Acta Materialia 147 (2018) 342–349

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

Microstructural origin of hysteresis in Ni-Mn-In based magnetocaloric compounds

H. Sepehri-Amin [a, *], A. Taubel [b], T. Ohkubo [a], K.P. Skokov [b], O. Gutfleisch [b], K. Hono [a]

[a] Research Center for Magnetic and Spintronic Materials, National Institute for Materials Science, Tsukuba 305-0047, Japan
[b] Technische Universität Darmstadt, Materialwissenschaft, D-64287 Darmstadt, Germany

ARTICLE INFO

Article history:
Received 27 September 2017
Received in revised form
24 January 2018
Accepted 24 January 2018
Available online 6 February 2018

Keywords:
Hysteresis
Magnetocaloric
Heusler alloys
Microstructure
In-situ TEM

ABSTRACT

Microstructures of magnetocaloric Ni-Mn-In-based Heusler alloys, $Ni_{50.2}Mn_{35.0}In_{14.8}$ and $Ni_{46.1}Mn_{37.9-}Fe_{3.0}In_{13.0,}$ were studied to understand the origin of a large difference in thermal hysteresis in these two alloys. *In-situ* transmission electron microscopy (TEM) observation showed that the Fe containing sample with a large hysteresis shows a discontinuous phase transition due to the existence of nano-scale Fe-rich bcc phase, along with Fe-lean B2 and $L2_1$ phases in the austenite state. The Fe-free sample with a low hysteresis shows a uniform phase transition from martensite to austenite initiated by the nucleation of austenite at the twin boundaries. Ni segregation was found at the twin boundaries of the low hysteresis sample that is considered to facilitate the nucleation of the austenite. The phase transition progresses by the growth of the nucleated austenite to the neighboring twins. 5M and 7M modulated martensites in the low hysteresis sample give rise to a slight difference in the phase transition temperatures in the twin bands contributing to the small hysteresis of 4.4 K in the Fe-free sample. Based on these results, we conclude that to minimize the thermal hysteresis of the Ni-Mn-In based magnetocaloric compounds, one of the key factors is to achieve a uniform composition and crystal structure in the alloy.

1. Introduction

The discovery of the giant magnetocaloric effect has opened up the possibility of magnetic refrigeration technology as an environmental-benign alternative to the conventional gas compression/expansion cooling systems [1–7]. Magnetic refrigeration is based on the magnetocaloric effect (MCE) defined as isothermal magnetic entropy change (ΔS_T) or adiabatic change of temperature (ΔT_{ad}) in a magnetic solid upon applying a magnetic field. Magnetic refrigeration using Gd can reach an efficiency of 60% of the theoretical limit while the conventional gas-compression technology shows a maximum efficiency of about 45% [8]. However, this high efficiency can be obtained only when a large magnetic field above 5 T is applied, which is not feasible for household appliances. Such a large magnetic field is necessary due to the insufficient MCE in the existing magnetocaloric compounds [9]. Thus, in order to move magnetic cooling at ambient temperature towards application, it is necessary to develop new magnetic materials with larger MCE and, at the same time, to reduce the magnetic field required for a complete ferromagnetic transition in these materials.

Many studies have been conducted to develop magnetic materials with large MCE under the magnetic field changes of $\Delta(\mu_0 H) = 1–2$ T at room temperature [10,11]. One promising material system are the martensitic Ni-Mn-based Heusler alloys that undergo the first order magneto-structural phase transition from austenite to martensite upon cooling [12–14]. As a result, a giant magnetocaloric effect has been reported in the Ni-Mn-In-(Co) system with an adiabatic temperature change of $\Delta T_{ad.} \approx 3–4$ K and isothermal entropy change of $\Delta S_m \approx 10–20$ J/kgK under $\Delta(\mu_0 H) = 1$ T [7,11]. However, the large thermal hysteresis originating from the martensitic transformation in the Ni-Mn-based Heusler alloys causes a large irreversible energy loss, which adversely affect the cyclic performance of the magnetocaloric Heusler alloys [11–18]. There are two origins for the thermal hysteresis; one is an intrinsic one coming from the crystallographic compatibleness of austenite and martensite, and the other is an extrinsic one originating from composition variations and internal stresses that can cause inhomogeneous phase transitions [11,16–24]. Microscopic observations of the phase transitions in Ni-Mn-based Heusler alloys have shown non-uniform phase

