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Effect of rare earth doping on the hydrogen storage performance of $Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6}$ alloy for hybrid hydrogen storage application

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ABSTRACT

In order to improve the activation behavior of $Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6}$ alloy with high hydrogen desorption pressure for hybrid hydrogen storage vessel application, the rare earth (RE) doped $Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6}RE_{0.03}$ (RE = La, Ce, Ho) alloys were prepared by induction levitation melting. The effect of rare earth doping on the microstructures and hydrogen storage properties was also investigated systematically. The results show that $Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6}$ alloy displays a single C14 Laves phase, and there is a secondary phase of rare earth oxide in the RE doped alloys. The RE doping strategy can expand the unit cell volume of C14 Laves main phase. After RE doping, the activation behavior of the $Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6}RE_{0.03}$ alloy is obviously improved and the hydrogen storage capacity is increased, while the hydrogen desorption plateau pressure is decreased. Moreover, the RE-free alloy can hardly absorb hydrogen at room temperature under 34–43 MPa hydrogen pressure, but all RE-doped alloys can absorb hydrogen to saturation under the same condition. The decline of pressure plateau is inversely proportional to the atomic number of RE. Among the studied alloys, the $Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6}La_{0.03}$ alloy shows the best overall properties and can be fully activated at room temperature. Its hydrogen absorption pressure is 39.31 MPa and 51.27 MPa under 298 K and 318 K, respectively. Its hydrogen storage capacity is up to 1.715 wt% and the dissociation enthalpy is 16.63 kJ/mol H_2 with a desorption plateau slope of 0.098.

1. Introduction

Hydrogen is a promising energy carrier in the near future because of both its cleanliness and high combustion value. The key of using hydrogen as an energy carrier is to store it safely and efficiently [1,2]. Among the accessible different hydrogen storage systems, Takeichi et al. [3] have proposed a novel hybrid hydrogen storage vessel (*i.e.* a high-pressure hydrogen storage vessel combined with metal hydride), which provided the technical approach to realize a hydrogen storage system advantageous in both gravimetric and volumetric hydrogen density. Some metal hydrides including AB_2-type and other hydrogen storage alloys have also been investigated for hybrid hydrogen storage vessel application [4–12]. Among them, AB_2-type Ti-Cr based alloy represented one of the most promising hydrogen storage alloys due to its high dehydrogenation pressure and high hydrogen storage capacity, as well as the stability of the main phase and the relatively low cost [13–20]. It is well known that the activation process is very important in the application of hydrogen storage materials and the mild activation condition is preferred. The high-pressure hydrogen storage vessel is always made of aluminum-carbon fiber reinforced plastics which are very temperature dependent. The Ti-Cr-Mn-Fe based alloys are hard to be activated which might be a hinder for the practical application. Yan et al. [21] investigated the effect of Ce on the structure and hydrogen storage properties of $V_{55}Ti_{22.5}Cr_{16.1}Fe_{6.4}$. They have found that all Ce-containing alloys could absorb hydrogen rapidly at room temperature. Wu et al. [22] have also found that rare earth (RE) doped to $V_{55}Ti_{22.5}Cr_{16.1}Fe_{6.4}$

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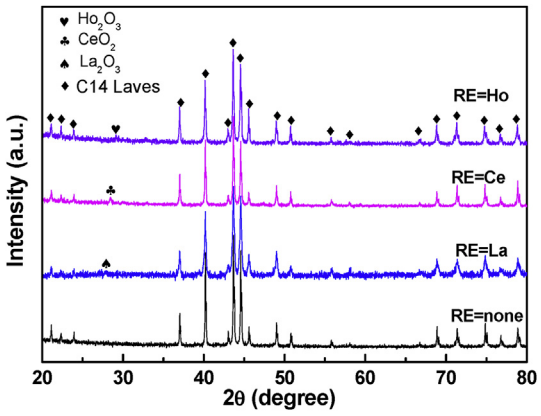

Fig. 1. XRD patterns of $Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6}RE_{0.03}$ based alloy samples.

Table 1
The crystallographic data of $Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6}RE_{0.03}$ based alloy samples.

