Journal of Alloys and Compounds 774 (2019) 586–592

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Magnetocaloric effect enhancement driven by intrinsic defects in a $Ni_{45}Co_5Mn_{35}Sn_{15}$ alloy

V. Sánchez-Alarcos [a, b, *], J. López-García [a, c], I. Unzueta [d, e], J.I. Pérez-Landazábal [a, b], V. Recarte [a, b], J.J. Beato-López [a, b], J.A. García [e, f], F. Plazaola [d], J.A. Rodríguez-Velamazán [c]

[a] Departamento Física, Universidad Pública de Navarra, Campus de Arrosadia, 31006 Pamplona, Spain
[b] Institute for Advanced Materials (INAMAT), Universidad Pública de Navarra, Campus de Arrosadía, 31006 Pamplona, Spain
[c] Institut Laue Langevin, 71, Avenue des Martyrs, 38042 Grenoble Cedex, France
[d] Elektrizitate eta Elektronika Saila, Euskal Herriko Unibersitatea UPV/EHU, p.k. 644, 48080 Bilbao, Spain
[e] BC Materials (Basque Centre for Materials, Applications and Nanostructures), 48080 Leioa, Spain
[f] Fisika Aplikatua II Saila, Euskal Herriko Unibersitatea UPV/EHU, p.k. 644, 48080 Bilbao, Spain

ARTICLE INFO

Article history:
Received 20 July 2018
Received in revised form
27 September 2018
Accepted 3 October 2018
Available online 4 October 2018

Keywords:
Ni-Mn-Sn-Co
Magnetocaloric effect
Defects
Vibrational entropy

ABSTRACT

The influence of mechanically-induced defects on the magnetostructural properties is analyzed in a Ni-Co-Mn-Sn alloy subjected to soft milling and subsequent annealing treatments. It is found that, opposite to what occurs in Ni-Mn-Sn ternary alloys, the annealing treatment affects the magnetic properties in a different way in martensite and in austenite. In particular, the saturation magnetization significantly increases in martensite after annealing whereas just a very slight variation is observed in austenite. This leads to the interesting fact that the presence of microstructural defects, far for worsening, makes the magnetocaloric effect to be higher in the as-milled state than after annealing. This behavior is explained as the result of the combination of the effect of defects on the Mn-Mn distance, the effect of Co on the magnetic exchange coupling between Mn atoms, and the effect of defects on the vibrational entropy change at the martensitic transformation.

1. Introduction

Ni-Mn-based metamagnetic shape memory alloys are being widely studied during the last decade because of the unique multifunctional features they show as a result of the interplay between a structural transformation and a complex magnetic ordering. Due to the strong dependence of the magnetic exchange interactions on the Mn-Mn distances [1–3], the change in the interatomic distances caused by the occurrence of a thermoelastic martensitic transformation (MT) in some of these alloys results in a large magnetization change (ΔM) at the transformation temperature that favors the induction of the structural transformation by an applied magnetic field [4–7]. Such magnetic induction of the MT, and the different features of the different structural phases (austenite and martensite), give rise to interesting properties such as the magnetic shape memory effect, large magnetoresistance or giant inverse magnetocaloric effect, that make these alloys very attractive for practical applications in sensing and magnetic refrigeration [8–18].

The most promising alloys for magnetocaloric applications are those alloys in the Ni-Mn-X (X = In, Sn, and Sb) systems in which the MT takes place between a ferromagnetic austenite and a weaker-magnetic martensite. The MT characteristics and the magnetic properties of these alloys depend on composition, atomic order and, to a lesser extent, on microstructure. The compositional dependence has been widely studied, being the complete phase diagrams of the appearing structural and magnetic phases well stablished [19–22]. Atomic order has been also systematically studied. In Ni-Mn-In and Ni-Mn-In-Co alloys it has been shown that the magnetostructural properties can be properly tuned varying the long-range atomic order, which can be easily controlled by means of thermal treatments [23–25]. In Ni-Mn-Sn and Ni-Mn-Sb alloys, in turn, the $L2_1$ structure is highly stable and the atomic order is then hardly modifiable by means of conventional thermal treatments [26]. In these alloys, the modification of the microstructural parameters (grain size, defects, internal stresses…) is the

* Corresponding author. Departamento Física, Universidad Pública de Navarra, Campus de Arrosadia, 31006 Pamplona, Spain.
E-mail address: vicente.sanchez@unavarra.es (V. Sánchez-Alarcos).

https://doi.org/10.1016/j.jallcom.2018.10.016
0925-8388/

only way to modify the functional properties for a selected alloy composition. Mechanical milling and subsequent annealing treatments are one of the simplest and most used method to modify the microstructure. Typically, the grain size reduction and the presence of defects and internal stresses induced by milling degrade the MT and the magnetic properties, which can be then partially restored upon microstructural recovery processes brought by subsequent annealing [27–32]. In this respect, by comparing a Ni-Mn-Sn alloy in both the as-milled and the annealed states, we have recently shown that, even though no appreciable long-range atomic disorder was induced by milling, the saturation magnetization of both martensitic and austenitic phases are considerably higher after annealing, due to the reduction of the density of the anti-phase boundaries (linked to dislocations) which promote the antiferromagnetic coupling between Mn moments [32]. A similar magnetic deterioration at anti-phase boundaries was indeed evaluated in Ni-Mn-Al-Ga alloys by electron holography, and explained as a consequence of a local atomic disordering in the boundary region [33].

