The high-temperature hydrogenation behavior of LaFe$_{11.6}$Si$_{1.4}$ and splitting of LaFe$_{11.6}$Si$_{1.4}$H$_y$ magnetocaloric transition

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ABSTRACT

LaFe$_{11.6}$Si$_{1.4}$ samples were hydrogenated at the same initial hydrogen-filling pressure of 0.6 MPa and different temperatures (from 393 K to 478 K). The hydrogen absorption kinetics performance, phase structures and Curie temperature (T$_C$) of these alloys were investigated. The results show that all samples have excellent hydrogen absorption kinetics performance, the NaZn$_{13}$-type main structure of these LaFe$_{11.6}$Si$_{1.4}$H$_y$ alloys is stable during the fore-and-aft hydrogenation processes and their T$_C$s vary from 326.9 K to 277.7 K by adjusting hydrogen content from 1.26 to 0.936. The high-temperature hydrogenation can markedly save the hydrogen saturation time of LaFe$_{11.6}$Si$_{1.4}$ alloys and precisely adjust the T$_C$ of these alloys. In addition, the split of magnetocaloric transition is observed by analyzing Differential Scan Calorimetry curves of the alloys hydrogenated from 443 K to 463 K. Further investigation of two typical samples hydrogenated at 443 K and 463 K shows that the split transition peaks change into a sharp single transition peak after annealing these samples at 373 K for 24 h and the split transition peaks re-emerge after storing the annealed samples near T$_C$ for 14 days. The recovery and split of the peaks imply that the fully hydrogenated LaFe$_{11.6}$Si$_{1.4}$ alloys at high treatment temperature are all partially hydrogenated LaFe$_{11.6}$Si$_{1.4}$ alloys when stored or used at room temperature.

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1. Introduction

The LaFe$_{13-x}$Si$_x$ alloys crystallizing in the cubic NaZn$_{13}$ structure are one of the most promising solid state refrigerants for magnetic refrigeration due to many advantages, such as giant magnetocaloric effects (MCEs), low cost of raw materials, adjustable Curie temperature (T$_C$) and large cooling capacity [1,2]. It is well known that the T$_C$ of LaFe$_{13-x}$Si$_x$ ($1.2 \leq x \leq 1.6$) alloys, changing from 175 K for $x = 1.2-199$ K for $x = 1.6$, is far from room temperature [3–6]. In order to adjust the T$_C$ of LaFe$_{13-x}$Si$_x$ alloys, a great deal of effort has been done, such as substituting Fe with Mn [7,8], Co [9] or Cr [10], substituting La with Ce [11], Pr [12] or Ca [13] and adding interstitial atoms H [14,15], C [16,17] or B [18,19]. It has been reported that the introducing of interstitial H atoms is the most efficient method to improve the T$_C$ to near room temperature as well as to keep the large magnetocaloric effect [20,21]. Some researchers used LaFeSiH

alloys as refrigerants materials to obtain the large cooling power in a large-scale rotary magnetic refrigerator [22]. It is known that, in LaFe$_{13-x}$Si$_x$H$_y$ system, the T$_C$ is strongly dependent on the H content y and LaFe$_{13-x}$Si$_x$H$_y$ alloys with a first order magnetic transition at the same x but varying y show different T$_C$s [14,15]. A positive linear relationship between the H content y and T$_c$ for the La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$H$_y$ compounds was found by A.Fujita [23]. The hydrogen absorption effect of LaFe$_{13-x}$Si$_x$ alloys is influenced by many process parameters, such as the treatment temperature, hydrogen gas pressure, hydrogenation time and particle size [24–27]. With a given particle size, the hydrogen saturation time as well as the hydrogen absorption capacity decreases with the increase of the treatment temperature [24]. In addition, small particle size and narrow size range benefit the homogeneity of hydrogen distribute in LaFe$_{13-x}$Si$_x$ alloys [27]. The usual way to control H content during the hydrogenation process is firstly to hydrogenate alloys until saturation, and then to desorb some H by thermal desorption [28]. However, the concentration of H desorption during this process is difficult to control. Recently, a new process route [29], called Hydrogen-Decrepitation-Sintering-Hydrogenation

(HDSH), is proposed as a possible alternative to fabricate bulk parts of La(Fe,Si)$_{13}$H$_y$, but it didn't show how to prepare LaFe$_{13-x}$Si$_x$H$_y$ alloys with varying y. So it is necessary to find a method to precisely adjust the H content in LaFe$_{13-x}$Si$_x$H$_y$ alloys.

