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Mechanical and magnetocaloric properties of $La(Fe,Mn,Si)_{13}H_8$/Cu plates prepared by Cu-binding prior to hydrogenation

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ABSTRACT

$La(Fe,Si)_{13}H_8$ hydrides with large magnetocaloric effect (MCE) have been demonstrated as promising magnetic refrigerants around room temperature. To meet the shape requirements in a refrigerator, hot-pressing technique was usually employed. However, hydrogenation prior to hot-pressing is inappropriate sometimes because the dehydrogenation occurs at about 450 K, and the incorporation of large amount of metal as binder often makes the MCE reduce a lot. Here, we report a new way to prepare the metal-bonded $LaFe_{11.4}Mn_{0.3}Si_{1.3}H_8$ hydride plates as thin as 0.5 mm by metal-binding prior to hydrogenation instead. By adding a small amount 4 wt% of Cu, $LaFe_{11.4}Mn_{0.3}Si_{1.3}$/Cu plates were firstly prepared. Afterwards, hydrogen absorption can be still conducted because lots of holes and naked surfaces still left, which favor hydrogen atoms into lattice. As a result, saturated hydrogenation can be achieved. The MCE keeps large, and good mechanical properties and thermal conductivity have been demonstrated.

1. Introduction

Solid state refrigeration based on caloric effect has attached tremendous attentions owing to the superiority of energy saving and environmental concerns [1–3]. The cubic $NaZn_{13}$(1:13)-type $La(Fe,Si)_{13}$ compounds with large magnetocaloric effect (MCE) have been demonstrated as promising magnetic refrigeration materials in recent years [4–7]. However, it is hard to apply $La(Fe,Si)_{13}$ materials as room temperature refrigerants directly due to the low Curie temperature (T_C, lower than 210 K) and bad mechanical properties. By hydrogen absorption, T_C can be raised to room temperature, and the first-order nature of transition and large MCE can be maintained. Meanwhile hysteresis loss can be reduced [6,8]. These characteristics make the $La(Fe,Si)_{13}H_8$ hydride a very promising candidate for magnetic refrigerant. However, the bad mechanical properties of $La(Fe,Si)_{13}$-based compounds become even worse after hydrogenation, which make the hydrides only exist in powder form, which is unfavorable to produce into required shapes like thin plates or spheres to meet the shape requirements in magnetic refrigerators [9].

In order to overcome the intrinsic brittleness of $La(Fe,Si)_{13}$ materials and improve the mechanical stability, lots of effort have been dedicated to machine the $La(Fe,Si)_{13}$-based materials, such as Fe-rich composition [10,11], hot pressing [12–14], metal- or epoxy-bonding [12–15], electroless copper plating [16], sintering technique [17], and etc. Off-stoichiometric $La(Fe,Co,Si)_{13}$ with extra-Fe was prepared and enhanced mechanical properties has been observed in expense of some reduction of entropy change [10]. The epoxy-bonded technique can enhance mechanical properties and maintain the large MCE, but it is unfavorable to thermal conductivity due to the inclusion of low thermal conductive epoxy [9]. Hot-pressing technique was tried by several groups by combining metal as binder, and good mechanical and thermal conductive properties have been demonstrated. For example, by mixing 10 wt% Cu [13] or 25 wt% Sn [12], $LaFe_{11.6}Si_{1.4}$/Cu and $LaFe_{11.6}Si_{1.4}H_y$/Sn composites were prepared by hot pressing, and

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satisfactory compressive strength can be obtained by setting appropriate hot pressing temperature, pressure, and duration according to the specific character of the metal binder. However, MCE reduces a lot due to the incorporation of large amount of metal as binder. The $LaFe_{11.65}Si_{1.35}$/Cu core-shell powders with a little amount 1 wt% Cu prepared by magnetron sputtering and then solidified by hot-pressing show an enhanced compressive strength without significant decrease of the MCE [18]. For $La(Fe,Si)_{13}H_{\delta}$, however, hydrogenation prior to hot-pressing is sometimes not a suitable means to improve mechanical properties since the dehydrogenation effect occurs at about 450 K [19]. Meanwhile, the core-shell structure or the incorporation of large amount of metal coating on the surface of $La(Fe,Si)_{13}$ will hinder the hydrogen atoms into the lattice of 1:13 lattice if hydrogenation was performed after hot-pressing.

