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Research articles

Simultaneous plate forming and hydriding of La(Fe, Si)$_{13}$ magnetocaloric powders

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ABSTRACT

In this work, we propose a way to simultaneously realize the plate forming and hydriding of La(Fe, Si)$_{13}$ powders by mixing hydride MgNiYH$_x$ and solder powders Sn$_{3.0}$Ag$_{0.5}$Cu. Under the annealing of the green compact, the hydriding of La(Fe, Si)$_{13}$ was realized through absorbing the released hydrogen from the metallic hydride MgNiYH$_x$. The Curie temperature of La(Fe, Si)$_{13}$ alloy increased from 213 K to 333 K and hysteresis reduced from 3.3 J/kg·K to 1.33 J/kg·K. Due to the bonding of Sn$_{3.0}$Ag$_{0.5}$Cu powders, the mechanical strength of the composite compact was highly improved in comparison to the compact of La(Fe, Si)$_{13}$ powders alone.

1. Introduction

La(Fe, Si)$_{13}$ alloys have drawn wide attentions as the magnetic refrigerant due to their high magnetocaloric effect and cheap price. On the other hand, the low Curie temperature is the shortcoming of the ternary La(Fe, Si)$_{13}$ alloys for the high temperature refrigeration applications [1–4]. Several methods of improving the Curie temperature have been proposed [5–16]. Through implanting the interstitial hydrogen La(Fe, Si)$_{13}$H$_y$ was fabricated to increase the Curie temperature to fulfill the requirements of the room temperature magnetic refrigeration materials [9–16]. Gas hydriding was widely performed to form La(Fe, Si)$_{13}$H$_y$ to adjust the Curie temperature under the high pressure hydrogen [9–14]. Recently, the electrolytic hydriding was also confirmed to be an effective way to form the hydrides of La(Fe, Si)$_{13}$ type alloys [15–16]. Both gas and electrolytic hydriding are carried out on the powders. Therefore, the plate forming of such hydriding powders must be performed subsequently in the case the plate shape of magnetocaloric media is designed to build the refrigeration system.

However, the brittle feature of La(Fe, Si)$_{13}$ -based alloys increase the difficulties of plate shaping. In order to get the bulk plate and overcome the shortcoming of materials brittleness, resin [17], polymer [18], eutectic alloy [19] and amorphous metal matrix [20] were tested to bond La(Fe, Si)$_{13}$ particles, which strengthen the magnetic powder material molding and promote the practical application of magnetic refrigeration. It was also found that sintering the broken LaFe$_{11.6}$Si$_{1.4}$ powders could improve the structural stability and decrease the magnetic hysteresis [14]. Regarding La(Fe, Si)$_{13}$H$_y$ powders, the plate shaping usually causes the decomposition of hydrides to degrade the magnetocaloric effect. It was reported that the desorption of the hydrogen atoms starts at the temperature over 150 °C [6]. Thus, the way of fabricating the plate of La(Fe, Si)$_{13}$H$_y$ powders with the relatively good magnetocaloric performance is highly deserved to be developed.

In this work, we simultaneously realize the plate shaping and solid hydriding of La(Fe, Si)$_{13}$ based alloy powders through mixing the metallic hydride MgNiYH$_x$ (MgNiYH$_x$ represents the hydrogenated Mg$_2$NiY, which usually includes MgNiH$_4$ hydrides and MgH$_2$ hydrides) and solder powders Sn$_{3.0}$Ag$_{0.5}$Cu. It was observed that the Curie temperature increased from 213 to 313 K. Through adding solder powders, the compressive strength and ductility were highly improved in comparison to the compact of the naked La(Fe, Si)$_{13}$ powders. The stability of the obtained La(Fe, Si)$_{13}$H$_y$ was evaluated through ageing too. Note that the Curie temperature of magnetocaloric powders can be experimentally controlled through varying the ratio of MgNiH$_4$ hydrides and annealing temperature. In this paper, the results with a fixed ratio of additions are focused to demonstrate the feasibility of the current experimental method.

