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Production and properties of metal-bonded $La(Fe,Mn,Si)_{13}H_x$ composite material

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ABSTRACT

Due to their excellent magnetocaloric properties hydrogenated $La(Fe,Mn,Si)_{13}$ are considered as promising and cost efficient materials for active magnetic regenerators operating near room temperature. However, due to their poor mechanical and chemical stability this alloys can not be directly implemented in a cooling machine. A solution of the problem is the production of a composite $La(Fe,Mn,Si)_{13}H_x$ magnetocaloric materials by using adhesive-bonding techniques similar to those used for production of polymer-bonded permanent magnets. Upon bonding one has to consider that the thermal stability of the polymer binder is rather low. Main disadvantage of a polymer-bonded composite is the fatigue due to the mechanical stress caused by the large magnetovolume effect in $La(Fe,Mn,Si)_{13}H_x$. Our article reports on a new method and equipment to produce metal-bonded magnetocaloric material using the low melting eutectic Field's alloy as a binder. A comprehensive investigation of the magnetocaloric, mechanical, chemical and thermal transport properties of polymer-bonded and metal-bonded magnetocaloric material is presented.

1. Introduction

Due to their outstanding magnetocaloric (MC) properties, hydrogenated $La(Fe,Mn,Si)_{13}H_x$ are considered as very promising materials for use as solid-state refrigerants in magnetic cooling machines working at ambient temperatures [1–7]. However, in order to be used as a magnetic refrigerant, the magnetocaloric material should be machined into heat exchangers with fine porous structures, designed to provide the largest possible contact surface area to the heat-transfer liquid. For this purpose, a good machinability of the material is requested [8–10]. In spite of an extensive experimental work done on the topic, the problem of the decrepitation of $La(Fe,Mn,Si)_{13}H_x$ alloys during the hydrogenation process has not been solved yet, and till now these materials are available only as a powder, obstructing the practical application of $La(Fe,Mn,Si)_{13}H_x$. Their rather low mechanical and chemical stability explain why expensive Gadolinium is still preferably used as a refrigerant in prototypical magnetic cooling machines [11].

The production of a functional composite, where the powderized magnetocaloric material is embedded in a protective polymer matrix is complex but a promising solution. This composite material can be rather easily consolidated in the desired geometry via a net shape manufacturing. Recent reports show that by proper choice of the epoxy adhesive and the production routine, heat exchangers made from polymer-bonded composite material can retain the magnetocaloric properties of the $La(Fe,Mn,Si)_{13}H_x$ loose powder in combination with better mechanical and chemical stability [12,13].

The main disadvantage in using of polymer binders for the consolidation of MC powder is their relatively low thermal conductivity impeding the fast heat transfer between the polymer-bonded composite and the heat exchange liquid. As discussed in the literature [14], the thermal conductivity of an epoxy adhesive can be increased from typical $\lambda = 0.2–0.4\ W\ m^{-1}\ K^{-1}$ up to $\lambda = 1–3\ W\,m^{-1}\,K^{-1}$ by adding fine particles of a material (filler) with high thermal conductivity. According to a recent report [15], $\lambda = 8–9\ W\,m^{-1}\,K^{-1}$ can be achieved by adding a few weight percent

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of nano sized graphene sheets. However, the best commercially available adhesives have only $\lambda = 1{-}3$ W m^{-1} K^{-1} [16] and they are rather expensive. Indeed, the addition of a filler to the epoxy adhesives results not only in an increased density (from 1 g cm^{-3} up to 4 g cm^{-3}), but more essentially, it leads to a drastic increase of the cost. In addition, composite materials prepared from epoxy adhesives with fillers have worse magnetocaloric properties in comparison to composites made by using a conventional epoxy (this is caused by the higher density and lower viscosity of thermoconductive epoxy [12]).

Another disadvantage of polymer-bonded La(Fe,Mn,Si)$_{13}$H$_x$ is the cyclic aging. When a functional composite is working near its transition temperature in an alternating magnetic field, it undergoes thermal and mechanical stresses caused by the giant magnetovolume effect of La(Fe,Mn,Si)$_{13}$H$_x$ [17,18]. This leads to aging and fatigue effects of the epoxy adhesive and results in the step-by-step degradation of thermal conductivity and mechanical stability of composite as indicated in Ref. [13].

The thermal conductivity and mechanical stability of the composite can be improved more efficiently, when ductile metals with a low melting point are used as binder instead of the epoxy adhesive with filler. Due to their good thermal conductivity, pure metals (Tin, Copper) are considered to be most appropriate natural candidates [19–21]. The main challenge is to find an alternative approach for the incorporation of magnetocaloric material into the metal-bonded composite, because commonly used compaction and sintering techniques are not appropriate for La(Fe,Mn,Si)$_{13}$H$_x$. Indeed, as it was previously discussed in the literature [12], a compaction pressure above 0.1 GPa reduces the magnetocaloric properties, while a heat treatment at temperatures above 350 K causes dehydrogenation and consequently deteriorates the adiabatic temperature change [22]. These specific material limitations can be overcome by implementing a new embedding technique where an alloy with a melting point below 350 K is used as binder material.

