Effect of Hydrogen Absorption-Desorption Treatment on the Magnetocaloric Effect of La0.6Pr0.4Fe11.4Si1.6B0.2 Alloy (Postprint)

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Abstract

La0.6Pr0.4Fe11.4Si1.6B0.2 alloy was prepared using raw materials of industrial purity. The precipitated phases, Curie temperature, and magnetocaloric properties were analyzed by XRD and VSM, and the influence of hydrogen absorption and desorption treatments on the magnetocaloric properties was investigated. The results show that the Curie temperatures of the annealed alloy after hydrogen absorption treatment at 0.13 and 0.2 MPa reached 320 and 321 K, respectively; samples with higher hydrogen absorption pressure exhibited difficulty in hydrogen desorption; after hydrogen desorption at 473 K, the Curie temperature of the sample hydrogenated at 0.13 MPa decreased to the room temperature range. Hydrogen desorption led to a decrease in the maximum magnetic entropy change of the hydride and an enhancement of the relative cooling power (RCP).

Full Text

Influence of Hydrogen Absorption and Desorption on Magnetocaloric Effect of $La_{0·6}Pr_{0·4}Fe_{11·4}Si_{1·6}B_{0·2}$ Alloy

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Abstract

The $La_{0·6}Pr_{0·4}Fe_{11·4}Si_{1·6}B_{0·2}$ alloy was prepared using industrial-grade raw materials. The precipitated phases, Curie temperature, and magnetocaloric properties of the alloy were analyzed using X-ray diffraction (XRD) and vibrating sample magnetometry (VSM). The influence of hydrogen absorption and desorption treatments on the alloy’ s magnetocaloric properties was investigated. Results show that after hydrogen absorption at 0.13 and 0.2 MPa, the Curie temperatures of the annealed alloy reached 320 and 321 K, respectively; samples hydrogenated at higher pressure exhibited more difficult hydrogen desorption. For the sample hydrogenated at 0.13 MPa, desorption at 473 K reduced the Curie temperature to the room temperature range. Desorption led to a decrease in the maximum magnetic entropy change of the hydride and an increase in the relative cooling power (RCP).

Keywords: metallic materials, magnetic materials, magnetocaloric properties, hydrogen desorption, stability, Curie temperature

Introduction

The development of magnetic materials with large room-temperature magnetocaloric effects represents a major research focus for universities and research institutions worldwide [1-4]. In particular, La(Fe,Si)$_{13}$-based alloys with the NaZn$_{13}$-type crystal structure have attracted considerable attention due to their large magnetocaloric effect, low rare-earth content, absence of toxic elements, and ease of alloying and preparation [5]. The Curie temperature of La(Fe,Si)$_{13}$-based alloys is far below room temperature, and hydrogenation treatment is commonly employed to increase their Curie temperature [6-8]. While hydrogenated materials maintain a relatively large magnetocaloric effect, the hydrogen absorption process readily reaches saturation, causing the Curie temperature to exceed the room temperature range. Partial substitution of Fe with antiferromagnetic Mn can yield hydrides with Curie temperatures in the room temperature range even after saturated hydrogen absorption, but this approach reduces the material’ s magnetocaloric performance [9-11]. Parameters such as hydrogen absorption temperature and pressure significantly influence the magnetocaloric properties, with numerous studies focusing on the effects of the hydrogen absorption process on magnetic properties [12,13]. Research has shown that controlling hydrogen desorption after absorption can regulate the amount of hydrogen uptake [14-16]. Hydrogen atoms profoundly affect the Curie temperature but have minimal impact on the maximum magnetic entropy change. Therefore, controlling hydrogen content represents an effective method for obtaining materials with large room-temperature magnetocaloric effects [3,17], making control of hydrogen absorption a critical issue for developing room-temperature magnetic refrigeration materials.

Partial substitution of La with Pr can enhance the maximum magnetic entropy change of the material, and hydrogenation treatment for preparing materials with large magnetocaloric effects also helps reduce magnetic hysteresis [15,18-20]. Adding trace amounts of elements such as B or C can shorten the annealing time [17,21], but excessive addition leads to the formation of secondary phases and weakening of the first-order transition, degrading the alloy's magnetocaloric performance [22,23]. Trace additions of B and C help reduce magnetic hysteresis, promote formation of the main magnetocaloric phase, and improve preparation efficiency [24]. In this work, $La_{0\cdot6}Pr_{0\cdot4}Fe_{11\cdot4}Si_{1\cdot6}B_{0\cdot2}$ alloy was prepared using industrial-grade raw materials. After annealing and hydrogen absorption, desorption control was applied to investigate the influence of hydrogen absorption pressure on the desorption process and magnetocaloric effects of the material.

