Acta Materialia 107 (2016) 1–8

Contents lists available at ScienceDirect

Acta Materialia

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

Full length article

On the S(T) diagram of magnetocaloric materials with first-order transition: Kinetic and cyclic effects of Heusler alloys

Tino Gottschall [a, *], Konstantin P. Skokov [a], Ramon Burriel [b], Oliver Gutfleisch [a]

[a] Institut für Materialwissenschaft, TU Darmstadt, 64287 Darmstadt, Germany
[b] Instituto de Ciencia de Materiales de Aragón (ICMA) and Departamento de Física de la Materia Condensada, CSIC - Universidad de Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza, Spain

ARTICLE INFO

Article history:
Received 1 December 2015
Received in revised form
20 January 2016
Accepted 22 January 2016
Available online xxx

Keywords:
Magnetocaloric effect
Heusler alloys
Calorimetry
Martensitic transition

ABSTRACT

For magnetocaloric materials the total entropy diagram $S(T)$ in different magnetic fields is of central importance. From such a plot the isothermal entropy change ΔS_T and the adiabatic temperature change ΔT_{ad} can be well-defined. Aim of this work is to investigate the reversible magnetocaloric effect of Heusler alloys under cycling in terms of the $S(T)$ diagram. For this purpose we selected three different Heusler alloys of Ni–Mn–In with transition temperatures between 200 k and room temperature. The $S(T)$ diagrams of the three materials cover all conceivable shapes and are therefore representative for inverse magnetocaloric Heusler alloys. First we comprehensively analyzed the magnetocaloric properties of this model system using calorimetry, magnetometry and direct measurements of the adiabatic temperature change ΔT_{ad} and subsequently combined those results into the $S(T)$ diagram. It turns out that under certain measurement conditions significant discrepancies can appear. With the help of in-situ optical microscopy, this effect could be attributed to kinetic relaxation effects in the pure martensite phase before the actual ΔT_{ad} experiment. Furthermore we found that the $S(T)$ diagram obtained under continuous heating and cooling fails to describe the reversible magnetocaloric properties of minor loops under cycling. Utilizing cyclic measurements of the adiabatic temperature change together with calorimetric data it is however possible to determine the reversible magnetic field induced entropy change ΔS_T in fast operation comparable to real device conditions which can be applied to every magnetocaloric material with a first-order transition.

1. Introduction

Recently, magnetic refrigeration at ambient temperature draws a lot of attention because of its great potential for energy efficient cooling [1–6]. Especially Heusler alloys are interesting candidates as rare-earth free refrigerants because of the large magnetocaloric effect of the martensitic transition [7–10]. The ternary Heusler compounds Ni_{50} Mn_{50-x} In_x with $14 \leq x \leq 16$ exhibit a magneto-structural transition of first-order type between paramagnetic martensite and ferromagnetic austenite [11–13]. This so-called inverse magnetocaloric effect is due to the fact that the isothermal entropy change ΔS_T as well as the adiabatic temperature change ΔT_{ad} have an opposite sign in comparison to ΔS_T and ΔT_{ad} of conventional magnetocaloric materials [14,15].

Fig. 1 shows a schematic of the $S(T)$ diagram for an inverse magnetocaloric effect. The magnetic field lowers the transition temperature and for instance under isothermal conditions a heat transfer from the surroundings to the sample takes place and an increase in entropy is observed (vertical arrow in Fig. 1). If the magnetization process is done adiabatically the total entropy does not change and the temperature of the material is decreased (horizontal arrow in Fig. 1). From a thermodynamic point of view both ΔS_T and ΔT_{ad} are well defined by the $S(T)$ diagram in different magnetic fields [16].

For the application of magnetic refrigeration, materials are needed which can operate in magnetic field changes limited to about 1 T in cycling frequencies up to 10 Hz with large reversible magnetocaloric effects [17]. However, standard characterization techniques like magnetic measurements and calorimetry are quasi-static and do not fulfill these operational conditions. On the other hand, the adiabatic temperature change can be obtained in field rates comparable to the alternating fields in magnetic refrigerators

* Corresponding author.
E-mail address: gottschall@fm.tu-darmstadt.de (T. Gottschall).

http://dx.doi.org/10.1016/j.actamat.2016.01.052
1359-6454/

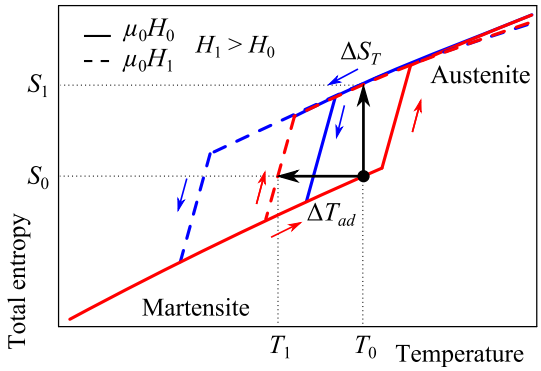

Fig. 1. Illustration of the $S(T)$ diagram of an inverse magnetocaloric transition between martensite and austenite for heating and cooling. A magnetic field lowers the transition temperature resulting in a ΔS_T or ΔT_{ad} depending on the conditions.

and also can be measured under cycling. Unfortunately, such measurements are only rarely reported in the literature [18–21]. More often only the isothermal entropy change ΔS_T obtained from quasi-static $M(T)$ or $M(H)$ curves is considered, calculating ΔT_{ad} indirectly from this data [22,23].

