

# Indium-Bonded $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$ Magnetocaloric Composites by Hot Pressing

Pang Wenkai, Chen Yungui, Tang Yongbai, Zhou Lingtong, Guo Huaqiang

Sichuan University, Chengdu 610065, China

**Abstract:** The advanced magnetocaloric composites in active magnetic regenerator (AMR) are required to meet the good mechanical properties, magnetocaloric effect (MCE) and thermal conductivity. However there are challenges in the shape up and heat conduction of most of the magnetocaloric composites currently. In this paper, we reported  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  magnetocaloric composites which was pressed together with a low melting point metal of indium (In) and the different compaction pressures of 0~800 MPa at 430 K. The results show that the MCE of the composite is deteriorated when compaction pressure exceeds 200 MPa. The In-bonded  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  composite sheet with a thickness of 0.8 mm pressed with 100 MPa has the maximum adiabatic temperature change of 5.88 K at the magnetic field change of 0~2 T.

**Key words:** magnetocaloric effect (MCE); hot pressing;  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  composites

The magnetic refrigeration based on the magnetocaloric effect (MCE) is a high efficiency and environment-friendliness technique and has attracted increasing attention especially in room temperature refrigeration<sup>[1-3]</sup>. After the long-term exploration of magnetic refrigeration materials, the cubic  $\text{NaZn}_{13}$ -type compounds  $\text{LaFe}_{13-x}\text{Si}_x$  with a first-order phase transition and obvious lattice contraction are regarded as the most promising magnetic refrigeration material owing to their low cost, giant magnetocaloric effect and continuous-adjustable Curie temperature<sup>[4-6]</sup>. However the Curie temperature of  $\text{LaFe}_{13-x}\text{Si}_x$  is around 200 K; hence it needs to be adjusted to room temperature by hydrogen absorption<sup>[7,8]</sup>. The powder metallurgy process has been developed as an attractive technique in fabricating magnetic refrigerants because of  $\text{LaFe}_{13-x}\text{Si}_x\text{H}_y$  existing almost in powders<sup>[9]</sup>. There are many approaches to prepare magnetocaloric composites by powder metallurgy, such as epoxy-bonded<sup>[10,11]</sup>, and hot pressing with metals binder<sup>[12]</sup>. It has been proposed that epoxy-bonded magnetocaloric composites obtain good mechanical properties and magnetocaloric effects<sup>[10,11]</sup>. But the low thermal conductivity of epoxy weakens the heat transmission of magnetocaloric composites. Good heat-

transfer properties of the active magnetic refrigerator (AMR) are the key to its cooling efficiency. In order to enhance the heat-transfer properties,  $\text{LaFe}_{11.6}\text{Si}_{1.4}/\text{Cu}$  is prepared by electroless copper plating<sup>[13]</sup>. The thermal conductivity can be improved by 300%, but its plating solution has some disadvantages, such as difficult recovery and environment pollution.  $\text{LaFe}_{11.6}\text{Si}_{1.4}/\text{Cu}$  magnetocaloric composites prepared by hot pressing had also been proposed<sup>[14]</sup>. M. Krautz et al. compacted  $\text{La}(\text{Fe},\text{Si})_{13}$  particles together with an amorphous  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$  (at%) matrix<sup>[12]</sup>. H. Zhang et al. prepared  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_y/\text{Sn}$  composites by hot pressing in which minimum compaction temperature is 498 K<sup>[15]</sup>. However, the higher the temperature, the greater the hydrogen-releasing capacity<sup>[8]</sup>, so some metals of low melting points may be more suitable. Owing to a low melting point (429.63 K) and non reaction with  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_y$  at pressing temperature, indium is selected as an adhesive for  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_y$  magnetocaloric composites in this research.

In the present work, we compacted  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  particles together with indium powders by hot pressing. The influence of applied pressure on phase, microstructure, porosity and magnetocaloric effects of In-bonded  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$

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Corresponding author: Chen Yungui, Ph. D., Professor, College of Materials Science and Engineering, Sichuan University, Chengdu 610065, P. R. China, Tel: 0086-28-85405670, E-mail: ygchen60@aiyun.com

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magnetocaloric composites were investigated.