Experimental Methods

1.1 Alloy Preparation Industrial-grade La-Fe alloy ingots, B-Fe alloy powder, and Pr ingots were used as raw materials, with La comprising 69.11% and B comprising 29.3%. Fe and Si were used as bulk raw materials with purities above 99%. The nominal composition of the samples was $La_{0\cdot6}Pr_{0\cdot4}Fe_{11\cdot4}Si_{1\cdot6}B_{0\cdot2}$. The alloy was melted by medium-frequency induction melting and cast into square plate ingots weighing 6 kg with a thickness of 15 mm. Samples were taken from the middle of the ingot cross-section for annealing. The samples were placed in an annealing furnace, evacuated and then filled with argon gas, and annealed at 1473 K for 16 and 30 h before cooling naturally.

1.2 Hydrogen Absorption Treatment The annealed alloy was crushed and placed in a vacuum hydrogenation furnace for hydrogen absorption at 553 K for 5 h. After hydrogen absorption, the hydrogen pressure was maintained while naturally cooling to room temperature, yielding $La_{0\cdot6}Pr_{0\cdot4}Fe_{11\cdot4}Si_{1\cdot6}B_{0\cdot2}H$ hydrides. The hydrogen absorption pressures used in the experiments were 0.13 MPa and 0.2 MPa.

1.3 Hydrogen Desorption Treatment Hydrides of equal weight were placed in a desorption furnace, evacuated, and then filled with high-purity argon gas before heating to 473 K for desorption treatment for 75-240 min, yielding desorbed hydrides.

1.4 Property Testing A Philips PW1830 X-ray powder diffractometer (XRD, CuKα) was used to analyze the phases of annealed samples. A LakeShore 7407 vibrating sample magnetometer (VSM) was employed to measure the M-T and M-B curves of the samples. The magnetic field for M-T curve measurement was 0.05 T, while the magnetic field range for M-B curve measurement was 0-1.5 T with a step size of 0.05 T. The Curie temperature (TC) of the material was determined from the M-T curve (the temperature corresponding to the extremum point in the dM/dT-T curve). Several isothermal magnetization curves (M-B) were measured near TC, and the isothermal magnetic entropy change of the samples was calculated using the formula where M and M $_1$ are the magnetization values at magnetic field B and temperatures T and T $_1$, respectively:

$$S_m = -\sum_i$$

The maximum magnetic entropy change reflects the magnetocaloric performance of the material. The relative cooling power (RCP) provides a more accurate representation of the material’ s magnetic refrigeration capability, defined as the product of the maximum magnetic entropy change and the full width at half maximum of the magnetic entropy change versus temperature curve [25]. Therefore, the RCP values of the samples were calculated in this study.

Results and Discussion

Figure 1 [Figure 1: see original paper] shows the XRD patterns of samples annealed at 1473 K for 16 and 30 h. The patterns exhibit no diffraction peaks from α-Fe or La-rich phases, only diffraction peaks from the $NaZn_{13}$-type phase, indicating that a substantial amount of the main magnetocaloric phase formed in the alloy. Extending the annealing time facilitates formation of a single-phase magnetocaloric microstructure and improves compositional homogeneity of the main magnetocaloric phase, but excessively long annealing times reduce the alloy’ s maximum magnetic entropy change and increase its TC [26]. The heating M-T curves of annealed samples were measured at a magnetic field of 0.05 T (Figure 1b), and the TC values for samples annealed for 16 and 30 h were determined to be 198.7 and 201.7 K, respectively, by taking the derivative of the curves and identifying the extremum points. This result indicates that prolonged annealing time increases the TC of this alloy composition. M-B curves were measured at various temperatures near TC for both 16 and 30 h annealed samples, and the magnetic entropy change versus temperature curves for the annealed samples were obtained using equation (1) (inset in Figure 1b). Under a magnetic field of 0-1.5 T, the maximum magnetic entropy change values for the 16 and 30 h annealed samples were 9.1 and 8.6 J/kg · K, respectively. The more uniformly annealed 30 h sample was used for magnetocaloric performance analysis to investigate the effects of hydrogen absorption pressure, desorption time, and desorption temperature on the Curie temperature and magnetocaloric effect of the hydrides.

Figure 2 [Figure 2: see original paper] presents the thermomagnetic M-T curves of annealed and hydrogenated samples. As shown in Figure 2, the annealed sample exhibited a TC of 201.7 K, while hydrogenation substantially increased the TC beyond room temperature. After hydrogen absorption at 0.13 and 0.2 MPa, the TC values increased to 320 and 321 K, respectively. Different hydrogen absorption pressures resulted in different TC values for the hydrides, and for $La(Fe,Si)_{13}$-based alloys doped with trace B, the variation in TC of hydrogenated materials still follows the trend that higher hydrogen absorption pressure yields higher Curie temperature [3].

