EPOXY-BONDED La-Fe-Co-Si MAGNETOCALORIC PLATES

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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.

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

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 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. 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 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, 12, 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 as 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 $\text{LaFe}_{13-x-y}\text{Co}_x\text{Si}_y$ 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 minutes 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 hours, 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 0.4 mm. In general, it is possible to perform even smaller plate thickness. However, because of the mechanical stability of a plate during operation, the thickness of 0.4 mm has been selected. This is still thinner than the 0.5 mm La(Fe,Co,Si)_{13} -based plate in the sintered state-of-the-art AMR.

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 ($<10 \mu\text{m}$)
D	Amerlock	45	19 vol. % of milled graphite powder ($<10 \mu\text{m}$)
E	high conductive epoxy (OB-101)	45	/
F	high conductive epoxy (OB-101)	55	/
G	silver epoxy	45	/
H	silver epoxy	60	/

The analysis of the magnetocaloric and thermal properties of the epoxy-bonded magnetocaloric plates were initially performed for the Amerlock epoxy-bonded magnetocaloric plates (A-D) where the impact of the plate composition (the impact of the additional elements) was analyzed. Additionally, a sintered (state-of-the-art) $\text{La}(\text{Fe,Co,Si})_{13}$ -based magnetocaloric plate (produced by Vacuumschmelze) was evaluated in parallel, in order to compare its magnetocaloric and thermal properties with the epoxy-bonded magnetocaloric plates. The initial composites (A-D) and sintered sample prepared at Vacuumschmelze were tested regarding their magnetization, magnetic entropy change, its cyclic stability and thermal diffusivity. In the next step four additional samples with two different epoxies and two different volume fractions of the La-Fe-Co-Si powder were analyzed regarding the adiabatic temperature change and specific heat as they are the most representative properties for the implementation of the magnetocaloric material in the AMR. The measurements of the magnetization as a function of temperature and isothermal measurements of the magnetization as a function of magnetic field were carried out on the Quantum Design PPMS (Physical Property Measurement System) equipped with VSM (Vibrating Sample Magnetometer). The magnetic entropy change Δs_M was calculated from isothermal magnetization curves using Maxwell equation:

$$\Delta s_M = \mu_0 \int_{H_i}^{H_f} \left(\frac{\partial M}{\partial T} \right)_H dH, \quad (1)$$

where H_i is the initial magnetic field, H_f is the final magnetic field, and M is the magnetization of the specimen. The Curie temperatures T_C were obtained from the measurements of the magnetization as a function of temperature performed on heating in the temperature range of 250-330 K (with the temperature step of 1 K) in magnetic field of 0.005 T. The magnetization was also measured in the temperature range of 240-330 K in magnetic field change between 0 T and 2 T. From this data the Δs_M has been calculated by Eq. (1). Furthermore the specific heat as a function of temperature was measured on the same device, with the relaxation calorimetric measurement platform, at the magnetic field of 0 T and 2 T. In the next step the adiabatic temperature change has been measured by using a direct method in a custom-made measurement device at TU Darmstadt [18]. The device consists of a concentric Halbach array (magnetic field generator based on the Nd-Fe-B permanent magnets) placed in a vacuumed space, which assures the adiabatic conditions. The measurements were performed during the simultaneous heating for a magnetic field change between 0 and 1.9 T. Additionally, one of the composites was tested also during the simultaneous cooling to examine the thermal hysteresis effect. The adiabatic temperature change ΔT_{ad} of all samples was measured also on a custom-made device at IFW Dresden [19] in the magnetic field of 0.85 T. On this device composites (A-D) and sintered sample were tested for its cyclic stability, which is crucial for the application of materials in the magnetic refrigerator. The cyclic stability was analyzed regarding its adiabatic temperature change after 90,000 cycles at the cycling frequency of 3 Hz. One cycle consists of a magnetization and demagnetization process. Samples were further analyzed also regarding their mechanical stability. Using optical microscope Nikon Epiphot 300 the microstructure of samples was analyzed before and after the cycling. Additional pictures of all magnetocaloric plates prepared with Ameron epoxy were taken to analyze the distance between particles and its distribution. Furthermore, samples were measured also for its thermal diffusivity, which is one of the most important properties of the material used in an AMR in order to transport the heat generated by the magnetocaloric effect from/to the material as fast as possible. It is defined as:

