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Hydrogen absorption and desorption properties of $Ho_{1-x}Mm_xCo_2$ alloys

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Abstract

The hydrogen absorption–desorption pressure-composition (PC) isotherms and kinetics of $Ho_{1-x}Mm_xCo_2$ ($x = 0, 0.1, 0.2, 0.3$ and 0.4, Mm = mischmetal) have been carried out in the temperature and pressure ranges 50–200 °C and 0.001–1 bar using Sieverts-type apparatus. The effect of Mm on the equilibrium plateau pressure and hydrides stability has been discussed. The kinetics of hydrogen absorption at near equilibrium plateau region have been analyzed by a rate function. The reaction rate constants in the two-phase coexistence region and diffusion coefficient in the hydride phase region were calculated and its pressure and temperature dependence have been discussed. The hydrogen desorption from interstitial sites of $Ho_{1-x}Mm_xCo_2H$ has been performed using differential scanning calorimetry (DSC) and thermogravimetry (TG) analysis. The results are explored to identify the preferential occupation of different interstitial sites of hydrogen atoms and complete desorption temperature. The observed phase transformations as a function of hydrogen concentration and temperature have been discussed.

Keywords: Cubic Laves phase; Hydrogen absorption; Kinetics of hydrogen absorption; SEM; DSC; TG

1. Introduction

The Laves phase AB_2-type alloys are well-known class of hydrogen storage materials. A large number of Laves alloys, especially those in which a rare-earth element is one of the components, easily absorb hydrogen up to 4.5 H atoms per formula unit and form stable hydrides [1–10]. The AB_2-type C15 cubic Laves-phase (space group $Fd\bar{3}m$) alloy hydrides are generally formed with hydrogen occupying tetrahedral interstitial sites. There are total 17 tetrahedral interstitial sites per AB_2 formula unit containing 12 (2A2B)-sites, four (1A3B)-sites and one 4B site. The occupation of these sites is limited through the nearest neighbor distances between two sites available for hydrogen, so that tetrahedral sites with shared faces cannot be occupied by hydrogen atoms at the same time [10].

There are a few investigations on the hydrogen absorption and desorption properties of Laves phase RM_2-hydrides (R = rare earth elements, M = Mn, Fe, Co and Ni), because of very lower plateau pressures and complex behavior of hydrogen absorption and desorption properties [3–6,9]. For example, $ErFe_2$-H [3,5] exhibits multi-plateau behavior with five different hydride phases, whereas GdB_2-H (B = Mn, Fe, Ni, Rh, Ru) [4] exhibit a single plateau region and complete desorption of hydrogen cannot be possible even by evacuating the hydride down to 10^{-5} mbar near room temperatures. The hydrogen absorption and desorption properties can be tuned by partial replacement or alloying with different kinds of elements without changing the structure [11–13]. Most of the hydrogen absorbing materials are of multi-element alloys and a lot of effort has been spent to optimize the materials for the best practical performance. However, relatively much less importance has been given for fundamental understanding of the mechanism and kinetics of hydrogen absorption reaction. In order to understand the hydrogen absorption and desorption properties, the PC isotherms and kinetics of hydrogen absorption of $Ho_{1-x}Mm_xCo_2$ ($x = 0, 0.1, 0.2, 0.3$ and 0.4, Mm = mischmetal, a natural mixture of the light rare earth metals, 50% Ce, 35% La, 8% Pr, 5% Nd and 1.5% other rare earth elements and 0.5% Fe [14]) have been investigated. The effect of Mm on the plateau pressure and hydride stability

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has been discussed. In addition, the DSC and TG studies of hydrides of $Ho_{1-x}Mm_xCo_2$ have been studied. The existence of different hydride phases, the hydriding reaction mechanism in each phase and its temperature and pressure dependence properties were discussed with respect to Mm concentration. Furthermore, the preferential occupation of interstitial sites and complete desorption of hydrogen from interstitials were discussed.

