Journal of Magnetism and Magnetic Materials 375 (2015) 65–73

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

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

Epoxy-bonded La–Fe–Co–Si magnetocaloric plates

Barbara Pulko [a,*], Jaka Tušek [a], James D. Moore [b], Bruno Weise [c], Konstantin Skokov [d], Oleg Mityashkin [b], Andrej Kitanovski [a], Chiara Favero [e], Peter Fajfar [f], Oliver Gutfleisch [d], Anja Waske [c], Alojz Poredoš [a]

[a] University of Ljubljana, Faculty of Mechanical Engineering, Aškerčeva cesta 6, 1000 Ljubljana, Slovenia
[b] IFW Dresden, Institute for Metallic Materials, Helmholtzstraße 20, D-01069 Dresden, Germany
[c] IFW Dresden, Institute for Complex Materials, Helmholtzstraße 20, D-01069 Dresden, Germany
[d] TU Darmstadt, Department of Materials Science, D-64287 Darmstadt, Germany
[e] Parker Hannifin Manufacturing Srl, Hiross Zander Division, Strada Zona Industriale 4, S. Angelo di Piove, 35020 Padova, Italy
[f] University of Ljubljana, Faculty of Natural Sciences and Engineering, Aškerčeva cesta 12, 1000 Ljubljana, Slovenia

ARTICLE INFO

Article history:
Received 23 April 2014
Received in revised form
12 August 2014
Available online 2 September 2014

Keywords:
Magnetocaloric effect
Magnetic refrigeration
La–Fe–Co–Si
Active magnetic regenerator
Epoxy

ABSTRACT

We report the processing, analysis and testing of magnetocaloric composite materials consisting of La–Fe–Co–Si particles of various size fractions and a polymer matrix. All of the composites have working temperatures close to room temperature. The composites were pressed into thin plates, a geometry favorable for testing the composites in an active magnetic regenerator (AMR). In order to investigate the influence of particle size and binder type (epoxy), eight different epoxy-bonded La–Fe–Co–Si plates were made and analyzed. We found that the higher filling factor that can be achieved by using a mixture of several particle size fractions has beneficial influence on the thermal conductivity. Tests in the AMR revealed that a maximum temperature span of approximately $\Delta T = 10$ K under magnetic field change of $\mu_0 H = 1.15$ T can be obtained at no cooling load conditions. The stability of the measured ΔT values and the mechanical integrity of sample after cyclic application of a magnetic field have been monitored for 90,000 cycles and showed no significant changes. We therefore conclude that epoxy-bonded La–Fe–Co–Si magnetocaloric composites have good magnetocaloric properties at low material-processing costs and hence represent a competitive way to produce magnetocaloric materials to be used in AMR.

1. Introduction

Magnetic materials can release heat when they are placed in a magnetic field and absorb heat when the magnetic field is removed. This phenomenon is called the magnetocaloric effect (MCE) and it is the highest around the phase transition, known as the Curie temperature T_C. When magnetic material is magnetized and the conditions are kept adiabatic the MCE manifests as temperature increase of the magnetocaloric material, usually denoted by the adiabatic temperature change (ΔT_{ad}). In the case of isothermal conditions the magnetic entropy (Δs_M) is reduced upon application of a magnetic field. When the magnetic field is removed adiabatically the material cools down and in case of isothermal conditions the magnetic entropy rises due to disorientation of the magnetic moments. The MCE can be utilized for room temperature magnetic refrigeration, which was first demonstrated by Brown [1]. The magnetic cooling technology has a great potential to become an alternative to the conventional vapor-compression refrigeration [2]. The potential advantages of magnetic refrigeration compared to conventional vapor-compression based refrigeration are higher energy efficiency, the absence of harmful gases, low-noise operation and more compact design. The research in the field of magnetic refrigeration covers a wide field of research. It includes detailed investigation and improvement of the magnetocaloric properties [3] as well as an extensive design and optimization of magnetic cooling devices from experimental [2] as well as numerical [4] point of view. To provide the best development these research fields must be linked.

Pure gadolinium has been favored in scientific community due to its Curie temperature close to room temperature ($T_C = 294$ K [5]). It is therefore the most often tested magnetocaloric material and thus it became a reference magnetocaloric material. It exhibits good magnetocaloric properties [6]. However, the high price of Gd limits its commercial use. The current research aims at magnetocaloric materials with a so-called giant MCE, which was discovered by Pecharsky and Gschneidner [7]. Among magnetocaloric materials, $La(Fe,Si)_{13}$-based compounds are currently the most promising. They show large magnetocaloric effect and represent low material costs compared to other, e.g. Gd-based, magnetocaloric alloys. Moreover, the T_C of

---

[*] Corresponding author.
E-mail address: pulko.barbara@gmail.com (B. Pulko).

http://dx.doi.org/10.1016/j.jmmm.2014.08.074

La–Fe–Si alloys are easily tunable by the doping e.g. with H or Co [8,9]. However, technical problems, such as industrial fabrication, challenges in shaping, mechanical stability, corrosion and thermal efficiency under working conditions are issues to be overcome before employing La(Fe,Si)$_{13}$-based materials as the refrigerant.