In this paper, the high-temperature hydrogenation method is used to prepare a set of fully hydrogenated LaFe$_{11.6}$Si$_{1.4}$H$_y$ alloys. The hydrogen absorption kinetics performance, phase structures and Curie temperature (T$_C$) of these alloys are investigated. Interestingly, it is found that some LaFe$_{11.6}$Si$_{1.4}$H$_y$ alloys split into two magnetocaloric transitions separated by a temperature interval at room temperature in Differential Scanning Calorimetry (DSC) curves. This phenomenon is similar to the age splitting of unsaturated LaFe$_{13-x}$Si$_x$H$_y$ alloys reported in Refs. [30–32].

2. Experimental

The LaFe$_{11.6}$Si$_{1.4}$ alloys with nominal composition were prepared by arc melting under the protection of high-purity argon atmosphere. The purities of raw materials La, Fe and Si were 99.4, 99.9 and 99.9999 wt. %, respectively. Considering the loss of lanthanum, an excess of 4% of La was systematically added. The alloy buttons were re-melted five times to ensure homogeneity. To obtain NaZn$_{13}$-type main phase, the as-cast LaFe$_{11.6}$Si$_{1.4}$ alloy was annealed in a ZM-40-16 vacuum molybdenum wire furnace at 1473 K for 5 h [33,34].

The hydrogen absorption kinetics curves of the alloys were measured by the PCTPro-2000 Sieverts Gas Sorption Analyzer made by Hy-Energy Company. The powder samples were made through mechanical shattering process and the particle size measured by the Standard sample sieve was in the range of 0.15−0.45 mm. Before the hydrogen absorption test, the annealed alloy was activated twice as follows: putting the powder samples into the reactor, and then the reactor was firstly vacuumized at 298 K for 30 min and subsequently vacuumized at 653 K for 60 min. When hydrogenating, H$_2$ with a high purity of 99.999 wt. % was introduced. Considering the practical application and production cost, 0.6 MPa was chosen as the hydrogen-filling pressure, and the samples were kept at different high treatment temperatures (from 393 K to 478 K) for 1 h to saturate, followed by cooling slowly to room temperature. Finally, a series of samples with different H contents were prepared, the hydrogen content in the LaFe$_{11.6}$Si$_{1.4}$H$_y$ alloys was determined by the ideal gas law.

The X-ray diffraction (XRD) analysis was performed in a DX-2600 powder diffractometer with CuK$_\alpha$ radiation to analyze the phase structure. A stepping scanning mode with a scanning step of 0.04° (2θ) was adopted. The transition temperatures of the LaFe$_{11.6}$Si$_{1.4}$ hydrides were measured by the TA.Q200 DSC with a heating velocity of 10 K/min under the protection of N$_2$ atmosphere.