Here, we report a new way to prepare the metal-bonded $La(Fe,Si)_{13}H_{\delta}$ hydride plates as thin as 0.5 mm. The composition $LaFe_{11.4}Mn_{0.3}Si_{1.3}$ with Mn was chosen to ensure the Curie temperature, T_C, of $LaFe_{11.4}Mn_{0.3}Si_{1.3}H_{\delta}$ with saturated hydrogenation to be located around room temperature. T_C of $LaFe_{11.7}Si_{1.3}$ is at around 190 K, and the introduction of Mn can rapidly lower the T_C because Mn atoms carry antiparallel magnetic moment to Fe [20]. $LaFe_{11.4}Mn_{0.3}Si_{1.3}$ with Mn shows T_C at ~137 K. By adding a relative small amount of Cu power 4 wt%, $LaFe_{11.4}Mn_{0.3}Si_{1.3}$/Cu composites were prepared at first by spark plasma sintering technique, and then cut into plates as thin as 0.5 mm. Afterwards hydrogen absorption can be still conducted because the small amount of bonding Cu only appears at partial surfaces of $LaFe_{11.4}Mn_{0.3}Si_{1.3}$ powders. Lots of holes and naked surfaces still left, which favor hydrogen atoms into 1:13 lattice. As a result, saturated hydrogenation can be achieved. The magnetic transition remains sharp and the MCE keeps large for the resulted $LaFe_{11.4}Mn_{0.3}Si_{1.3}H_{\delta}$/metal. Moreover, good mechanical properties, thermal conductivity, and excellent aging stability have been demonstrated.

2. Experimental

$LaFe_{11.4}Mn_{0.3}Si_{1.3}$ alloys were prepared by conventional arc-melting technique followed by annealing at 1323 k for 60 days and then quenched in liquid nitrogen. Powder X-ray diffraction (XRD) measurement confirms that the $LaFe_{11.4}Mn_{0.3}Si_{1.3}$ crystallizes in a $NaZn_{13}$-type structure with a minor amount of impurity phase α-Fe (4.67 wt %). Then, the ingots were ground into 30–80 μm particles and mixed with 4 wt% commercial metal powders, i.e. Cu in size of 48 μm. The mixture was put into cylindrical mold with size of φ15 × 15 mm and then sintered by using spark plasma sintering technique (SPS−20C) under different temperature, pressure, and duration. The details can be found in Table 1. The resulted composites $LaFe_{11.4}Mn_{0.3}Si_{1.3}$/Cu were cut into plates as thin as 0.5 mm by wire cutting technique. Afterwards, hydrogen absorption was performed at 523 K in H_2 atmosphere by using a commercial P−C-T (pressure-composition-temperature) instrument. During the process, gas pressure was gradually increased to 3 MPa by step of 0.15 MPa at the constant temperature of 523 K, where 15 min was held at each step, and then 5 h was held at the maximal pressure (3 MPa) to ensure full hydrogenation. The density of bonded materials was examined by Archimedes method. The microstructure was examined by scanning electron microscopy (SEM) in backscattered electron (BSE) mode. The compressive strength was tested by compressing overlapped four plates under ambient temperature using a universal material testing machine, while the bending strength was measured using the standard three-point bending method for a single plate with size of $15 \times 5 \times 0.5\ mm^3$. Magnetic measurements were carried out using a Quantum Design SQUID vibrating sample magnetometer. Thermal conductivity κ was measured using thermal transport option (TTO) equipped on quantum design physical property measurement system (PPMS).

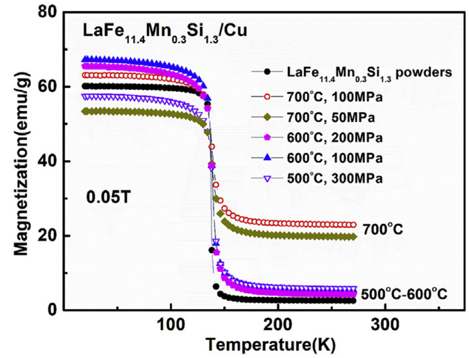

Fig. 1. Temperature dependent magnetization measured on warming under a magnetic field of 0.05 T for the $LaFe_{11.4}Mn_{0.3}Si_{1.3}$/Cu plates sintered at different conditions compared to the naked $LaFe_{11.4}Mn_{0.3}Si_{1.3}$ powders before hydrogenation.