In this work, a method for the production of La(Fe,Mn,Si)$_{13}$H$_x$-based composites by using a metal binder is proposed. The magnetocaloric properties, the chemical and mechanical stability of the metal-bonded composite are investigated and compared with polymer-bonded composite, produced from the same La(Fe,Mn,Si)$_{13}$H$_x$ material. Finally, the applicability and functionality of polymer-bonded and metal-bonded composite were evaluated and discussed.

2. Sample characterization

The magnetocaloric properties, the chemical and mechanical stability of both polymer- and metal-bonded composite materials were measured on a rectangular 10×5 mm^2 plates with thickness of 0.3 mm.

The adiabatic temperature change was obtained by direct ΔT_{ad} measurements performed in a home-built experimental set-up [4]. The $\Delta T_{ad}(H)$ dependance were measured in an external magnetic field up to $\mu_0 H = 1.93$ T. A sweeping rate of 0.5 T s^{-1} was used to prevent heat losses during the measurement. To ensure adiabatic conditions, the sample was encapsulated in thermal insulating material and the sample space was evacuated. Detailed description of the experimental set-up is given in Ref. [23].

Magnetization measurements were performed on rectangular shaped $3 \times 3 \times 0.3$ mm^3 samples using a Quantum Designs Physical Properties Measurement System (PPMS 14) with standard VSM option. Isothermal field dependance of magnetization $M(H)_T$ were measured in temperature interval from 280 K to 320 K with 2 K steps. The field-sweeping rate was set to 0.12 T min^{-1}. Magnetization values at 280 K (ferromagnetic state) were used to confirm the ratios between the binder and the magnetocaloric material in the composite samples. The magnetic entropy change ΔS_m was calculated from $M(H)_T$ dependance using the Maxwell relation.

The thermal conductivity λ of the composite material was measured by a direct steady-state method. Measurements were performed on a rectangular shaped sample with a cross section of 2×1 mm^2 and a length of 10 mm. The cold end of the sample was fixed to the sample holder frame (the thermal bath), a calibrated resistive heater (heat source) was attached to the hot end. When heat is injected to the hot end, a temperature gradient along the sample builds up. This gradient was measured between two points in a rod sample by differential T-type thermocouple, and then, taking into account the known heat flux through a cross-section of the sample and the distance between the two junctions of the thermocouple, the thermal conductivity λ was calculated using the Fouriers law.

The dynamics of the convective heat transfer between the composite material and the heat transfer fluid was investigated by a home-built experimental set-up. Detailed description of the setup and the sample preparation is given in section 5.1.

The mechanical stability of the composite material on bending was investigated by a standard three-point bending set-up. The flexural strength σ calculated for samples with 10 mm width and 0.3 mm thickness is presented in Table 1.

3. Sample preparation

3.1. Magnetocaloric La(Fe,Mn,Si)$_{13}$H$_x$ material

The commercial magnetocaloric powder LaFe$_{11.38}$Mn$_{0.32}$Si$_{1.30}$ H$_x$ with a transition temperature of $T_{tr} = 297$ K produced by Vacuumschmelze GmbH was used in this work as a precursor. According to XRD results, the main phase with NaZn$_{13}$ cubic structure had a unit cell with a = 11.568 ± 0.002 Å. SEM and XRD data indicated the presence of about 5% secondary phases. The amount of α-Fe in individual fragments of the alloy was evaluated based on magnetization measurements at a temperature of 340 K, where the main phase is paramagnetic. The residual magnetic polarization of the α-Fe, confirmed a NaZn$_{13}$ phase concentration of 95 ± 3%. The hydrogen content in the samples was determined to be x = 1.6 by weighting the sample before and after dehydrogenation for 2 h in high vacuum at 493 K.

The initial La(Fe,Mn,Si)$_{13}$H$_x$ powder was sieved and sorted by particles size: a fraction with large particles (160–250 μm) and fraction with small particles (40–60 μm) were selected for our study. Two types of composite samples were prepared and investigated: Monomodal composites containing 100% of 160–250 μm particles and bimodal composites containing a mixture of 160–250 μm and 40–60 μm powders. The exact mixing ratio for the bimodal samples will be discussed later in this chapter.

3.2. Metal binder

The metal binder needs to fulfill two main requirements: (1) the melting temperature should be in the range of 330 K–350 K in order to prevent the dehydrogenation of the magnetocaloric powder during the heat treatment process [22] and (2) its thermal conductivity should be not worse than λ of bulk La(Fe,Mn,Si)$_{13}$H$_x$. Many well-known and commercially available Bi - Sn - Pb - In - Cd based low temperature solders meet these criteria. The Pb and Cd containing alloys are more cost efficient, but environmentally harmful and health hazardous, therefore eutectic Bi$_{32.5}$Sn$_{16.5}$In$_{51}$ alloy (known as Field's metal or Field's alloy) was selected for dip coating. This alloy has a melting temperature of T$_m$ ≈ 335 K, a density of ρ = 9.23 g cm^{-3} and a thermal conductivity of $\lambda = 17.5{-}18$ W m^{-1} K^{-1} in the temperature range 280–320 K.