3. Results and discussion

3.1. Hydrogen absorption kinetics performance

Fig. 1 shows the hydrogen absorption kinetics performance of LaFe$_{11.6}$Si$_{1.4}$ alloys. The hydrogen absorption of all samples can approach to a saturation state within about 1 h at the same initial hydrogen-filling pressure of 0.6 MPa but varying treatment temperature. The hydrogen saturation time of these samples decreases from 45 min (at 393 K) to 4 min (at 478 K). Compared with the hydrogen saturation time of 670 min at initial hydrogen-filling pressure of 2 MPa and room temperature [35], it can be seen that the hydrogen absorption kinetics performance of samples in this work is extremely excellent, indicating that high-temperature
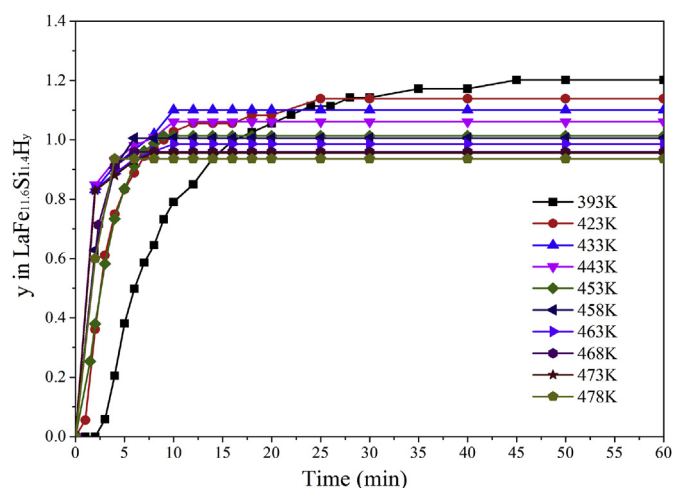

Fig. 1. The hydrogen absorption kinetics curves of the LaFe$_{11.6}$Si$_{1.4}$ alloys at 0.6 MPa hydrogen-filling pressure and different treatment temperatures.

hydrogenation is an efficient way to save the hydrogenation time and improve the production efficiency.

As shown in Fig.1, the hydrogen absorption capacity of LaFe$_{11.6}$Si$_{1.4}$ alloys decreases with the increase of temperature. The hydrogen content y of LaFe$_{11.6}$Si$_{1.4}$H$_y$ alloys changes from 1.26 to 0.936 while the treatment temperature varies from 393 K to 478 K. The treatment temperature T dependence of the hydrogen content y for the LaFe$_{11.6}$Si$_{1.4}$H$_y$ alloys is shown in Fig. 2. A linear correlation between T and y with negative slope indicates that high-temperature hydrogenation is available to obtain the LaFe$_{11.6}$Si$_{1.4}$H$_y$ alloys with varying H content y where given particle size and hydrogen-filling pressure are required.

3.2. Phase structure analysis

The X-ray diffraction patterns of the annealed LaFe$_{11.6}$Si$_{1.4}$ alloy and their hydrides are shown in Fig. 3. In these alloys, the major phase is cubic NaZn$_{13}$ structure (space group Fm3c) with minor α-Fe phase marked by solid black star. Contrasting to the peaks of the XRD patterns for unhydrogenated LaFe$_{11.6}$Si$_{1.4}$ alloys, the peaks of NaZn$_{13}$ structure for hydrogenated LaFe$_{11.6}$Si$_{1.4}$ alloys shift slightly to low degree, which implies that hydrogen atoms enter the NaZn$_{13}$
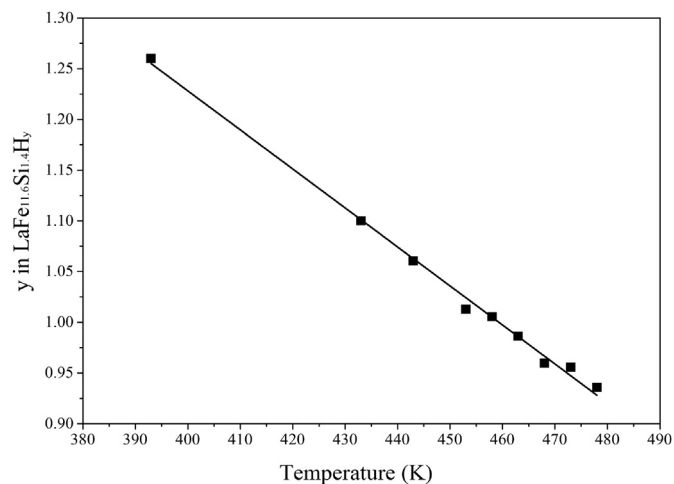

Fig. 2. The hydrogen content y as a function of treatment temperature T for LaFe$_{11.6}$Si$_{1.4}$H$_y$ alloys.