3. Results and discussion

For the initial $LaFe_{11.4}Mn_{0.3}Si_{1.3}$, x-ray diffraction measurements and Rietveld refinements indicate that the compounds crystalize in 1:13 structure, while a little amount (~4.67 wt%) of α-Fe impurity coexists. Temperature dependent magnetization (M-T curves) denotes that the T_C of naked $LaFe_{11.4}Mn_{0.3}Si_{1.3}$ locates at 137 K due to the incorporation of Mn atoms, which carry antiparallel moments to Fe, as shown in Fig. 1. For the composites $LaFe_{11.4}Mn_{0.3}Si_{1.3}$/Cu sintered at different conditions (500°C-700 °C, 50 MPa-300 MPa, 5min, Table 1), the T_C keeps nearly unchanged, but the amount of α-Fe impurity increases more or less depending on the sintering pressure and temperature. The elevated magnetization at temperatures above T_C reflects the growth and different amount of α-Fe impurity caused by sintering. One can note that a sintering temperature as high as 700 °C will lead to precipitation of a large amount of α-Fe, as shown in Fig. 1. However, as appropriate sintering conditions were chosen, such as 500 °C and 300 MPa, magnetic transition still keeps sharp and enhanced mechanical properties can be achieved while the coexist amount of α-Fe is acceptable for the resulted $LaFe_{11.4}Mn_{0.3}Si_{1.3}H_{\delta}$/Cu hydride plates. The thermal hysteresis is approaching zero for the $LaFe_{11.4}Mn_{0.3}Si_{1.3}$/Cu plates both before and after hydrogenation. This is relative to the introduced porosity during preparation, which partially removes the grain boundaries that restrain volume expansion in the bulk material, and hence reduces the hysteresis [21]. For clarity, only the branch on heating is presented in Fig. 1. Some investigations were performed on the effect of introducing porosity by spark plasma sintering or hot

Table 1
Sintering conditions of the composites $LaFe_{11.4}Mn_{0.3}Si_{1.3}$/Cu.

Ratio of the metal binder	Metal	Sintering temperature	Sintering pressure	Sintering Duration	wire-electrode cutting	Polish surface	Density	porosity
4 wt%	Cu	700 °C	50 MPa	5min	able	–	6.16 g/cm^3	15.0%
		700 °C	100 MPa		able	–	6.87 g/cm^3	5.2%
		600 °C	100 MPa		able	unable	5.92 g/cm^3	28.4%
		600 °C	200 MPa		able	unable	5.19 g/cm^3	18.2%
		500 °C	300 MPa		able	able	6.09 g/cm^3	15.9%
		500 °C	100 MPa		unable	unable	4.93 g/cm^3	31.9%

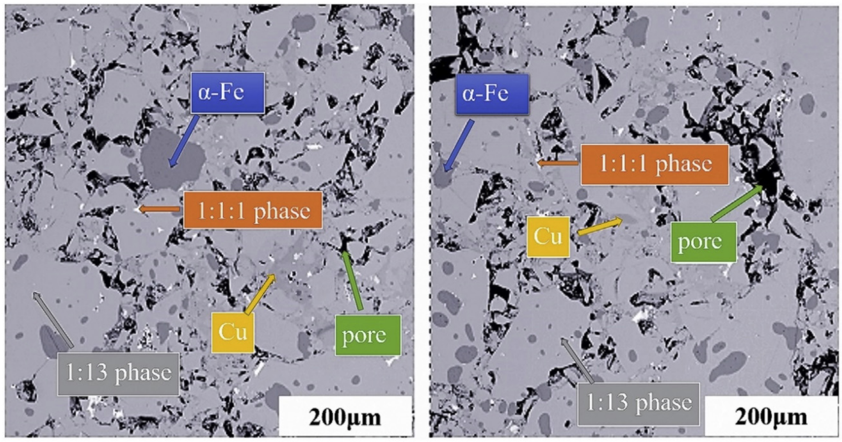

Fig. 2. SEM backscattered electron (BSE) images for $LaFe_{11.4}Mn_{0.3}Si_{1.3}$/Cu plate (500 °C, 300 MPa). The left and right images come from different parts of the plate.

pressing for $La(Fe,Si)_{13}$ powders [21,22], but few involve the mechanical and comprehensive performance for the plates as thin as 0.5 mm particularly with hydrogen.