The problem is that the reversibility of the magnetocaloric effect under cycling is normally not accessible by utilizing the Maxwell relation or the Clausius–Clapeyron equation. One possible way is to perform calorimetry under cycling [24] but as already mentioned these techniques are not as fast as in cooling device application. In principle also the reversible ΔS_T and ΔT_{ad} can be extracted from the $S(T)$ diagram (Fig. 1). In order to drive the transition reversibly, the applied magnetic field should be strong enough to overcome the thermal hysteresis of the material. Therefore the entropy curve under heating in field (dashed line in the center of Fig. 1) needs to be moved beyond the cooling curve without magnetic field (solid line in the center of Fig. 1) because the reversible transition only takes place between these two curves.

The aim of this work is to compare measurement techniques using different magnetic field sweeping rates to evaluate both parameters ΔS_T and ΔT_{ad}, combining them in the $S(T)$ diagram and finally investigate the reversible magnetocaloric effect of three selected Heusler alloys of the Ni_{50} Mn_{50-x} In_x system. As will be pointed out later, the different character of the martensitic transition in these three compounds is representative and monitors the transition behavior of Heusler alloys in general. We will show for this model system that in some cases significant deviations can appear when comparing measurements obtained on different temperature heating rates due to kinetic effects. As a consequence the $S(T)$ diagram (quasi-static mode) fails to predict the magnetocaloric properties reasonably.

2. Experimental details

Samples of $Ni_{49.8}$ $Mn_{35.0}$ $In_{15.2}$, $Ni_{49.6}$ $Mn_{35.6}$ $In_{14.8}$ and $Ni_{50.2}$ $Mn_{35.0}$ $In_{14.8}$ were prepared by arc melting and subsequent annealing at 1173 K for 24 h under Argon atmosphere followed by water quenching. Scanning electron microscopy confirmed that the material is single-phase. The exact stoichiometry was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES). Magnetic measurements were obtained by a commercial vibrating sample magnetometer (LakeShore VSM). For the experimental determination of the entropy change a differential scanning calorimeter (DSC200 F3 Maia) with a heating and cooling rate of 10 K min^{-1} was used.

We used a home built instrument for the determination of the adiabatic temperature change ΔT_{ad}, described in detail in Ref. [25]. The noise level of the measurement amounts to ±0.01 K and the absolute error of the ΔT_{ad} is about ±0.05 K. The attainable magnetic field in this device is limited to $\mu_0 H = 1.93$ T. Measurements were obtained in both the continuous mode (constantly heating or cooling) and the discontinuous mode (overheating by 50 K to T_1 and undercooling by −50 K to T_2 after each field application). A detailed discussion on the differences between the continuous and the discontinuous protocol can be found in the supplemental material.

The heat capacity at various fields has been measured in an adiabatic calorimeter integrated in a cryocooler and provided with a superconducting magnet of 9 T. This adiabatic installation has also been used for quasi-static cooling measurements of the heat capacity, with heating and cooling rates of around 1 mK s^{-1}, following the method described in Ref. [26]. With the adiabatic insulation provided by the calorimeter, the ΔT_{ad} and ΔS_T parameters have been directly measured applying field changes at a slow rate lower than 1 T min^{-1}. The temperature increases upon field changes, ΔT_{ad}, have been measured adiabatically and the heat absorbed to maintain a constant temperature when changing the field, $T \cdot \Delta S_T$, has been determined as described in Ref. [27]. The measurement errors are below 5%.

Temperature and magnetic field dependent in-situ optical imaging was performed in a magneto-optical Kerr microscope with polarized light and a 2.5× objective. The heating and cooling rates of the cryostat were varied from 3 K min^{-1} down to 0.05 K min^{-1}. A magnetic field of 1.1 T was applied by a magnet assembly with a rate of approximately 0.2 Ts^{-1}.

3. Results and discussion

3.1. Calorimetric study

In the Ni_{50} Mn_{50-x} In_x Heusler system large entropy changes can be observed due to the martensitic transformation. In Fig. 2 (a) the magnetization curves of the three compounds under investigation are shown in 0.1 T, 1 T and 2 T. These materials have been selected for this study since their transition temperatures and also the characteristics of the transformation are representative for Ni–Mn based Heuslers in general. The compound $Ni_{50.2}$ $Mn_{35.0}$ $In_{14.8}$ transforms near room temperature close to the Curie point of the austenite phase $T_C^A = 314$K and shows a sharp transition with small thermal hysteresis. In contrast to that, the alloy $Ni_{49.8}Mn_{35.0}In_{15.2}$ transforms at low temperatures of about 240 K. The thermal hysteresis and the transition width are much larger in this case. The third compound $Ni_{49.6}Mn_{35.6}In_{14.8}$ transforms in a mid-region between the other two. Therefore, the three materials together reflect the typical transition behavior of Heusler alloys with magnetocaloric effects in general.

For first-order magnetocaloric materials the driving force of the effect is the shift of the transition temperature by the application of a magnetic field because the phase with higher magnetization is stabilized [28]. This is clearly evident from the magnetization measurements shown in Fig. 2(a). In addition to that, calorimetric measurements of the heat capacity under heating protocol in 0 T, 1 T and 2 T are shown in Fig. 2(b). The shift of the transition temperature can also be observed. For instance the peak position of the compound $Ni_{49.8}Mn_{35.0}In_{15.2}$ with the lowest transition temperature shifts by about −6.9 KT^{-1}.

Furthermore it can be seen that the peak heights and areas of the three representative alloys differ significantly. The material $Ni_{50.2}Mn_{35.0}In_{14.8}$ shows a very sharp and high transition peak. However, this is tailing off with decreasing transition temperature in the other two materials. In order to quantify this behavior the entropy change of the complete transition ΔS_t was determined