## 1 Experiment

The magnetocaloric alloy with nominal composition of  $\text{LaFe}_{11.6}\text{Si}_{1.4}$  was prepared by arc melting under the protection of high-purity argon atmosphere. The purities of raw materials La, Fe and Si are 99.4%, 99.9% and 99.9999%, respectively.

The sample was turned over and re-melted five times to ensure good composition homogeneity. The as-cast  $\text{LaFe}_{11.6}\text{Si}_{1.4}$  alloys were annealed in a ZM-40-16 vacuum molybdenum wire furnace at 1473 K for 5 h to obtain  $\text{NaZn}_{13}$ -type main phase as many as possible<sup>[16,17]</sup>.

The  $\text{LaFe}_{11.6}\text{Si}_{1.4}$  powders were made through mechanical crushing process and the powders were sieved into the size of 0.15~0.45 mm. Indium powders as adhesion agents were provided by China New Metal Materials Technology Co. Ltd, and their average size was 20  $\mu\text{m}$ . The mass fraction of indium was 7.5wt% approximately. The hydrogen absorption process was carried out in a reactor filling with  $\text{H}_2$  atmosphere at 453 K for 1 h. Considering the practical application and production cost, 0.6 MPa was chosen as the hydrogen charging pressure. Finally, the hydrogen content in  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_y$  was determined by the ideal gas law. The specific chemical equation of hydrogenated  $\text{LaFe}_{11.6}\text{Si}_{1.4}$  is  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$ . Since the melting point of indium is 429.63 K, the composites were heated up at 430 K which is below the dehydrogenation temperature. The hot pressing pressure of 100, 200, 400 and 800 MPa, were applied for 10 min.

The phase characterizations of the In-bonded  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  magnetocaloric composites were characterized by X-ray diffraction (XRD, DanDongFangYuan, DX-2600) with  $\text{Cu K}\alpha$  radiation. The microstructure and the element distribution were analyzed using a scanning electron microscope (SEM) and an energy dispersive spectrometer (SEM-EDS, Cambridge S360), respectively.

The specific heat was measured using differential scanning calorimetry. The measurements were performed on differential scanning calorimeter (DSC, METTLER TOLEDO, DSC1) in the temperature range between 280 and 315 K (at zero magnetic field). The specific heat ( $C_p$ ) of the samples was calculated by the following equation<sup>[18]</sup>:

$$C_p = \frac{(Y_1 - Y_0)m_1}{(Y_2 - Y_0)m_2} C_{p1} \quad (1)$$

Where,  $m_1$  is the mass (g) of sapphire,  $m_2$  is the mass (g) of sample,  $Y_1$  is the DSC value of sample at the temperature,  $Y_2$  is the DSC value of sapphire at the temperature,  $Y_0$  is the baseline DSC value, and  $C_{p1}$  is the specific heat of sapphire at the temperature.

The density of the samples was determined by the Archimedes method at room temperature. Each group of data was measured three times. The details of porosity measurement have been reported elsewhere as follows<sup>[19]</sup>:

$$K = 1 - \rho \sum_{i=1}^n \frac{C_i}{\rho_i} \quad (2)$$

Where  $C_i$  is a ratio and  $\rho_i$  is a density of the component in In-bonded  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_y$  magnetocaloric composites.

For the calculation of theoretical density  $\rho$  of samples, the following equation was used:

$$\rho = \sum_i \text{vol}\% \cdot \rho_i \quad (3)$$

Where  $\rho_i$  is a density of the component in In-bonded  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_y$  magnetocaloric composites.

The magnetic measurements of the magnetocaloric sheets were performed on a vibrating sample magnetometer (VSM, Quantum Design). The magnetic entropy change  $\Delta S$  was calculated from isothermal magnetization curves using the Maxwell relation:

$$S_M(T, H) = \int_{H_1}^{H_2} \left( \frac{\partial M}{\partial T} \right)_H dH \quad (4)$$

Where  $H_1$  is the initial magnetic field,  $H_2$  is the final magnetic field, and  $M$  is the magnetization of the specimen.