To know the microstructure and distributions of Cu binder for the sintered composites, backscattered SEM micrographs were investigated. As representative displays, the SEM images of composite sintered under 500 °C and 300 MPa for 5 min are shown in Fig. 2, where different phases, Cu binder, and pores in the composites can be identifies. Based on EDS (energy-dispersive spectroscopy) analysis, the light grey, grey, dark grey, and white areas correspond to Cu binder, 1:13 structure, α-Fe, and 1:1:1 structure, respectively, while black areas correspond to the pores among the particles. One can notice that the Cu binder only appears in some areas while a large quantity of pores remains unfilled due to the small amount of Cu (4 wt%) as binder. The sintering temperature 500 °C–700 °C is not high enough to make the Cu binder melt and well diffuse noting the melting point of Cu is as high as 1083 °C. This means that many $LaFe_{11.4}Mn_{0.3}Si_{1.3}$ particles remain uncoated after sintering, hence hydrogen absorption can be still carried out for the composites with metal binder. Moreover, α-Fe and Cu_2Sb-type 1:1:1 (LaFeSi) impurities, which normally appear during the formation of 1:13 phase [23,24], were also detected besides the main phase of 1:13 structure. The considerable amount of α-Fe distributed in the SEM image verifies the α-Fe precipitation caused by sintering, which is in line with the elevated magnetization at temperatures above T_C in the M-T curves (Fig. 1).

We also evaluated the porosity by measuring density using Archimedes method. The results are shown in Fig. 3. The density ρ is ranging between 4.93 g/cm^3 and 6.87 g/cm^3 for the composites $LaFe_{11.4}Mn_{0.3}Si_{1.3}$/Cu sintered at different conditions (500°C-700 °C, 50 MPa-300 MPa, 5min, Table 1), as shown in Fig. 3a. By taking into account the theoretical full density of the composite (7.245 g/cm^3), the evaluated porosity of the composites is in the range between 5.1% and 31% (Fig. 3b) based on the porosity calculation model,

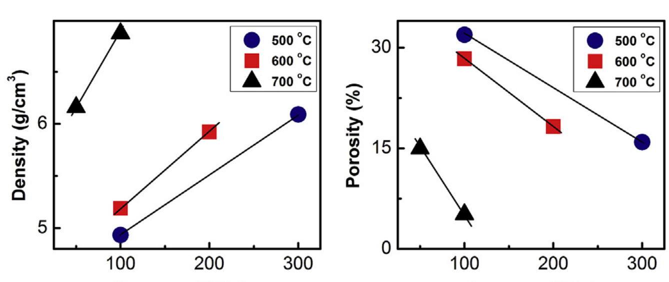

Fig. 3. (a) Density and (b) porosity of $LaFe_{11.4}Mn_{0.3}Si_{1.3}$/Cu composites sintered at different temperatures and pressures. The linked lines guide eyes.

$$P = \left(1 - \frac{\rho_a}{\rho}\right) * 100\%$$

where P, ρ_a, ρ represent porosity, apparent density, and full density, respectively. It can be seen that the porosity decreases with the increase of sintering pressure and temperature (Fig. 3b). Decreasing the porosity is beneficial to thermal conductivity and mechanical properties. The coarse particles of $LaFe_{11.4}Mn_{0.3}Si_{1.3}$ are brittle, and inclined to break apart during hot compaction, leading to an increased number of fractured smaller particles with increasing pressure. These smaller particles accumulate in the space among larger particles, hence the porosity is reduced with increasing the sintering pressure, as shown in Fig. 3.

Fig. 4 shows the temperature dependent magnetization (*M-T* curves) measured under 0.05 T magnetic field for the $LaFe_{11.4}Mn_{0.3}Si_{1.3}$/Cu plate (sintered at 500 °C and 300 MPa) and its hydride. Hydrogen absorption can be still conducted because the small amount of bonding metal Cu only appears at partial surfaces of $LaFe_{11.4}Mn_{0.3}Si_{1.3}$ powders. Lots of holes and naked surfaces still left, which favor hydrogen atoms into 1:13 lattice. As a result, saturated hydrogenation can be achieved. The phase transition around the Curie temperature upon hydrogenation still keeps sharp while shifts from 140 K to 292 K, which is close to room temperature. These results also indicate that $LaFe_{11.4}Mn_{0.3}Si_{1.3}$/Cu plate with a little incorporation of Cu still remains high capacity of hydrogen absorption.