Figure 3 [Figure 3: see original paper] shows the isothermal magnetization curves M-B at various temperatures near TC and the SM-T curves obtained using equation (1) for $La_{0}·_{6}Pr_{0}·_{4}Fe_{11}·_{4}Si_{1}·_{6}B_{0}·_{2}$ alloy before and after hydrogenation. Figures 3a, b, and c present the M-B curves under a magnetic field of 0-1.5 T for the annealed sample, the 0.2 MPa hydrogenated sample, and the 0.13 MPa hydrogenated sample, respectively. As shown by the curves in Figure 3d, the maximum magnetic entropy changes under a 0-1.5 T magnetic field for the annealed sample, the 0.2 MPa hydrogenated sample, and the 0.13 MPa hydrogenated sample were 8.6, 8.0, and 7.9 J/kg · K, respectively, with corresponding relative cooling power (RCP) values of 98, 88, and 88 J/kg. These results demonstrate that while hydrogenation reduced the magnetic entropy and RCP of $La_{0}·_{6}Pr_{0}·_{4}Fe_{11}·_{4}Si_{1}·_{6}B_{0}·_{2}$ samples, the values remained relatively large.

Controlling the desorption time to reduce the hydrogen content of hydrides can lower their TC to the room temperature range. The relationship between TC and desorption time for hydrides obtained under different hydrogen absorption processes during desorption at 473 K is shown in Figure 4 [Figure 4: see original paper]. Within the experimental time frame, the TC of the 0.2 MPa hydrogenated sample remained constant after a certain desorption time, whereas the TC of the 0.13 MPa hydrogenated sample continuously decreased with increasing desorption time. Both hydrides exhibited a similar trend where the rate of TC reduction slowed with longer desorption time. This occurs because desorption was conducted in a sealed furnace, where the released hydrogen gas and hydrogen atoms within the hydride gradually reached equilibrium.

For the sample hydrogenated at higher pressure, the TC decreased to 304 K after 180 min of desorption, and further extension of desorption time made it difficult to reduce TC further. For the sample hydrogenated at lower pressure, the TC decreased below 300 K after 75 min of desorption, and increased desorption time to 90 min reduced the TC to 295 K. When desorption time reached 105 min, the TC further decreased to 294 K, but the desorption rate clearly slowed. For the same desorption temperature, samples hydrogenated at higher pressure exhibited lower desorption rates. Therefore, samples hydrogenated at higher pressure undergo more difficult desorption and possess higher stability. Considering the effect of Curie temperature, hydrides with higher Curie temperature have lower desorption rates. Since the Curie temperature of hydrides is closely related to hydrogen content, the high stability of samples hydrogenated at higher pressure originates from their higher hydrogen content. Desorption treatment can reduce the TC of materials and also affect their magnetocaloric properties.

Figure 5 [Figure 5: see original paper] shows the isothermal magnetization curves M-B at various temperatures near TC and the magnetic entropy change versus temperature curves (SM-T) for desorbed samples. Figures 5(a, b, c) present the M-B curves for the 0.2 MPa hydrogenated sample after 180 min desorption, and the 0.13 MPa hydrogenated samples after 75 min and 105 min desorption, respectively. As shown by the SM-T curves in Figure 5d, the maximum magnetic entropy changes under a 0-1.5 T magnetic field for the 0.2 MPa hydrogenated sample after 180 min desorption and the 0.13 MPa hydrogenated samples after 75 min and 105 min desorption were 6.5, 6.8, and 6.8 J/kg·K, respectively, with corresponding RCP values of 91, 102, and 102 J/kg. It should be noted that the RCP value for the 0.13 MPa hydrogenated sample after 75 min desorption is an estimated value because the measurement range of its SM-T curve did not cover the entire half-width. This value was obtained by extrapolation based on the curve trend and differs somewhat from the actual value, serving only to indicate the trend. The above analysis indicates that while the maximum magnetic entropy change of desorbed samples is lower than that of hydrogenated samples, the RCP values of desorbed samples are higher than those of hydrogenated samples, and desorbed samples still possess considerable room-temperature magnetic refrigeration capability.

Conclusions

1. During the desorption process of $La_{0\cdot6}Pr_{0\cdot4}Fe_{11\cdot4}Si_{1\cdot6}B_{0\cdot2}$ alloy, the released hydrogen gas establishes equilibrium with hydrogen within the metal. After a certain desorption time, TC approaches a constant value that is related to the hydrogen content in the hydride. Hydrogenated samples subjected to desorption treatment at 473 K exhibited reduced maximum magnetic entropy change but increased relative cooling power (RCP) values.
2. Hydrogen absorption pressure significantly influences the desorption process; higher absorption pressure makes hydrogen more difficult to release, resulting in higher stability of the resulting hydride. The high stability of hydrides produced at higher absorption pressure originates from their higher hydrogen content.
3. Using industrial raw materials combined with hydrogen absorption and desorption treatment enables preparation of hydride magnetic refrigeration materials with large room-temperature magnetocaloric effects. For the 0.13 MPa hydrogenated sample subjected to desorption treatment at 473 K, the hydride exhibited a TC of 294 K, a maximum magnetic entropy change of 6.8 J/kg·K under a 0-1.5 T magnetic field, and an RCP of 102 J/kg.

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Note: Figure translations are in progress. See original paper for figures.