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2. Experimental details

The alloy of $LaFe_{11.65}Si_{1.35}$ was arc-melted and vacuum annealed at 1323 K for 3 days. The grounded powders with the size of 30–110 μm [21] was obtained and mixed with the metallic hydride $MgNiYH_x$ powder (<30 μm) uniformly with the weight ratio of 9:1. The mixed powders were pressed into Φ 10 mm × 10 mm cylinder under 280 MPa, and was sealed in vacuum quartz tubes to be sintered at 663 K for 20 min, in which the $LaFe_{11.65}Si_{1.35}$ powders will absorb the released hydrogen atoms from metallic hydride $MgNiYH_x$ and simultaneously remain as the plate shape. The solder powders $Sn_{3.0}Ag_{0.5}Cu$ (20 wt%, the main component is Sn) was further added to improve the strength of green compacts. Phase constitution and lattice parameters of the samples was determined by powder X-ray Diffraction (XRD) on a Philips X'Pert Plus Diffractometer with Cu *Ka* radiation. Magnetic measurements were performed using superconducting quantum interference device (Verse-Lab) magnetometer. The isothermal magnetic entropy change was calculated from isothermal magnetization curves in the vicinity of T_C by using the thermodynamic Maxwell relation. The compressive stress–strain curves were analyzed by the metal compressive strength tester, and the surface microstructure of the sample was analyzed by scanning electron microscope (SEM).

3. Results and discussion

The formation of $LaFe_{11.65}Si_{1.35}H_y$ was characterized by XRD patterns for the sintered samples: the naked sample $LaFe_{11.65}Si_{1.35}$, its composite materials of ($LaFe_{11.65}Si_{1.35}$ + $MgNiYH_x$) and ($LaFe_{11.65}Si_{1.35}$ + $MgNiYH_x$ + $Sn_{3.0}Ag_{0.5}Cu$), as shown in Fig. 1. The sintered $LaFe_{11.65}Si_{1.35}$ consisted of $NaZn_{13}$-type matrix phases and the trace remaining α-Fe. The phase constituents were not affected after mixing the hydride $MgNiYH_x$ or $Sn_{3.0}Ag_{0.5}Cu$, other than some diffraction peaks from the mixed components. In comparison to the naked sample, the peak shift of $NaZn_{13}$-type matrix phase is obvious for the mixed composite samples, which indicate an increase of the lattice parameters. Therefore, it can be deduced that the hydrogen atoms were released from the metallic hydride $MgNiYH_x$, and successfully absorbed by $LaFe_{11.65}Si_{1.35}$ phases during the sintering process.

The hydriding can be further confirmed by measuring the temperature dependence of the magnetization (*M*). Fig. 2 gives the curves of *M* versa *T* of the sintered samples under a magnetic field of 100 Oe, in which the curves were also included for the composite sample ($LaFe_{11.65}Si_{1.35}$ + $MgNiYH_x$) after ageing at 333 K (close to the Curie temperature) for 24 h under the vacuum or environmental atmosphere. All samples present a clear magnetic transition from ferromagnetic to paramagnetic features. After mixing the metallic hydride $MgNiYH_x$, the Curie temperature of 1:13 phase increased from 213 K to 333 K, and the addition of $Sn_{3.0}Ag_{0.5}Cu$ had no significant influence on the Curie temperature, in agreement with the XRD results. The increase of T_C after adding metallic hydride $MgNiYH_x$ can be attributed to the strengthened ferromagnetic coupling caused by the lattice expansion due to the introduction of interstitial hydrogen atoms [22]. In addition, the Curie temperature remains close to the original 333 K after long time ageing at 333 K under a vacuum or environmental atmosphere, implying the high stability of the achieved $LaFe_{11.65}Si_{1.35}H_y$ phase.