Magnetic entropy change, *ΔS*, was evaluated based on the isothermal magnetization as a function of magnetic field (*M-H* curves) by using Maxwell relation. Fig. 5 shows the *ΔS* as a function of temperature

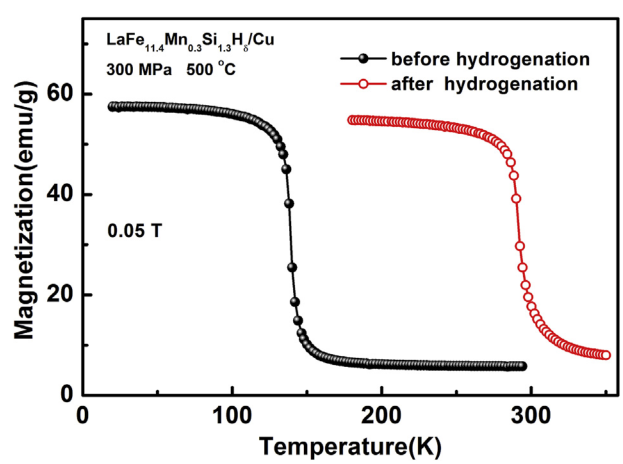

Fig. 4. The comparison of temperature dependent magnetization measured on warming under a magnetic field of 0.05 T for the $LaFe_{11.4}Mn_{0.3}Si_{1.3}$/Cu plates before and after hydrogenation.

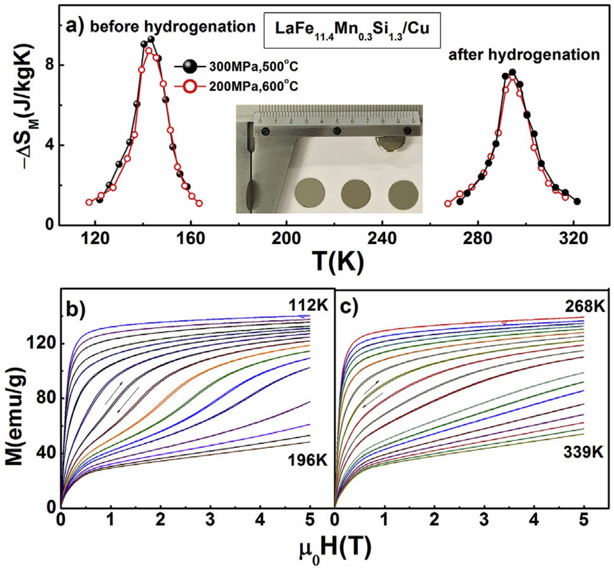

Fig. 5. (a) Entropy change under a magnetic field change of 0–2 T for the $LaFe_{11.4}Mn_{0.3}Si_{1.3}/Cu$ plates sintered at different conditions before and after hydrogenation, where the inset displays the morphology of the plates. The M-H curves for the plate sintered at 300 MPa and 500 °C (b) before and (c) after hydrogenation.

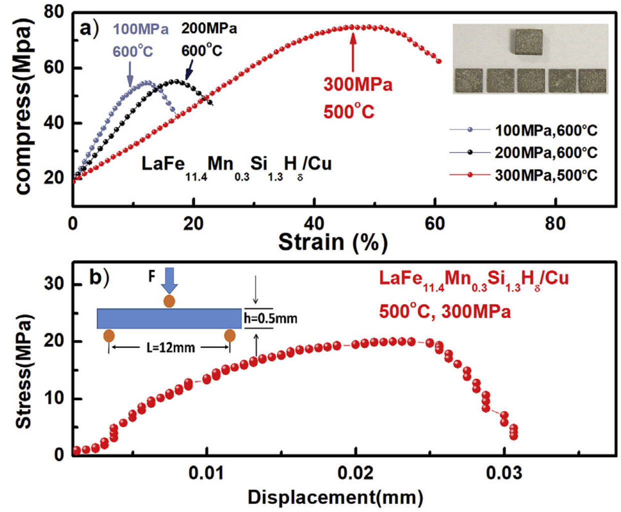

Fig. 6. (a) Compressive pressure as a function of strain for the $LaFe_{11.4}Mn_{0.3}Si_{1.3}H_{\delta}/Cu$ hydride plates of 0.5 mm thickness. Inset shows the photographs of the plates. Four plates were overlapped for the measurements, as shown on the top. (b) Bending strength of a single plate of 0.5 mm thickness measured by the three point bending method for $LaFe_{11.4}Mn_{0.3}Si_{1.3}H_{\delta}/Cu$ hydrides plates prepared at 500 °C and 300 MPa. The inset is the schematic of the three-point bending test.