* Corresponding author.
E-mail address: h.sepehriamin@nims.go.jp (H. Sepehri-Amin).

https://doi.org/10.1016/j.actamat.2018.01.044
1359-6454/

transitions in micro-scale during thermal hysteresis [19,21–23]. However, the underlying mechanism is not yet clarified. Gottschall et al. proposed that one can use a minor hysteresis loop to remain in the mixed phase region, which can result in a significant reversible ΔT_{ad} in an applied magnetic field of 1.95 T [19]. However, only a part of the giant MCE can be used within minor loops. Hence, it is important to study how the nucleation and growth of the austenite and martensite take place during the thermal hysteresis in the Ni-Mn-based Heusler compounds. In this work, we studied the microstructure of Ni-Mn-In based Heusler alloys with different hysteresis using *in-situ* transmission electron microscopy to elucidate the microstructural origins of the hysteresis in Ni-Mn-based Heusler alloys.

2. Experiment

Ni-Mn-In based Heusler alloys with composition of $Ni_{50.2}Mn_{35.0}In_{14.8}$ and $Ni_{46.1}Mn_{37.9}Fe_{3.0}In_{13.0}$ were prepared by induction melting. The alloys were annealed at 950 °C for 100 h and quenched in water for homogenization. The composition of the alloys were measured using inductively coupled plasma optical emission spectrometry. The magnetic properties of the samples were measured using a vibrating sample magnetometer (VSM) equipped with a cryostat. Magnetization versus temperature was measured by sweeping temperature at 2 K min^{-1} with 30 s holding time at each data point under applied field range of 0.0–2.0 T. The adiabatic temperature change (ΔT_{ad}) was directly measured under a maximum applied cyclic magnetic field of 1.9 T using a home-built measurement setup [23,25]. Measurements ΔT_{ad} were performed in discontinuous mode, meaning that after each field application the sample was overheated and afterwards undercooled by 50 K, respectively. Transmission electron microscopy (TEM) was performed using a JEOL JEM-2100F and a FEI Titan G2 80–200 with a probe aberration corrector. Three-dimensional atom probe (3DAP) analysis was carried out using a locally built laser assisted 3DAP. The specimens for the TEM and 3DAP analysis were prepared by a focused ion beam (FEI Nanolab Helios 650) with the lift out method.

3. Results

Fig. 1 (a) and (b) show magnetization versus temperature curves for the $Ni_{50.2}Mn_{35.0}In_{14.8}$ and $Ni_{46.1}Mn_{37.9}Fe_{3.0}In_{13.0}$ samples in two different applied magnetic fields of 0.1 and 2.0 T. A sharp magneto-structural transition from low temperature martensite to high temperature austenite at a austenite start temeperature (A_s) of ~291 K to austenite finish temeperature (A_f) of ~301 K, measured during heating under magnetic field of 2.0 T, is observed for the $Ni_{50.2}Mn_{35.0}In_{14.8}$ sample, while this transition temeprature range is A_s = ~300 K to A_f = ~318 K for $Ni_{46.1}Mn_{37.9}Fe_{3.0}In_{13.0}$ sample suggesting a broader transition temperature. Note that upon applying a magnetic field, the tranistion temperatures shift to lower temperatures, which is due to the inverse-magnetocaloric effect in this material accompanied by stabilization of ferromagnetic phase at increased magnetic fields. The Curie temperature of ferromagnetic austenite in both samples is ~320 K. The martensite state of $Ni_{50.2}Mn_{35.0}In_{14.8}$ sample shows a very weak magnetization which is larger for that of the $Ni_{46.1}Mn_{37.9}Fe_{3.0}In_{13.0}$ sample. Fig. 1 (c) and (d) show the isothermal entropy change (ΔS_T) of the alloys upon cooling (blue line) and heating (red line) calculated from M-T curves obtained in different magnetic fields from 0.1 T to 2.0 T with a field step of 0.1 T. The samples show transition temperatures around room temperature. Nevertheless, $Ni_{50.2}Mn_{35.0}In_{14.8}$ shows a