$$\alpha = \frac{\kappa}{\rho \cdot c_H}, \quad (2)$$

where α , κ , ρ , c_H presents thermal diffusivity, thermal conductivity, density and specific heat, respectively. The measurements of thermal diffusivity were performed with the NETZSCH LFA 457 MicroFlash device which uses Cape-Lehman model [20]. The measurements were performed at the temperature range between 240 and 340 K (at zero magnetic field). The main goal of this analysis was to measure the thermal diffusivity of sample and to evaluate the impact of the carbon on the thermal diffusivity of the epoxy-bonded magnetocaloric plate. The thermal conductivity κ was calculated using Eq. 2. In this calculation the ρ of samples was theoretically calculated and c_H was specific heat measured at magnetic field of 0 T and at Curie temperature of samples. For the calculation of theoretical density ρ of samples the next equation was used:

$$\rho = \sum_i \text{Vol.}\%_i \cdot \rho_i, \quad (3)$$

where ρ_i is a density of specific component in epoxy-bonded sample.

2. 2 Experiments with the Epoxy-bonded AMR

In order to evaluate the performance of the epoxy-bonded magnetocaloric plates in the magnetic refrigerator an epoxy-bonded AMR has been constructed. Its performance was compared with the previously analyzed sintered (state-of-the-art) AMR (two-layered) produced by Vacuumschmelze [16]. The plates used to make the epoxy-bonded AMR were produced with the technique presented previously in the paper. Since the magnetocaloric effect of the La-Fe-Co-Si alloy is limited to relatively narrow temperature range the La-Fe-Co-Si powder (average particle size 130 μm) with two different Curie temperatures has been used in order to enlarge the temperature span (layered-bed AMR). The two-layered plates with the Curie temperatures of 286 K and 293 K one have been produced. The epoxy-bonded AMR was manufactured with the Amerlock Sealer epoxy (sample A). To assure the distance between plates the stainless-steel ribbons with thickness of 0.1 mm were glued on epoxy-bonded plates. Afterwards, all plates were glued with each other into the rigid structure. Fig. 1 shows the sketch and the photography of the epoxy-bonded AMR. The geometry of the epoxy-bonded AMR is presented in the Table 2.

Fig. 1. The sketch (left) and the photo (right) of the epoxy-bonded AMR and the photo of a single plate with the spacers at the edges (bottom).

Table 2
Geometry of the epoxy-bonded AMR.

Outer dimensions, $h \times w \times L$	10 mm $\times$ 40 mm $\times$ 80 mm
Plate thickness, d	0.4 mm
Plate spacing, s	0.1 mm
Hydraulic diameter	0.2 mm
Total heat-transfer area	0.0768 m ²
Total mass, m_s	82.3 g
Porosity	0.22
Vol. % of powder	45
Mass % of powder	90

The epoxy-bonded AMR was then applied in the experimental device of the University of Ljubljana and which has been presented in Tušek *et al.* [11]. The magnet assembly of device provides a magnetic field change of about 1.15 T. The varied parameters were hot-side temperature, operating frequency (number of thermodynamic cycles per unit of time) and the utilization factor U , which is defined as:

$$U = \frac{A_f \cdot v_f \cdot \tau_f \cdot \rho_f \cdot c_f}{m_s \cdot c_s}, \quad (4)$$

where A_f is the cross-sectional area of regenerator available for fluid flow, v_f is the fluid velocity, τ_f is time for fluid flow (in one direction), ρ_f is the fluid density, c_f is the specific heat of the working fluid, m_s is the mas of the solid regenerator material and c_s is the specific heat of regenerator material. The utilization factor was changed with adjusting the fluid velocity. Different frequencies were obtained with changing the time for fluid flow τ_f , while keeping the magnetization and demagnetization time constant (0.75 s). Initially, the maximum temperature span of epoxy-bonded AMR was measured at different hot-side temperatures in order to define the optimal operating temperature range at the constant operating conditions (constant operating frequencies and constant utilization factor). Further tests were performed at the optimal hot-side temperature and at different operating conditions (different operating frequencies and different utilization factors) in order to measure the maximum possible temperature span of the AMR.