The magnetocaloric effect of all known magnetocaloric materials is not sufficiently large to allow a direct implementation of magnetocaloric materials in a magnetic cooling device. Therefore, the magnetic cooling devices apply active magnetic regeneration (AMR). This was first introduced by Barclay and Steyert [10] and served for increase of the temperature span of between the heat source and heat sink [2,11–13]. The AMR is a porous structure made of magnetocaloric material through which a working fluid flows in an oscillatory (counter-flow) manner. Good heat-transfer properties of the AMR are crucial for its good cooling characteristics. It has been shown [14] that the geometry of the AMR is of great importance to achieve high cooling and efficient performance of the magnetic regenerator. An equally spaced parallel-plate AMR with as thin plates as possible shows the largest potential [14,15]. The La–Fe–Co–Si-based magnetocaloric plates are usually produced by sintering technique and it is rather impossible to make them thin enough to assure efficient heat transfer geometry. Moreover the plates are very brittle, what represents further obstacle for applications in a magnetic refrigerator. One of the challenges is therefore to improve the mechanical properties of the La–Fe–Co–Si-based AMR as well.

In this work epoxy-bonded magnetocaloric composites have been studied as a possible solution to problems, such are related to mechanical and forming properties. We are well aware that the second component of the material influences (decreases) the magnetocaloric effect of the plate and its thermal properties. Therefore a large effort was put on the study of the magnetocaloric and thermal properties of different compositions of epoxy-bonded magnetocaloric plates. Eight different composites were made and tested regarding the magnetization, magnetic entropy change, adiabatic temperature change, its cyclic stability, thermal diffusivity and specific heat. The impact of the plate composition and the impact of the epoxy were investigated separately. Additionally, the two-layered epoxy-bonded AMR (made of epoxy-bonded magnetocaloric composite plates) has been constructed and experimentally verified in the linear-type of magnetocaloric device [11]. As the La(Fe,Co,Si)$_{13}$-based AMR is limited with the plate thickness of 0.5 mm (state-of-the-art) and the corresponding spacing between the plates of 0.2 mm [16] our goal was to improve heat transfer geometry of the La(Fe,Co,Si)$_{13}$-based AMR (i.e. increase the total heat transfer area and decrease the hydraulic diameter) and consequently its cooling characteristics. Results were then compared to cooling characteristic of the two-layered parallel-plate La(Fe,Co,Si)$_{13}$-based AMR, made by sintering technique. This has been previously tested on the same prototype that was applied in this study. The characteristics of the prototype have been reported in [16].

2. Experimental section

2.1. Manufacturing and testing of the epoxy-bonded magnetocaloric plates

The initial set of experiments was focused on the characterization of epoxy-bonded magnetocaloric plates. The plates were made by the cold plate pressing method. As a magnetocaloric powder, 130 μm particles of $LaFe_{13-x-y}Co_xSi_y$ material have been applied (produced by Vacuumschmelze), while as a binder, an epoxy Amerlock Sealer was used (produced by Ameron). In the initial stage the epoxy was not selected regarding its thermal properties. The preconditions for the selection of the epoxy were good mixing properties with the La-powder (in order to have as large volume ratio of the powder as possible) and low (room temperature) curing points. The latter is further related to the chemical stability of the La–Fe–Co–Si powder at higher temperatures (above 373 K). In the next step, in order to analyze the impact of the epoxy we have focused on the selection of epoxy, which has high thermal conductivity and small specific heat. In order to study the effect of epoxy on magnetocaloric (and thermal) properties more in detail we additionally prepared high conductive epoxy-bonded and silver epoxy-bonded magnetocaloric plates. Silver epoxy-bonded magnetocaloric materials were studied before and are showing good magnetocaloric properties [17].

Table 1 presents the composition of all eight epoxy-bonded magnetocaloric plates. For all four Amerlock epoxy-bonded plates (A–D) the volume fraction of 130 μm La–Fe–Co–Si powder remains the same (45%). Sample A is composed without any additional elements. Sample B contains additional 12 μm, 21 μm and 57 μm La–Fe–Co–Si powder in the ratio of 1:1:1. Samples C and D contain additional milled La–Fe–Co–Si powder (< 10 μm) and milled graphite powder (< 10 μm), respectively. The graphite powder was used in order to increase the thermal conductivity of the plate. Samples E and F are made of high conductive epoxy OB-101 (produced by Omega), while samples G and H of silver epoxy (produced by Arctic Silver Incorporated), respectively. Furthermore, samples E and G are composed of 45% of the volume fraction of the La-powder (in order to compare it with previously analyzed Amerlock Sealer epoxy), while samples F and H are composed with the maximum possible volume fraction of the 130 μm La–Fe–Co–Si powder that was still possible to mix with each epoxy and to produce the magnetocaloric plate. These volumes are 55 vol% and 60 vol%, respectively for each type of epoxy. High possible volume fraction of powder is probably consequence of better wetting of La–Fe–Co–Si particles.

The plates were made in a special two-part Teflon mold. The La–Fe–Co–Si powder was mixed with epoxy resin and the mixture was spread on one half of Teflon mold in the form of a plate. This was vacuumed at 150 mbar for 10 min to reduce the porosity in the plate. After vacuuming, plates were cold pressed inside the two-part Teflon mold. The composite plate stayed in the mold for 24 h, when it was removed and subsequently cured at the ambient condition. The plates were finally cut into smaller pieces for experimental work. The thickness of plates was approximately

Table 1
Target compositions of the eight epoxy-bonded magnetocaloric plates.

Sample	Epoxy	vol% of the 130 μm La–Fe–Co–Si powder	Additional elements
A	Amerlock	45	–
B	Amerlock	45	19 vol% of 12 μm, 21 μm and 57 μm La–Fe–Co–Si powder in the ratio of 1:1:1
C	Amerlock	45	19 vol% of 12 μm La–Fe–Co–Si powder milled into smaller particles (< 10 μm)
D	Amerlock	45	19 vol% of milled graphite powder (< 10 μm)
E	High conductive epoxy (OB-101)	45	–
F	High conductive epoxy (OB-101)	55	–
G	Silver epoxy	45	–
H	Silver epoxy	60	–