The magnetization as a function of the temperature measured in a magnetic field of 0.01 T (inset of Fig. 1) does not show the presence of other magnetic transitions down to 5 K. The measurement of the magnetization as a function of the magnetic field at 5 K (Fig. S1 supplementary material) shows that the magnetization is almost saturated at a field of 2 T. The saturation magnetization at 5 K is 128 Am^2kg^{-1}, in agreement with Ref. [9].

The MC properties of the alloy were collected on a fragment by both direct and indirect methods. The isothermal entropy change Δs_T was derived from isofield $M(T)$ measurements by applying the Maxwell relation:

$$\Delta s_T\,(T,H) = \mu_0 \int_0^H \frac{\partial M\,(T,H')}{\partial T}\,dH' \qquad (1)$$

The $\Delta s_T(T)$ for an external magnetic field change $\mu_0 H = 2$ T is reported in Fig. 2 (red triangles). It presents a maximum of (3.3 ± 0.2) $Jkg^{-1}K^{-1}$ at 318 K. The $\Delta s_T(T)$ and the adiabatic temperature change $\Delta T_{ad}(T)$ of the sample (Fig. S2 supplementary material), directly measured by using a dedicated experimental setup [23], are in agreement with the results of Ref. [9].

The effects of cold working and of a subsequent heat treatment were investigated by measuring the magnetic and magnetocaloric properties of a powder sample, obtained by manual crushing in an agate mortar, and of the same sample annealed at 773 K for 24 h. The temperature dependence of magnetization of the untreated powder and of the annealed powder are reported in Fig. 1 with green squares and yellow circles. The $M(T)$ of the powdered sample shows a significant reduction of the saturation magnetization (about 26%) and a widening of the transition shifted to lower temperatures ($T_c \approx 317$ K, inset of Fig. 1). The annealed powder presents a partial, but not complete, restoration of the low-

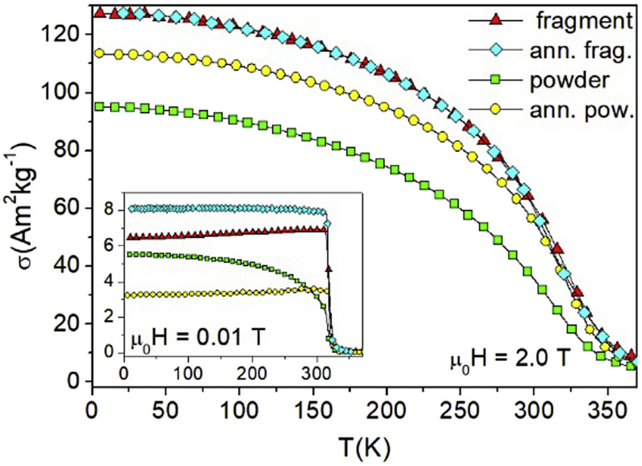

Fig. 1. Magnetization as a function of temperature in a magnetic field of 2 T of a $Ni_{50}Mn_{34}In_{16}$ fragment, untreated powder, annealed fragment and annealed powder from the same sample. Inset: their magnetic behaviour in a low magnetic field (μ_0H = 0.01 T).