3 Results and Discussion

3.1 The Impact of the Plate Composition

Fig. 2 shows the magnetization and specific entropy change of the four epoxy-bonded magnetocaloric plates and the sintered La(Fe,Co,Si)₁₃-based magnetocaloric plate. It is evident that the largest change in magnetization and further also in the magnetic entropy occurs in the

sintered La(Fe,Co,Si)_{13} -based magnetocaloric plate. Among the epoxy-bonded magnetocaloric plates the largest magnetic entropy change is obtained with sample A, followed by the D and B, while sample C has the smallest entropy change. That means that mixing smaller powder with $130\text{ }\mu\text{m}$ La-Fe-Co-Si powder does not increase the magnetocaloric properties but rather decrease them. The smallest change of magnetization and magnetic entropy occurs in Sample C which has additional 19 vol. % of $12\text{ }\mu\text{m}$ La-Fe-Co-Si powder milled into smaller particles (below $10\text{ }\mu\text{m}$). The main reason for that is because the magnetization of this sample is still relatively high in the paramagnetic region (above the Curie temperature). From the previous studies it is known that too long milling time can change the transition character from the first to the second order and correspondingly the magnetic entropy change is reduced [9]. Considering this we can conclude that the milling of La-Fe-Co-Si powder was carried out too long. The impact of the additional $12\text{ }\mu\text{m}$, $21\text{ }\mu\text{m}$ and $57\text{ }\mu\text{m}$ La-Fe-Co-Si powder and graphite powder apparently does not have significant influence on the magnetization and magnetic entropy change. On the other hand, especially the graphite powder influences the magnetization in the ferromagnetic region (below the Curie temperature), but those values are not of a great importance, since dM/dT is crucial for the large magnetocaloric effect.

a)

b)

Fig. 2. Specific magnetization at 0.005 T (a) and magnetic entropy change at the magnetic field change between 0 T and 2 T (b) of the four epoxy-bonded magnetocaloric plates (A-D) and the sintered La(Fe,Co,Si)_{13} -based magnetocaloric plate.

The measured values of the adiabatic temperature change of the four Amerlock Sealer epoxy-bonded magnetocaloric plates and the sintered La(Fe,Co,Si)_{13} -based magnetocaloric plate at the magnetic field change of 1.9 T are shown in Fig. 3. As it was expected from the results of the magnetization and magnetic entropy change, the sintered magnetocaloric plate exhibit the largest adiabatic temperature change. However, the difference in the adiabatic temperature change between the sintered and the epoxy-bonded magnetocaloric plates is even larger (~50 %) than in the case of the magnetic entropy change. It is evident that among the epoxy-bonded magnetocaloric plates sample B has the largest adiabatic temperature change; followed by sample A. Significantly smaller adiabatic temperature changes were measured on samples C and D. That means that the additional 19 vol. % of 12 μm , 21 μm and 57 μm La-Fe-Co-Si powder increases the adiabatic temperature change compared to sample A (due to smaller amount of the epoxy in the plate and further higher average thermal diffusivity). On the other hand, additional smaller (ball milled) particles (<10 μm) of La-Fe-Co-Si powder and graphite powder decreases the adiabatic temperature change compared to sample A. For sample C this was expected regarding its magnetic entropy change (see Fig. 2), while in sample D smaller adiabatic temperature change is most probably caused by lower thermal diffusivity (see Fig. 7). Furthermore there is no difference in adiabatic temperature change upon heating and cooling (no thermal hysteresis is present) in composite magnetocaloric plates (Fig. 4).

Fig. 3. The adiabatic temperature change in the magnetic field change of 1.9 T of the four epoxy-bonded magnetocaloric plates and the sintered La-Fe-Co-Si magnetocaloric plate.

Fig. 4. Thermal hysteresis of adiabatic temperature change of sample B measured in the field of 1.9 T.

Fig. 5 shows the adiabatic temperature change of five analyzed samples (A-D and sintered sample) as a function of the number of cycles. It is evident that the magnetocaloric effect (adiabatic temperature change) does not decrease with the number of cycles and remained almost unchanged for all 90,000 cycles. This is very important for the operation of magnetic cooling device. The measured values at different number of cycles of each sample vary mostly due to the measurement error (± 0.12 K). Fig. 6 shows the microstructure of sample C before and after the cycling at the same location of sample (such analysis was made also for all other samples). In all tested samples, the formation of cracks were not visible under the microscopy. Therefore it can be concluded that all the epoxy-bonded samples can withstand long-term cyclic loading, what is one of the prerequisites for their use in a magnetic refrigerator.

Fig. 5. Adiabatic temperature change as a function of a number of magnetic cycles for the magnetic field change of 0.85 T, at the operating frequency of 3 Hz (frequency of the applied magnetic field) and around the Curie temperature of each analyzed sample (290 K for the epoxy-bonded plates and 283 K for the sintered plate).