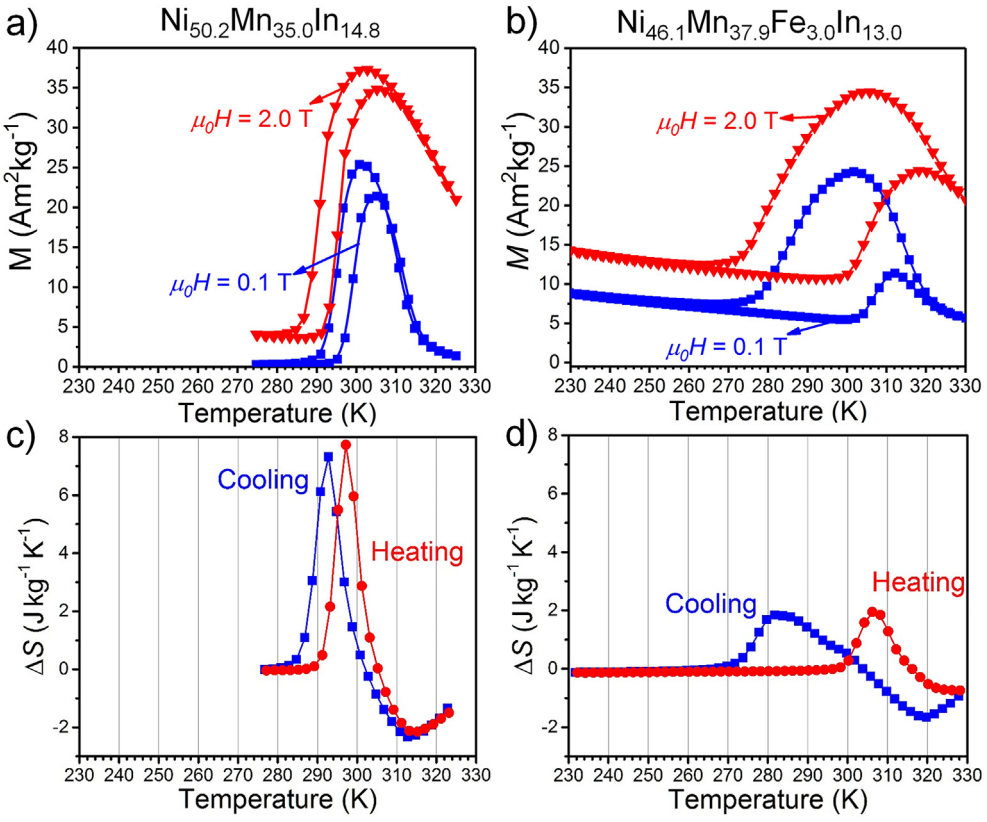

Fig. 1. Temperature dependence of magnetization measured in the fields ($\mu_0 H$) from 0.1 T to 2.0 T with field step of 0.1 T (shown data are just $\mu_0 H$ of 0.1 and 2.0 T) for (a) $Ni_{50.2}Mn_{35.0}In_{14.8}$, (b) $Ni_{46.1}Mn_{37.9}Fe_{3.0}In_{13.0}$. Magnetic entropy changes in a 2.0 T magnetic field change for alloys with composition of (c) $Ni_{50.2}Mn_{35.0}In_{14.8}$, (d) $Ni_{46.1}Mn_{37.9}Fe_{3.0}In_{13.0}$.