for $LaFe_{11.4}Mn_{0.3}Si_{1.3}/Cu$ composites sintered at different conditions before and after hydrogenation. For a magnetic field change of 0–2 T, the maximal $-\Delta S$ is about 9.2 J/kg·K (500 °C, 300 MPa) and 8.7 J/kg·K (600 °C, 200 MPa) around T_C ~140 K before hydrogenation, while the peak of entropy change shifts to 292 K after hydrogenation and the $-\Delta S$ value is ~7.6 J/kg·K (500 °C, 300 MPa) and 7.4 J/kg·K (600 °C, 200 MPa) for the $LaFe_{11.4}Mn_{0.3}Si_{1.3}H_6/Cu$ with hydrogen. Compared to the naked $LaFe_{11.4}Mn_{0.3}Si_{1.3}$ ($-\Delta S$ ~ 11.8 J/kg·K, 140 K, 0–2 T, not shown), the magnetic entropy change is reduced due to the growth of α-Fe impurities during the sintering process and the diluted effect by metal binder (ratio of $LaFe_{11.4}Mn_{0.3}Si_{1.3}$ is 95 wt%). But these $-\Delta S$ values are still higher than or comparable to those of the reported previously around room temperature, such as the hot press $La_{0.8}Ce_{0.2}(Fe_{0.95}Co_{0.05})_{11.8}Si_{1.2}/Sn_{42}Bi_{58}$ (6.79 J/kg·K, 246 K, 0–2 T) [25], $LaFe_{11.6}Si_{1.4}H_{1.02}/In$ (7.4 J/kg·K, 298 K, 200 MPa) [26], $LaFe_{11.0}Co_{0.8}Si_{1.2}$ ribbons (7 J/kgK, 283 K, 0-2 T) [27], $LaFe_{10.7}Co_{0.8}Si_{1.5}$ (7 J/kgK, 280 K, 0-2 T) [28], $La_{0.8}Pr_{0.2}Fe_{10.7}Co_{0.8}Si_{1.5}$ (7.2 J/kg K, 275 K, 0-2 T) [29], and also the recently reported $LaFe_{12.1}Co_{0.8}Si_{1.2}$(7.9 J/kgK, 278 K, 0-2 T) [10]. Moreover the magnetic hysteresis loss is approaching zero for the $LaFe_{11.4}Mn_{0.3}Si_{1.3}H_6/Cu$ composites (Fig. 5c) owing to the weakness of itinerant electron metamagnetic transition and the released strain upon the implantation of hydrogen atoms, which is performed at 250 °C [30]. Gschneidner et al. [1] pointed out that since the engineer or designer of magnetic refrigerator needs to know the cooling per unit volume, the |ΔS| using the unit of mJ/cm³ K is much more meaningful than J/kg K from a practical view [4]. Therefore, the density of all studied materials was examined (Table 1, Fig. 3) and then the unit of $-\Delta S$ was converted from J/kg K to mJ/cm³ K. The corresponding maximal $-\Delta S$ under 0-2 T is 52 mJ/cm³ K (500 °C, 300 MPa) and 49 mJ/cm³ K (600 °C, 200 MPa) for $LaFe_{11.4}Mn_{0.3}Si_{1.3}H_6/Cu$ plates sintered at different conditions. Refrigerant capacity (RC) is another measure characterizing magnetic refrigerants. According to $RC = \int_{T_1}^{T_2} |\Delta S| dT$, where T1 and T2 denote the positions of half width of the ΔS peak, the calculated RC is 121 J/kg (500 °C, 300 MPa), 114 J/kg (600 °C, 200 MPa), under 2 T for the present plates after hydrogenation.