Fig. 6. The microstructure of sample C before (a) and after (b) the 90,000 magnetic cycles. The pictures were taken with optical microscope Nikon Epiphot 300.

The results for thermal diffusivity of the five samples (A-D and sintered sample) are shown in Fig. 7. As it was expected the highest values of the thermal diffusivity were measured in the sintered magnetocaloric plate. Epoxy-bonded magnetocaloric plates have substantially lower values of the thermal diffusivity. Among them the best thermal properties were measured on sample C, followed by sample B, while samples A and D have the lowest values of the thermal diffusivity for the entire analyzed temperature range. Samples B and C are composed of additional 19 vol. % of smaller La-Fe-Co-Si particles. This is the main reason for their high thermal diffusivity compared to sample A. The higher vol. % of La-Fe-Co-Si material means smaller distance between La-Fe-Co-Si particles. This further leads to a faster and more efficient heat transfer through the composite material. The distance between La-Fe-Co-Si particles is evident from the Fig. 8, which was taken by the optical microscope. The distance between the particles in composites (see Fig. 8) inversely corresponds to its thermal diffusivity presented in Fig. 7. Sample D, which is composed of additional 19 vol. % of carbon particles, does not have as high thermal diffusivity as we expected, yet similar to thermal diffusivity of sample A. This is due to almost the same distance between La-Fe-Co-Si particles (see Fig. 8).

The calculated values of thermal conductivity at Curie temperature of samples are presented in Table 3. The calculation shows substantially higher thermal conductivity of sintered sample (8.93 W/mK) compared to epoxy-bonded samples (from 1.09 W/mK to 2.68 W/mK). This corresponds to thermal diffusivity measurements and to the distance between La-Fe-Co-Si particles in sample. The increase in thermal conductivity can be compared with literature [21] where Cu was used to increase the thermal conductivity of porous La-Fe-Si material. It is evident that the small La-Fe-Co-Si particles can increase thermal conductivity as much as deposited Cu.

Fig. 7. Thermal diffusivity of all the analyzed samples as a function of the temperature.

Fig. 8. Microstructure of magnetocaloric plates with Ameron epoxy taken with Nikon Epiphot 300 optical microscope. Samples are arranged from A-D (from left to right).

It is evident from Fig. 9 that the sintered sample has lower specific heat compared to samples A-C which was expected due to the content of epoxy. The trend of dependency of the specific heat as a function of temperature is similar to that of samples A, B and C. Sample D has on the other hand almost twice smaller values of the specific heat for the entire analyzed temperature range. It can be concluded that additional smaller magnetocaloric particles do not influence the specific heat by large amount, while small graphite particles drastically decrease the specific heat of sample. As possible reason for that we see in the chance of oxidation of graphite powder during preparation of composite. However, magnetocaloric properties and thermal diffusivity of sample

D is of the lowest among all tested composites. Therefore a suggestion can be made that one should avoid adding of the milled carbon powder to the composite magnetocaloric material.

Fig. 9. Specific heat of the epoxy-bonded (A-D) and sintered magnetocaloric plates at 0 T (a) and 2 T (b) of magnetic field.

3. 2 The Impact of the Epoxy

The results for the adiabatic temperature change and specific heat of composites based on highly conductive silver-epoxy are shown in Figs. 10 and 11. For the comparison, the results of sample A are included. The largest adiabatic temperature span (1.2 K) was obtained with the silver epoxy-bonded magnetocaloric plate with 60 % of the volume fraction of the La-Fe-Co-Si powder. Other samples have the maximum adiabatic temperature span between 0.8 and 1 K. Even though in samples F and H the volume fraction of the powder is larger than in other samples, the maximum adiabatic temperature change was not increased as much as might be expected. When comparing the adiabatic temperature change of samples A, E and G, which has the same volume fraction of the La-Fe-Co-Si powder (45 %), it is evident that Amerlock Sealer epoxy-bonded

sample (A) performed the largest adiabatic temperature change (see the later Table 3). On the other hand, results on the specific heat show that sample G and especially sample H, which are consisted of silver epoxy, have lower specific heat compared to samples containing Amerlock epoxy (A) and high conductive OB-101 epoxy (E and F).

Fig. 10. The adiabatic temperature change as a function of temperature for samples A and E-H for a magnetic field change of 0.85 T.