Alloys	Lattice parameters (10^{-1} nm)		c/a	Unit Cell volume $V/(10^{-3}$ nm$^3)$
	a	c		
$Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6}$	4.8543	7.9676	1.6413	162.60
$Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6}La_{0.03}$	4.8623	7.9746	1.6400	163.28
$Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6}Ce_{0.03}$	4.8613	7.9726	1.6400	163.16
$Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6}Ho_{0.03}$	4.8601	7.9710	1.6401	163.05

alloy can improve the activation property rather than kinetics, absorption capacity and plateau pressure. Liu et al. [23] found that Ce additive further improves the flatness of plateau. In this work, in order to improve the activation properties of the alloy, RE elements (La, Ce and Ho) were introduced into the $Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6}$ alloy and then the microstructures and hydrogen storage properties were also investigated systematically.

2. Experimental details

The raw materials including La, Ce, Ho used in this experiment have commercially available purity higher than 99%. The $Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6}RE_{0.03}$ (RE = La, Ce, Ho) samples were prepared by induction levitation melting the constituent metals (total weight of around 30 g) in a water-cooled copper crucible under argon atmosphere, and were remelted 3 times to ensure high homogeneity.

The structural characterization and lattice parameters of the alloy samples were determined by X-ray diffraction (XRD) using a Rigaku D/max-3B diffractometer with Cu Kα radiation. The metallographic microstructures were analyzed by scanning electron microscopy (SEM, Hitachi S4800) and element distribution of the samples were analyzed by energy dispersive X-ray spectrometer (EDS).

The pressure-composition-temperature (P-C-T) curves of the samples were measured using a homemade Sieverts-type apparatus. In the activation process, the ingots were crushed into 100-mesh powders in air and then put into a stainless steel reactor for measurements. Hereafter the reactor was vacuumed under room-temperature. In order to supply the high hydrogen pressure, we used a hydrogen storage material with low plateau pressure absorbing hydrogen under low hydrogen pressure and then it was heated to release high pressure hydrogen. The hydrogen pressure which varied from the saturation of the hydrogen storage material with low plateau and the heat temperature and other conditions was introduced into the system and reacted with the samples at room temperature. Then, the system was vacuumed for 30 min under 373 K to make sure the dehydriding reaction was completed. After activation, the P-C-T measurement was carried out at different temperatures.

3. Results and discussion

3.1. Effect of RE additives on the structure of $Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6}$ alloy

The XRD patterns of $Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6}$ and $Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6}RE_{0.03}$ (RE = La, Ce, Ho, separately) alloy samples are presented

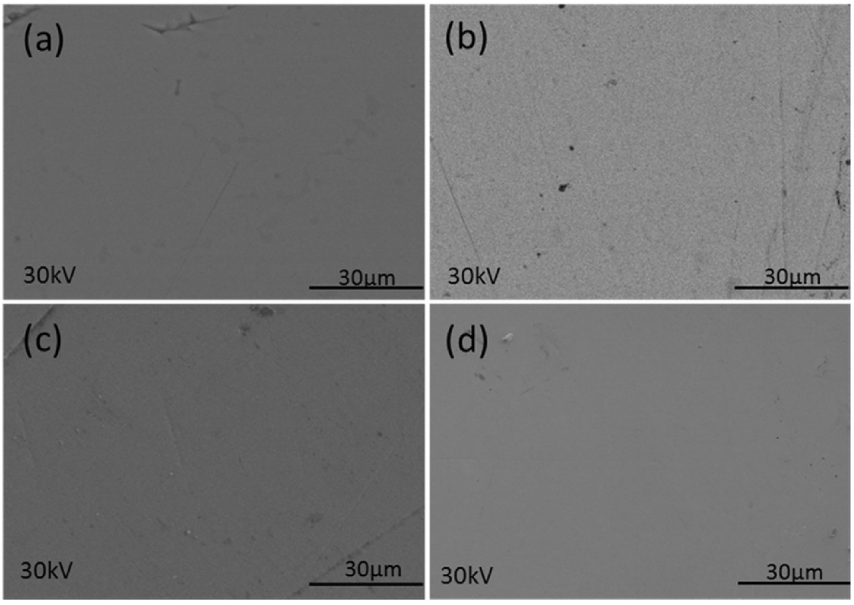

Fig. 2. SEM micrographs of $Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6}RE_{0.03}$ alloy samples: (a) $Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6}$; (b) $Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6}La_{0.03}$; (c) $Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6}Ce_{0.03}$; (d) $Ti_{1.02}Cr_{1.1}Mn_{0.3}Fe_{0.6}Ho_{0.03}$.