The adiabatic temperature change of  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  magnetocaloric composites were measured using the following equation<sup>[20]</sup>:

$$\Delta T_{ad} = -\frac{T}{C_p} \Delta S_m \quad (5)$$

Where  $T$  is the temperature and  $C_p$  is the specific heat at the temperature.

## 2 Results and Discussion

### 2.1 Phase and microstructure of the $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$ composites

Fig.1 shows the XRD patterns of In-bonded  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  magnetocaloric composites at different compaction pressures (from 100 to 800 MPa). The main phase of samples is  $\text{NaZn}_{13}$  and a small amount of  $\alpha\text{-Fe}$ . It can be seen the  $\text{NaZn}_{13}$  phase is still reserved after hot pressing. No other new phases are generated after hot pressing at different compaction pressures.

Considering the hot pressing pressure is beneficial for the formation of  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  magnetocaloric composites, the compaction pressure 100 MPa is applied firstly. Fig.2a shows the microstructure of In-bonded  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  magnetocaloric composites pressed with 100 MPa. It can be seen the liquid indium forms a homogenous continuous filler among the particles of  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  and porosity is hardly found. The density of the composites calculated by the Archimedes method is 6.87  $\text{g/cm}^3$  which is close to the theoretical full density of 7.2  $\text{g/cm}^3$ . The elemental mapping in In-bonded  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  magnetocaloric composites is illustrated in Fig.2b and Fig.2c. The element indium (green area) closely fills the blank of the iron region (red area) which represents  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$ . Owing to a good wettability between indium and Fe<sup>[21]</sup>, the liquid indium flowing into the porous space of the composites enables the compactness increasing when

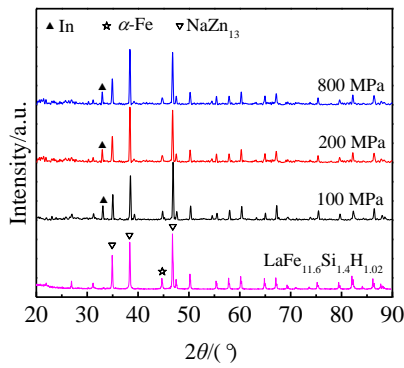


Fig.1 XRD patterns of In-bonded  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  magnetocaloric composites at different compaction pressures

heated up to 430 K; as a result,  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  particles are well bonded together by indium. Hence, for  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  magnetocaloric composites, indium can act as a ductile binder to form a continuous and tight composite during hot pressing.

## 2.2 Effect of pressures on the porosity of $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$ composites

Fig.3 shows the porosity of In-bonded  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  magnetocaloric composites compacted under different pressures. It can be seen clearly that the porosity decreases with the increase of compaction pressure. But there is little change under pressures from 100 to 200 MPa. It has been

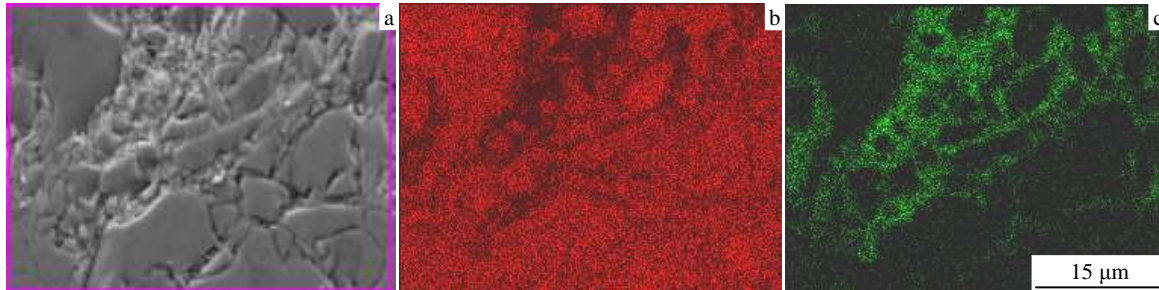


Fig.2 SEM image (a) and EDS mapping of element Fe (b) and In (c) for In-bonded  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  magnetocaloric composites under pressure of 100 MPa