Fig. 11. Specific heat of the epoxy-bonded plates (E-H) at the magnetic field of (a) 0 T and (b) 2 T. For easier comparison the specific heat of sample A is added to this chart.

All measured and calculated properties of all nine analyzed samples are summarized in the Table 3. Among the Amerlock Sealer epoxy-bonded plates, the best magnetocaloric properties were obtained with samples A and B, while substantially poorer performances have been observed for samples C and D. On the other hand, the best thermal properties were obtained with sample C, followed by B, D and A.

It is evident that additional smaller magnetocaloric particles do not increase the magnetocaloric properties, but rather decrease it, especially particles below 10 μm (sample C). This is related to the residual magnetization in the paramagnetic region. Compared to the epoxy-bonded sample A which consists only of 130 μm particles La-Fe-Co-Si and epoxy, smaller particles increase the thermal conductivity of the magnetocaloric plate. This has been for 86 % higher in sample B and 100 % higher in sample C, respectively. Carbon additives (sample D) do slightly decrease thermal conductivity. However, carbon addition drastically decreases the specific heat.

The impact of the epoxy is not as crucial as might be expected since samples with the same volume fraction but different epoxies (A, E, G) have relatively similar adiabatic temperature change. Among all prepared composite magnetocaloric samples the largest ΔT_{ad}^{max} was measured in sample H which contains silver epoxy and the highest volume fraction La-Fe-Co-Si powder. The main advantage of the high conductive epoxy (OB-101) and especially silver epoxy compared to Amerlock epoxy is the fact that those two epoxies allow higher volume fraction of the La-Fe-Co-Si powder, what further increases the adiabatic temperature change and especially the thermal diffusivity. Moreover these two epoxies cure faster and plates made of them have better mechanical properties as plate based on Amerlock Sealer epoxy.

Table 3

Measured magnetocaloric and thermal properties of all nine analyzed samples, sintered and epoxy-bonded magnetocaloric plates. κ was calculated using the Eq. 2.

	ΔS_M^{max} [J/kgK]	ΔT_{ad}^{max} [K]	ΔT_{ad}^{max} [K]	a (at T_C) [mm ² /s]	κ (at T_C and 0T) [W/mK]	κ^H (in paramagnetic region at 0 T) [J/kgK]
	$\Delta B=2$ T	$\Delta B=1.9$ T	$\Delta B=0.85$ T			
Sintered	8.7	3.3	1.85	1.86	8.93	455
A	7.5	2.2	1.15	0.54	1.29	625
B	7	2.4	1.07	0.68	2.4	580
C	5.3	1.9	1.06	0.83	2.68	560
D	7.3	1.9	0.80	0.58	1.09	440
E	/	/	0.85	/	/	650
F	/	/	0.95	/	/	595
G	/	/	0.9	/	/	610
H	/	/	1.2	/	/	560

3.3 The Cooling Characteristic of the Epoxy-Bonded AMR

The obtained results for the epoxy-bonded AMR (made using sample A) are presented in Figs. 12 and 13. It is evident from Fig. 12 that the optimal hot-side temperature of the epoxy-bonded AMR is 298 K. This value was expected regarding the distribution of Curie temperatures in the AMR (286 K and 293 K). Further tests were thus performed at 298 K of the hot-side temperature. The tests were performed at three different durations of the fluid flow period (i.e. operating frequencies with the constant (de)magnetization time) and at different utilization factors (i.e. mass flow rates). It is clear from Fig. 13 that the AMR performed the largest temperature span at 1 s of the fluid flow period (in one direction). This corresponds to the operating frequency of approximately 0.3 Hz. However, those results can be misleading. We have noticed that during the operation of the experimental device the performance of the epoxy-bonded AMR was decreasing

with time. The main reason for that was the maldistribution of the fluid flow in the AMR which was increasing with the number of the performed cycles. This was due to the magnetic force and not fully rigid epoxy-bonded plates. This caused bending of plates. The unequal spacing between the plates reduces the efficiency of the heat regenerator [22]. However, we noticed that the maximum temperature span was above 12 K, but we could not repeat the result (and thus this is not shown in Fig. 13). When one compares the two-layered epoxy-bonded AMR (Fig. 13) and two-layered sintered (state-of-the-art) AMR produced by Vacuumschmelze (see [16]) it can be concluded that sintered AMR still shows better results, as its maximum temperature span was approximately 17 K [16]. Even though it has poorer heat transfer geometry (thicker plates, larger spacing and smaller heat transfer area), the main advantage of the sintered AMR is smaller (or zero) maldistribution and of course better magnetocaloric and thermal properties. However, even though the goal to overcome the sintered AMR was not reached with the epoxy-bonded AMR the results are very promising. More suitable epoxy (e.g., silver epoxy) which would assure larger thermal conductivity of the plate and thinner plates with minimal maldistribution could overcome the performances of sintered (state-of-the-art) AMR.

