Hydrogen Absorption of LaFe$_{10.9}$Co$_{0.8}$Si$_{1.3}$ Compound under Low Hydrogen Gas Pressure

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Abstract. The effects of hydrogen absorption on structure, Curie temperature and phase transition property for the LaFe$_{10.9}$Co$_{0.8}$Si$_{1.3}$ compound are investigated by X-ray diffraction (XRD) and differential scanning calorimeter (DSC) in a 1-atm H$_2$ gas. The original compound and hydride present cubic NaZn$_{13}$-type structure. The Curie temperature of LaFe$_{10.9}$Co$_{0.8}$Si$_{1.3}$ shifts from 277K to 346K and temperature range of the phase transition becomes wider significantly after hydrogen absorption.

Introduction

Magnetic refrigerator research indicates, the La(Fe$_x$Si$_{1-x}$)$_{13}$-based compound with the itinerant-electron metamagnetic (IEM) transition is a kind of magnetic refrigeration material with very promising practicability[1-6]. But lower Curie temperature of La(Fe$_x$Si$_{1-x}$)$_{13}$ makes it difficult to be used in domestic and high temperature appliances. To realize room and high temperature magnetic refrigerators, it is necessarily to raise its $T_C$. It has been demonstrated that $T_C$ can be lifted by introducing Co or interstitial atoms such as H into La(Fe$_x$Si$_{1-x}$)$_{13}$[7-8]. After controlling hydrogen absorption in a 50-atm H$_2$ atmosphere, $T_C$ increases up to about 280~330K[9-11]. But the work in this aspect is mainly aimed at hydrogen absorption under a high H$_2$ pressure from 5 to 50 atm. Little study on hydrogen absorption under low H$_2$ pressure has been carried out so far.

For the sake of practical application, we prepare hydride of LaFe$_{10.9}$Co$_{0.8}$Si$_{1.3}$ compound in hydrogen gas under 1 atmospheric pressure at 623 K and study the effects of interstitial H atom on structure and Curie temperature in the present work. The phase transition properties of the compounds are also investigated.

Experiment

LaFe$_{10.9}$Co$_{0.8}$Si$_{1.3}$ compound was prepared from pure ($\geq$99.9%) elements by using arc-melting method in argon atmosphere. Each arc-melted ingot was flipped over and remelted at least three times to ensure its homogeneity. The ingots were annealed at 1373K for 10 days, and after that quenched in ice water. The hydrogen absorption took place in a furnace equipped with a gas supply plant. The samples were crushed into powder with about 0.8mm in size. Then the powders were kept in an unsealed tube with hydrogen gas flow, which was inserted into the centre of the furnace. The powders were heated while hydrogen was poured through the tube. By utilizing this system, the pressure of hydrogen was kept 1 atm stably. The temperatures of hydrogen absorption were measured by thermocouple in the tube. The duration of hydrogen absorption is selected to be 4 hours to ensure that the saturation was reached. The hydrogen concentration was determined by the weighing method. The structures of parent alloy and corresponding hydrides were identified by powder x-ray diffraction.
(XRD) and the phase transition of the compounds were carried out by differential scanning calorimeter (DSC).

Results and Discussion

X-ray diffraction analysis on powdered sample is shown in Fig.1. The main phase in LaFe$_{10.9}$Co$_{0.8}$Si$_{1.3}$ is a cubic NaZn$_{13}$-type structure, additionally a small amount of $\alpha$-Fe (indicated by symbol *). Results in the unsealed hydrogen absorption environment, content of $\alpha$-Fe increased after hydrogen absorption, but the hydride LaFe$_{10.9}$Co$_{0.8}$Si$_{1.3}$H$_{1.8}$ remain cubic NaZn$_{13}$-type structure. The diffraction peaks shift toward low angles compared with original compound LaFe$_{10.9}$Co$_{0.8}$Si$_{1.3}$. It is indicated that hydrogen atoms have entered interstices between crystal lattices as interstitial atoms, leading to an expansion of unit cell volume. After hydrogen absorptions at 623K, the values of lattice constant an increase from 11.4199 to 11.5604Å, and the volume expansibility reaches to 3.7365%.