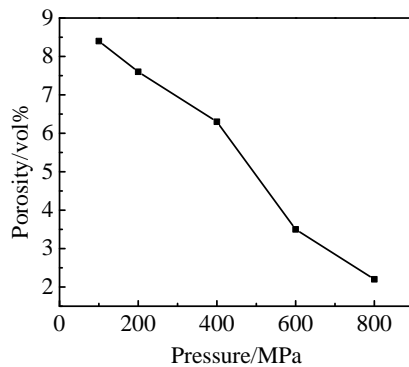


Fig.3 Dependence of the porosity on the compaction pressure for In-bonded  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  magnetocaloric composites

reported that the porosity leads to a reduction of thermal conductivity which is significantly important for active magnetic regenerator (AMR)<sup>[13]</sup>. Therefore decreasing the porosity is beneficial to thermal conductivity. However, there is another question that higher pressure may generate micro cracks<sup>[22]</sup>, which are also the great thermal resistance for composites. Therefore increasing the pressure blindly is unfavorable to the improvement of thermal conductivity.

## 2.3 Effect of pressures on the MCE of $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$ composites

Fig.4 shows the magnetization curves of pure  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  and indium-bonded composite under the pressure of 800 MPa. It can be seen clearly that the Curie temperature (defined as the point with the maximum value of  $dM/dT$  on cooling process) was both found to be  $(298 \pm 1)$  K. The magnetization of the indium-bonded composites at low temperature is slightly lower than that of the pure  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  due to indium existence diluting magnetocaloric effect. No change of  $T_c$  indicates that the indium atoms didn't diffuse into the lattice of  $\text{NaZn}_{13}$ -type structure, which is understandable since there is nearly no solid solubility of In in Fe at 430 K<sup>[21]</sup>. This is significantly important because even a few indium atoms diffusing into the  $\text{NaZn}_{13}$  would lead to the decrease of the magnetic entropy change drastically<sup>[23]</sup>. Therefore the In-bonded  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  magnetocaloric composites are able to maintain the good MCE after hot pressing.

The influence of the pressures applied on the magnetocaloric effects of the  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  composites is shown in Fig.5. In a magnetic field from 0~2 T, the loose  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  shows a maximum of  $\Delta S_{\text{max}}=8.05 \text{ J kg}^{-1} \text{ K}^{-1}$  (black line). Obviously, the maximum magnetic entropy change almost does not decrease under the pressure below 200 MPa. However increasing the pressing pressure does significantly reduce the magnetocaloric property as shown in Fig.5, such as 400 MPa (blue line) and especially 800 MPa (pink line). The main reason is the influence of particle size on  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$ <sup>[24,25]</sup>. The study by J. Liu et al.<sup>[26]</sup> indicated that the magnetic field-induced entropy change is reduced by the fine powderization process. Owing to the brittle characteristic of the intermetallic compound  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$ , it is easy to be crushed in pressing process. In contrast,

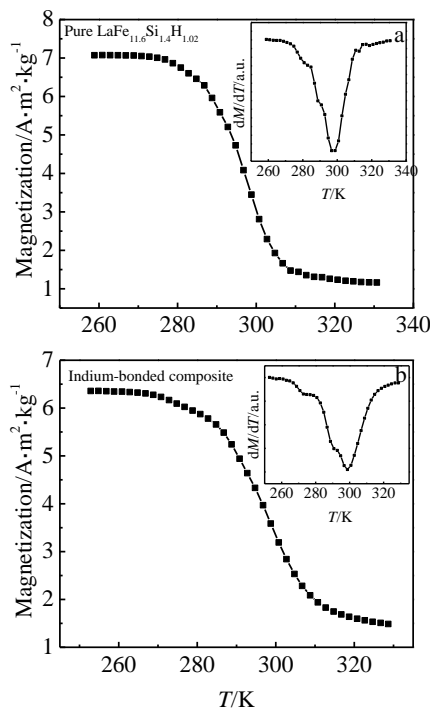


Fig.4 Magnetization change with the temperature of pure  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  (a) and indium-bonded composite (b) under 800 MPa (the magnetic field is 0.02 T)