Fig. 12. Temperature span T_{sp} of the epoxy-bonded AMR as a function of the hot-side temperature at constant operating conditions ($\tau_f = 1$ s; $U = 0.227$).

Fig. 13. Temperature span of the epoxy-bonded AMR as a function of the utilization factor for three different duration of the fluid flow period.

4 Conclusions

In this paper a detailed experimental work on epoxy-bonded La-Fe-Co-Si magnetocaloric plates was presented. The results were compared with those obtained on sintered La-Fe-Co-Si plate. Additionally, the AMR assembly made of stacked epoxy-bonded plates was fabricated and tested in the experimental magnetic cooling device. Based on the results presented in this paper, the following conclusions can be made.

1. The magnetocaloric epoxy-bonded plates with the thickness of 0.4 mm were produced and tested. Since no cracking was detected, the plates are mechanically stable. We showed that this method is more promising for the manufacturing of thinner plates compared to the sintered (state-of-the-art) technique.
2. As it was expected the sintered plates have better magnetocaloric and especially thermal properties compared to the epoxy-bonded plates. The main reason for that is the impact of the epoxy, since it has relatively high specific heat and low thermal conductivity. The difference in the adiabatic temperature change is larger than difference in the magnetic entropy change. This is mostly due to the impact of the higher specific heat of the epoxy-bonded plates compared to the sintered magnetocaloric plate. The impact on the thermal properties of the epoxy is the most clearly evident in the case of thermal diffusivity, where its value is in the case of the epoxy-bonded plates more than twice smaller compared to the sintered plate.
3. The addition of carbon powder does not increase the thermal diffusivity as it might be expected. The thermal diffusivity of sample A was drastically increased with the addition of smaller magnetocaloric particles (sample B and sample C). By mixing magnetocaloric particles of different sizes it is possible to keep magnetocaloric properties high and increase thermal diffusivity (conductivity).

4. Sample B (composed with additional 19 % of 12 μm , 21 μm and 57 μm La-Fe-Co-Si powder in the ratio of 1:1:1) seems to have the optimal composition regarding all the analyzed magnetocaloric and thermal properties of the Amerlock Sealer epoxy-bonded magnetocaloric plates. The adiabatic temperature change of 2.4 K and magnetic entropy change of 7 J/kgK for a field change of 1.9 T and 2 T respectively was measured for this sample. We can conclude that for the optimal magnetocaloric properties, high volume fraction of magnetocaloric material and corresponding low volume fraction of epoxy is necessary. Moreover, the particles of magnetocaloric material should not be too small (below 10 μm), since this leads to smaller MCE.
5. Regarding the mechanical stability of Amerlock Sealer epoxy-bonded magnetocaloric plates we can conclude that these materials can withstand long-term cyclic loading, which is crucial for its application in a magnetic refrigerator.
6. The special conductive epoxy and silver epoxy do not drastically increase the adiabatic temperature change. The positive effect of the silver epoxy reflects in low specific heat. Although the impact of the epoxy is not as crucial as it might be expected, it can be concluded that among all the analyzed epoxies and bonds, the silver epoxy currently shows a great potential, as 60 vol. % of powder can be used in the silver epoxy-bonded sample. This further results in higher adiabatic temperature change and corresponding lower specific heat compared with the other samples.
7. Although the highest measured temperature span of epoxy-bonded AMR was smaller compared to the sintered state-of-the-art AMR it can be concluded that the epoxy-bonded composite magnetocaloric plates is a promising solution for the manufacturing of the more efficient AMR with better mechanical properties compared to the sintered (state-of-the-art) AMR. Furthermore, epoxy based samples showed very good cyclic stability. However, the magnetocaloric and thermal performances of the epoxy-bonded plates are substantially lower compared to the sintered plates. Especially the thermal properties (thermal conductivity) and the adiabatic temperature change, which are crucial for the application of the magnetocaloric plate in the AMR should be improved. Further research of the most suitable epoxy or binder, presents the basis for our future work in this particular domain.

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