![Figure 1. The X-ray Diffraction Patterns of LaFe$_{10.9}$Co$_{0.8}$Si$_{1.3}$ Compounds before and after Hydrogen Absorption, Where Symbol * Refers to $\alpha$-Fe.](image)

DSC curves of LaFe$_{10.9}$Co$_{0.8}$Si$_{1.3}$ compound and hydrogenated sample are shown in Fig. 2 and Fig. 3, respectively. After hydrogen absorption, the endothermic peak of LaFe$_{10.9}$Co$_{0.8}$Si$_{1.3}$ shifts to a higher temperature obviously, that means the temperature of phase transition of LaFe$_{10.9}$Co$_{0.8}$Si$_{1.3}$ compound is increased by hydrogen absorption. In Fig.4, Curie temperature $T_C$ can be determined from differential of DSC (DDSC) curves. Hydrogen absorption lifts $T_C$ of LaFe$_{10.9}$Co$_{0.8}$Si$_{1.3}$ compound from 277 to 346K. The interstitial hydrogen atoms in LaFe$_{10.9}$Co$_{0.8}$Si$_{1.3}$ leads to the volume expansion (see Table 1), which enhances the exchange coupling between Fe-Fe atoms, and results in a significant increase of $T_C$. 

![Figure 2. DSC Curves of LaFe$_{10.9}$Co$_{0.8}$Si$_{1.3}$ Compounds before and after Hydrogen Absorption.](image)
Figure 2. DSC Measurement for LaFe10.9Co0.8Si1.3 Compound.

Figure 3. DSC Measurement for LaFe10.9Co0.8Si1.3H1.8 Compound.

Figure 4. DDSC Measurements for LaFe10.9Co0.8Si1.3 and LaFe10.9Co0.8Si1.3H1.8 Compounds.
A comparison between endothermic peaks before and after hydrogen absorption in Fig. 5. It shows that the temperature range of the phase transition becomes much wider, and indicates the property of phase transition change towards second order after hydrogen absorption.

For H₂ atmosphere at a high pressure, 50 atm for example, studies have shown that the lattice expansion due to the interstitial hydrogen atoms is highly symmetric, with keeping the IEM transition[9-11]. According to that, the first order phase transition could be weakened by asymmetrical hydrogen absorption in unit cell of LaFe_{10.9}Co_{0.8}Si_{1.3} compound in a 1-atm H₂ gas. In La(Fe, Si)_{13}H_y interstitial compounds, hydrogen atoms occupy the interstitial hole site at 24d, corresponding to the face-centre position in cubic lattice formed by the Fe atoms at 8b sites[12]. Due to the intrusion of hydrogen into the 24d site the Fe²⁻-Fe²⁻ (at 96i sites) is expanded, resulting in lattice expansion which yields a considerable increase in Curie temperature[12]. In compound after hydrogen absorption at a low pressure, hydrogen atoms might occupy different 24d sites in each cell, resulting in asymmetrical hydrogen absorption and widening of phase transition temperature range. The tendency of second order transition of LaFe_{10.9}Co_{0.8}Si_{1.3}H_{1.8} compound will decrease hysteresis loss and then increase the efficiency of magnetic refrigerator performance which is small energy loss during temperature change in the cycle operation system. Also, the wider DSC curve of LaFe_{10.9}Co_{0.8}Si_{1.3}H_{1.8} indicates it can be used in wide work temperature range.

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**Summary**

The effects of hydrogen absorption on structure, Curie temperature and phase transition property are investigated for the LaFe_{10.9}Co_{0.8}Si_{1.3} compound in H₂ gas under 1 atmospheric pressure. The room-temperature powder XRD patterns show that the LaFe_{10.9}Co_{0.8}Si_{1.3} and LaFe_{10.9}Co_{0.8}Si_{1.3}H_{1.8} compounds each crystallize into phase with a cubic NaZn_{13}-type structure. The Curie temperature T_C of LaFe_{10.9}Co_{0.8}Si_{1.3} compound increases from 277 to 346K after hydrogen absorption. The temperature range of the phase transition of LaFe_{10.9}Co_{0.8}Si_{1.3}H_{1.8} becomes much wider.
Acknowledgement

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