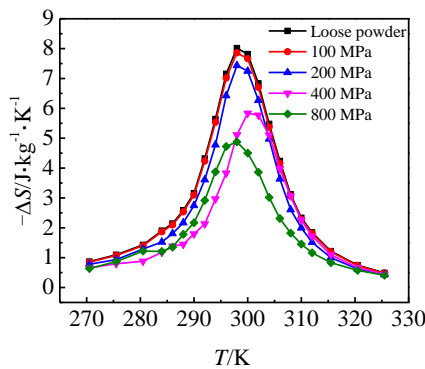


Fig.5 Magnetic entropy change of unpressed and In-bonded  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  magnetocaloric composites compacted under different pressures (the magnetic field changes from 0 to 2 T)

it is found that the Curie temperatures almost remain in the vicinity of 298 K under different pressures. Hence, comparing with the magnetic entropy change, the value of  $T_c$  is more stable under high pressures, which is beneficial to the practical process and application.

Fig.6 shows the adiabatic temperature change of four In-bonded  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  magnetocaloric composites compacted with different pressures. As it was expected from the results of magnetic entropy change, the  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  composites compacted with 100 MPa obtains the largest adiabatic temperature change of 5.88 K, and it significantly decreases

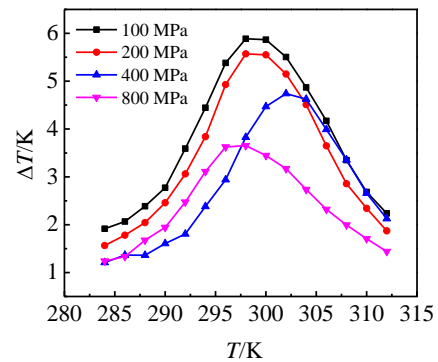


Fig.6 Adiabatic temperature change of In-bonded  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  magnetocaloric composites under different pressures (the magnetic field changes from 0 to 2 T)

once exceeding the pressure of 200 MPa. Currently the value of maximum adiabatic temperature change has already been larger than that of the previous reported  $\text{La}(\text{Fe},\text{Mn},\text{Si})_{13}\text{H}_x$  polymer-composites<sup>[10]</sup> and epoxy-bonded  $\text{La-Fe-Co-Si}$  magnetocaloric plates<sup>[11]</sup>. According to the Eq. (5), a low specific heat is beneficial to the adiabatic temperature change. Owing to the specific heat of indium only  $230 \text{ J kg}^{-1} \text{ K}^{-1}$  which is much lower than that of epoxy, the specific heat of In-bonded  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  composites reaches  $398 \text{ J kg}^{-1} \text{ K}^{-1}$ .

### 3 Conclusions

1) In-bonded  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  composites exhibit homogeneous continuous microstructure, and good magnetocaloric properties by hot pressing.

2) The compaction pressure is a key factor in preparation of In-bonded  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  magnetocaloric composites. It suggests the compaction pressure should not exceed 200 MPa.

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## 压力对热压法制备 $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}\text{-In}$ 复合材料组织与性能的影响

庞文凯, 陈云贵, 唐永柏, 周龄童, 郭华强  
(四川大学, 四川 成都 610065)

**摘要:** 主动式磁蓄冷器中的制冷材料需要满足优良的机械性能、磁热性能和导热性能。然而, 目前大多数磁制冷材料在成形和导热性能方面存在着一些问题。在本研究中, 介绍了一种在 430 K 的温度下, 将  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  和钢粉混合后在不同压力下进行压制成形的办法。结果显示, 当压制压力超过 200 MPa 时, 复合磁工质的磁热性能将会大幅度降低。在压制压力为 100 MPa 时, 厚度为 0.8 mm 的片状磁工质在 0~2 T 的磁场下, 达到的最大绝热温变为 5.88 K。

**关键词:** 磁热效应; 热压工艺;  $\text{LaFe}_{11.6}\text{Si}_{1.4}\text{H}_{1.02}$  复合材料

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作者简介: 庞文凯, 男, 1992 年生, 硕士生, 四川大学材料科学与工程学院, 四川 成都 610065, E-mail: pangwenkai309@163.com