The compressive strength was tested by compressing overlapped four plates at room temperature, while the bending strength was measured using the standard three-point bending method for a single plate with size of 15 × 5 × 0.5 mm³. Fig. 6a shows the compressive pressure as a function of strain for the fully hydrogenated $LaFe_{11.4}Mn_{0.3}Si_{1.3}H_6/Cu$ plates sintered at different temperatures and pressures. The compressive strength is 54 MPa for the plate under 600 °C and 100 MPa, 55 MPa for the one under 600 °C and 200 MPa, and 75 MPa for the one sintered at 500 °C and 300 MPa. These 3 kinds of plates can be successfully cut by wire electrical discharge machining while the plate sintered under 500 °C and 100 MPa is unable to be machined due to the bad mechanical properties. The plate prepared at 500 °C and 300 MPa shows the largest compressive strength, which can be further polished owing to the better mechanical properties while the latter two (600 °C and 100 MPa, 600 °C and 200 MPa) cannot (Table 1). Generally, for the materials sintered at relative low temperature (< 1300 °C), the mechanical strength depends on density. With increasing the sintered temperature and pressure, the pores formed during sintering process reduce and the density and mechanical properties increase. From Fig. 3, one can note that the plate prepared at 500 °C and 300 MPa shows the largest density compared to the other two cases (600 °C and 100 MPa, 600 °C and 200 MPa), hence the compressive strength is also the largest. The strength value (75 MPa) is higher than that of $La(Fe, Si)_{13}H_6$-Cu hydrides prepared through mixing the metallic $MgNiYH_x$ hydride (57.6 MPa) [31]. For the $LaFe_{11.4}Mn_{0.3}Si_{1.3}H_6/Cu$ plate (500 °C, 300 MPa) showing the largest compressive strength, we also measured the bending strength by using the standard three-point bending method. The result is shown in Fig. 6b. The bending strength is about 20 MPa, which is a little higher than the polymer-bonded $La(Fe,Mn,Si)_{13}H_x$ plates with 5 wt% epoxy adhesive (bending strength: 13 MPa) [32].

Our studies indicate that the introduction of Cu (though the amount is small, 4%) plays a critical role for the improved mechanical properties of such thin plates with hydrogen. Although the melting point of Cu is as high as 1083 °C, it can be softened at high temperature and shows a bonding effect in the composites under a relative high molding pressure. However, a high temperature (such as 700 °C) affects the stability of $La(Fe,Si)_{13}$ compounds and leads to a large amount of Fe precipitation (see Fig. 1), resulting in the reduction of magnetocaloric effect. Through careful investigations, the optimal conditions (500 °C, 300 MPa, 5min) were obtained, where Cu plays an appropriate bonding

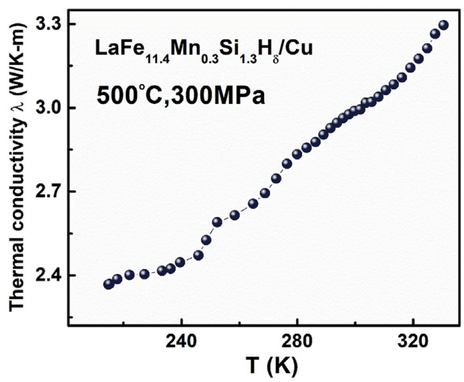

Fig. 7. Temperature dependence of the thermal conductivity λ measured in zero magnetic field for the $LaFe_{11.4}Mn_{0.3}Si_{1.3}H_8$/Cu hydride plate prepared at 500 °C and 300 MPa.

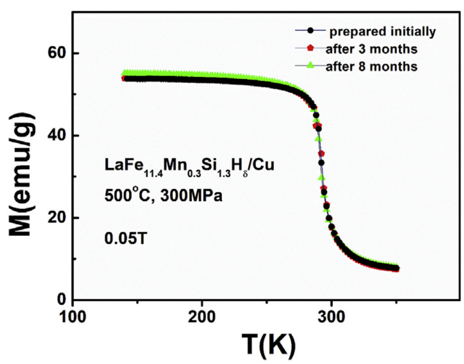

Fig. 8. Temperature dependent magnetization measured under a magnetic field of 0.05 T for the $LaFe_{11.4}Mn_{0.3}Si_{1.3}H_6$/Cu hydride plate (500 °C, 300 MPa) prepared initially, after 3 months and after 8 months.

effect. We also prepared the La(Fe,Mn,Si)$_{13}$H$_8$/Cu composites at many other conditions, as shown in Table 1. For condition (500 °C, 100 MPa), the composites cannot be cut into plates as thin as 0.5 mm owing to the poor mechanical properties, where the softened Cu particles have no bonding effect under such low molding pressure. For the conditions (600 °C, 100 MPa; 600 °C, 200 MPa), though the 0.5 mm thin plates can be successfully cut, the compressive strength is lower than that prepared at the optimal conditions (500 °C, 300 MPa) (see Fig. 6) and bend strength even cannot be measured, because the low molding pressure does not make Cu bond well and the mechanical properties are not good enough. The surface of the thin plates cannot be polished for measuring SEM backscattered electron (BSE) images (see Table 1).