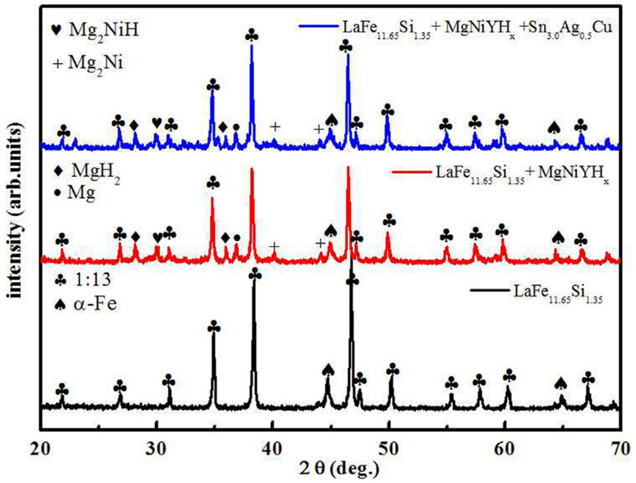

Fig. 1. XRD patterns of $LaFe_{11.65}Si_{1.35}$, its composite materials of ($LaFe_{11.65}Si_{1.35}$ + $MgNiYH_x$) or ($LaFe_{11.65}Si_{1.35}$ + $MgNiYH_x$ + $Sn_{3.0}Ag_{0.5}Cu$), respectively.

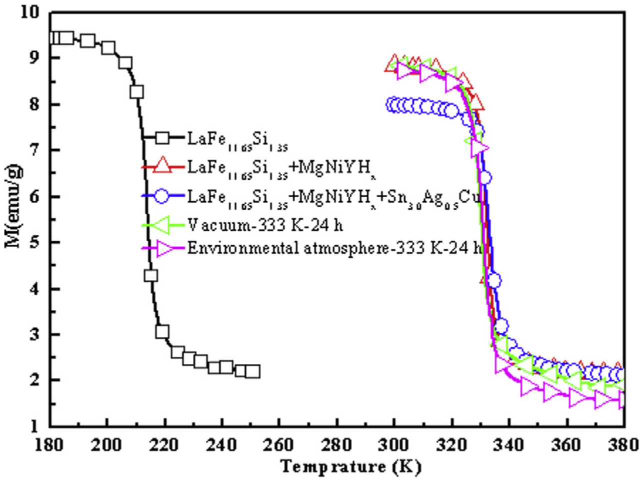

Fig. 2. Temperature dependence of the magnetization of $LaFe_{11.65}Si_{1.35}$ and its composite materials measured in the field-cooled (FC) process under a magnetic field of 100 Oe, including the ageing composite materials of $LaFe_{11.65}Si_{1.35}$ + $MgNiYH_x$ at a temperature close to Curie temperature for 24 h under vacuum or environmental atmosphere.

Magnetization isotherms of all the samples were measured in a wide temperature range, in which the temperature step was 3 K in the vicinity of T_C. The sweep rate of the field was slow enough to ensure that the *M*–*H* curves were recorded in an isothermal process. Fig. 3(a)–(c) show the magnetization isotherms of $LaFe_{11.65}Si_{1.35}$ and its composite materials. The saturation magnetizations M_s are 137 emu/g, 118 emu/g, 96 emu/g respectively for the naked $LaFe_{11.65}Si_{1.35}$, the composites with $MgNiYH_x$ or $MgNiYH_x$ + $Sn_{3.0}Ag_{0.5}Cu$. The decrease of the saturation magnetizations M_s is mainly attributed to the diluted effect from the mixed components. Valuably, the maximum magnetic hysteresis loss close to the Curie temperature was largely reduced from 3.3 J/kg·K to 1.3 J/kg·K and 0.7 J/kg·K respectively for the samples with $MgNiYH_x$ or $Sn_{3.0}Ag_{0.5}Cu$ based on the evaluation of the area of the isothermal magnetizing curves. There are two factors, which could reduce the magnetic hysteresis loss. Regarding the sample with metallic hydride $MgNiYH_x$, the reduced magnetic hysteresis loss is mainly owing to the implantation of hydrogen atoms, which weakens the trend of first-order magnetic transition [23]. The further reduction of the magnetic hysteresis loss could originate from the released strain owing to the melting solder powder during sintering [14].

The isothermal magnetic entropy change |ΔS| can be obtained in terms of the evaluation of the Maxwell relation $\Delta S(T,H) = \int_0^H (\partial M/\partial T)_H dH$ [24]. Fig. 3(d) shows the magnetic entropy change of $LaFe_{11.65}Si_{1.35}$ and its composite materials under the magnetic field of 3 T. The maximal |ΔS| are 12.4 J/kg·K, 10.6 J/