The addition of Cobalt has been shown to enhance the magnetism of the austenite and to hinder ferromagnetic ordering in martensite in Ni-Mn-X alloys, thus leading to an increase of ΔM and therefore to larger magnetically-induced shifts of the MT temperature and higher associated magnetocaloric effects [4,34–38]. In particular, in Ni-Mn-Sn alloys it has been also shown that the magnetic coupling between the Mn moments on the 4a (Mn sublattice) and 4b sites (Sn sublattice) of the austenitic cubic structure changes from being antiferromagnetic to ferromagnetic as a consequence of the substitution of Ni by Co [37] (the magnetic coupling between Mn atoms on the 4a sites is ferromagnetic both in the ternary and the quaternary alloys). In this regard, it could be thought that the influence of the presence of anti-phase boundaries (and any other microstructural defect resulting in local atomic disordering) on the magnetic properties will be different in the quaternary Co-doped alloys to that in the ternary ones. In this sense, the effect of mechanically-induced defects on the magnetostructural properties, and in particular on the magnetocaloric effect, is analyzed on a quaternary Ni-Co-Mn-Sn alloy subjected to soft milling and subsequent annealing. It is found that the presence of microstructural defects, far for worsening, can make the magnetocaloric effect to be higher in the as-milled state than after subsequent annealing. This unusual beneficial presence of defects is explained as the result of the combination of the effect of defects on the Mn-Mn distance, the effect Co on the magnetic exchange coupling between Mn atoms, and the effect of defects on the vibrational entropy change at the martensitic transformation.

2. Experimental

A $Ni_{45}Co_5Mn_{35}Sn_{15}$ alloy was prepared from high purity elements by arc melting under protective Ar atmosphere. The as-cast ingot was homogenized at 1173 K during 24 h and then slowly cooled to RT. The composition was analyzed by EDS in a Jeol JSM-5610LV Scanning Electron Microscope (SEM). In order to induce defects, the alloy was subjected to hand milling in an agate mortar until reaching a uniform particle-size distribution. The mean particle size of the powder, estimated from SEM images, was 60 ± 20 μm. A part of the obtained powder was then subjected to a 5 min annealing at 673 K in order to remove some of the defects induced by milling. In previous works, such annealing treatment has been shown (from Mössbauer spectroscopy and XR diffraction measurements) to cause a significant microstructural evolution in milled ternary Ni-Mn-Sn alloys [32,39]. The microstructural states obtained in the as-milled and the annealed samples were then analyzed and compared: the martensitic transformations were characterized by differential scanning calorimetry (Q-100 DSC, TA Instruments), on heating ramps performed from 140 K up to 300 K at 10 K/min; the magnetic properties (low and high field magnetization) by SQUID magnetometry (QD MPMS XL-7); and the crystallographic and magnetic structures were determined from powder neutron diffraction measurements performed on the D1B diffractometer, at the Institute Laue-Langevin (Grenoble, France), using a neutron wavelength of 1.28 Å. The structures were refined by the Rietveld method using the FullProf package programs [40].

3. Results and discussion

Fig. 1 shows the temperature dependence of the magnetization in the as-milled and annealed samples under (a) $7.95 \cdot 10^3$ A/m (100 Oe) and (b) $4.77 \cdot 10^6$ A/m (60 kOe) applied magnetic fields. The sequences of magnetostructural transformations can be clearly determined from the low-field $M(T)$ curves: in both samples, the high temperature paramagnetic austenite becomes ferromagnetic around 360 K and a subsequent magnetization jump takes place

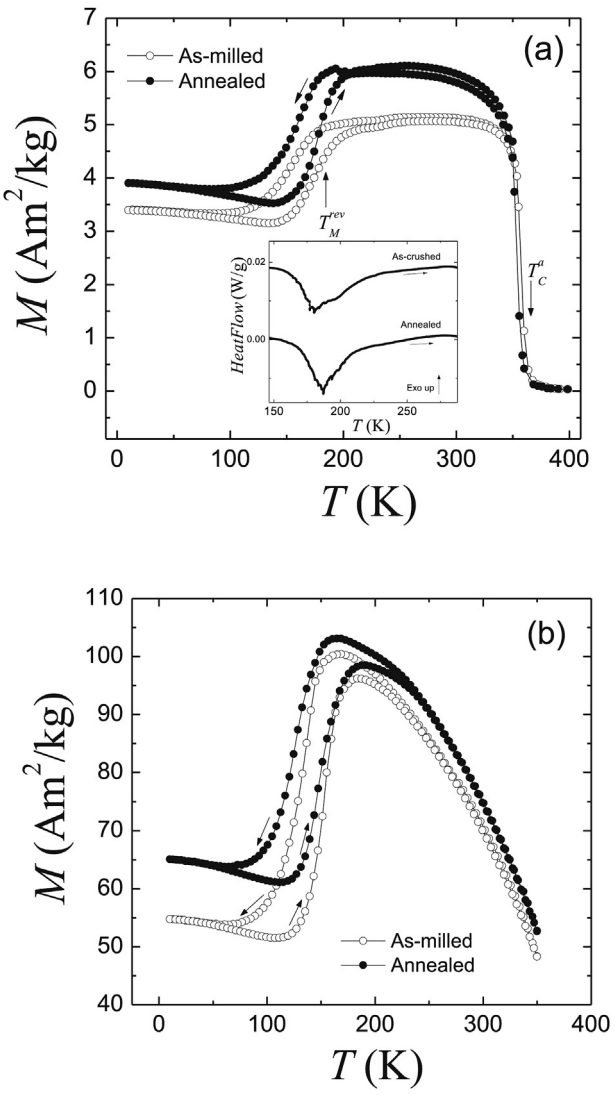

Fig. 1. Temperature dependence of magnetization of the as-milled and annealed samples under (a) $7.95 \cdot 10^3$ A/m and (b) $4.77 \cdot 10^6$ A/m applied magnetic field. Inset in Fig. 1a: detail of the heating curve of the DSC thermogram.