Thermal conductivity is a critical factor that affects the performance of refrigerants in a device. We also measured thermal conductivity λ for the $LaFe_{11.4}Mn_{0.3}Si_{1.3}H_6$/Cu plate that shows the best mechanical properties. The result is shown in Fig. 7. The λ is ranging from 2.4 W/Km to 3.3 W/Km in the temperature region from 215 K to 335 K, and it is 3.0 W/Km at 300 K. The value is higher than the previously reported, such as $LaFe_{11.6}Si_{1.4}H_y$ hydride (λ = 2.0 W/Km) [16], $LaFe_{11.6}Si_{1.4}H_y$/Cu(2-4 wt% Cu, λ = 2.3–2.5 W/Km) made by electroless plating [16], and the epoxy-bonded La–Fe–Co–Si (λ = 1.0–2.6 W/Km) [9]. However, such value is lower than those reported in some composites with metal at binder, such as La(Fe,Mn,Si)$_{13}$H$_y$ bound by silver-epoxy polymer (λ = 5 W/Km, 15 wt% silver-epoxy) [33], and $LaFe_{11.6}Si_{1.4}$Hy/Sn (λ = 6.8 W/Km, 25 wt% Sn) [12]. This result indicates that the lots of unfilled pores in the structure of present composites affect the thermal conductivity. For a multiphase system with pores, the thermal conductivity will be reduced if the pores were treated as isolated inclusions whose conductivity approaches zero.

Generally, hydrogen-unsaturated La(Fe,Si)$_{13}$H$_8$ hydrides show an unusual instability. When the hydride is held within a few K around its Curie temperature T_C, the single magnetic transition will split into two transitions with a gap as wide as ~20 K, i.e. the so-called "age splitting" [20]. Such unusual instability seriously affects the performance of refrigerants. We examined the age stability for the present hydrogenated $LaFe_{11.4}Mn_{0.3}Si_{1.3}H_6$/Cu plates by comparing the T_C before and after an aging treatment at room temperature. Specifically, Fig. 8 gives the comparison of temperature dependent magnetization measured under a magnetic field of 0.05 T for $LaFe_{11.4}Mn_{0.3}Si_{1.3}H_6$/Cu (500 °C, 300 MPa) hydride plates for initially prepared, after 3 months and 8 months. The three curves were nearly overlap and show no signs of T_C shift. This excellent stability can be ascribed to the full hydrogenation, as well as the incorporation of Mn, which can enhance the stability of $LaFe_{13\text{-}x\text{-}y}Mn_ySi_xH_z$ hydrides and avoid age splitting [20].

4. Conclusion

In summary, to produce fully hydrogenated metal-bonded La(Fe$_x$Si$_{1\text{-}x}$)$_{13}$H$_8$ plates with large entropy change, good mechanical properties and thermal conductivity, and excellent age stability, we propose to prepare [La(Fe$_{0.974}$Mn$_{0.026}$)$_{11.7}$Si$_{1.3}$]$_{1\text{-}x}$/Cu$_x$ (x = 4 wt%) plates as thin as 0.5 mm at first by using park plasma sintering and wire cutting technique, and then perform hydrogenation by annealing the plates in a hydrogen atmosphere. It is found that the introduced small amount of bonding metal (4 wt%) only appears at partial surfaces of $LaFe_{11.4}Mn_{0.3}Si_{1.3}$ powders. Lots of holes and naked surfaces still left, which favor hydrogen atoms into 1:13 lattice. As a result, saturated hydrogenation can be still achieved, and the T_C locates to be around room temperature and keeps excellent age stability. Meanwhile, the existence of the Cu can be softened at the optimal conditions (500 °C, 300 MPa), hence acts binder and improve the mechanical properties and thermal conductivity. All these characteristics favor the plates to be used as effective refrigerants in a room temperature magnetic refrigerator.

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