2. Experimental details

The $Ho_{1-x}Mm_xCo_2$ alloys were prepared by arc melting of stoichiometric amounts of constituting elements Ho, Mm and Co with a purity better than 99.9% under a protective argon atmosphere. A 6 wt% excess of Ho and Mm were taken in order to prevent the formation of Co-rich phases. The ingots were melted several times to ensure homogeneity. Samples thus obtained were sealed in an evacuated quartz tube and homogenized at 850 °C for 4 days. The structural characterization of the $Ho_{1-x}Mm_xCo_2$ were carried out by X-ray diffraction (XRD) (X'pert PRO, PANalytical diffractometer) using the Cu K_α radiation. Hydrogen absorption–desorption pressure-composition isotherms and kinetics of $Ho_{1-x}Mm_xCo_2$ alloys were performed using Sieverts-type apparatus in the pressure range 0.001–1 bar and temperature range 50–200 °C. The samples were activated by repeating hydrogen absorption and desorption cycles: (1) the absorption measurements have been carried out at 1 bar constant initial hydrogen pressure and temperatures at 100 and 150 °C, (2) desorption carried out in a vacuum and temperature increases up to 800 °C. A controlled amount of hydrogen gas has been admitted into the reaction chamber that holds a specimen and the pressure change has been monitored while maintaining constant temperature of the reaction chamber. The amount of hydrogen absorbed by the specimen is determined by calculating the amount of pressure change after the reaction. The DSC (NETZSCH DSC 200 PC) measurements have been carried out in the temperature range 30–450 °C with a constant heating rate of 10 °C/ min. A 20–50 mg sample, sealed in an aluminum pan with an aluminum lid of similar diameter using a standard press, was scanned under a constant flow of argon in the calorimeter against a reference pan sealed with the lid. The data were collected by simultaneously deducing a predetermined base line from the scan programmed through a computer. TG measurements (Perkin Elmer, TGA 6) were carried out under a protective argon atmosphere from room temperature to 450 °C with a constant heating rate of 10 °C/ min.

3. Results and discussion

3.1. Crystal structure and lattice constant

XRD patterns of homogenized $Ho_{1-x}Mm_xCo_2$ ($x = 0, 0.1, 0.2, 0.3$ and 0.4) alloys are shown in Fig. 1. All the homogenized alloys crystallize in cubic Laves phase with the $MgCu_2$-type structure (space group $Fd\bar{3}m$). The lattice constant (a), at room temperature (inset of Fig. 1), increases linearly with increasing Mm concentration due to the larger radius of the Mm than that of Ho.

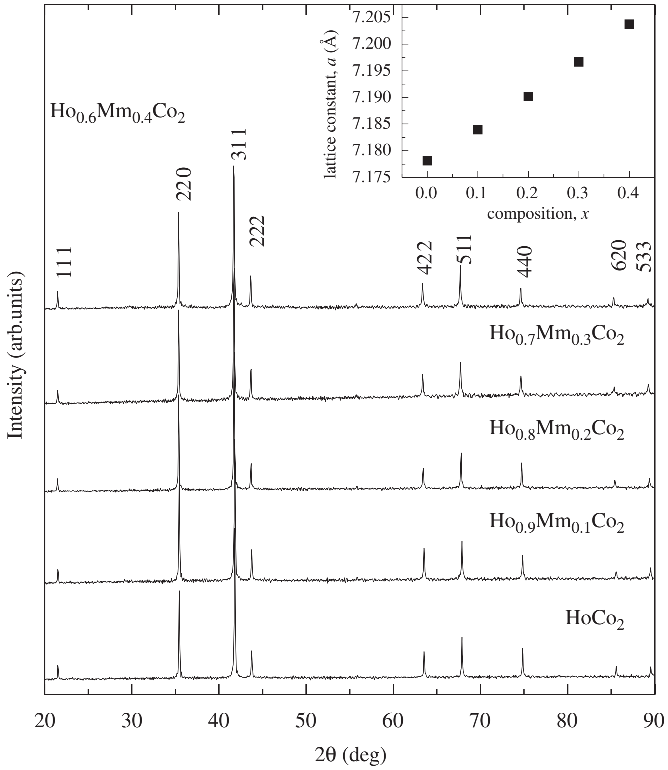

Fig. 1. XRD patterns of $Ho_{1-x}Mm_xCo_2$ ($x = 0, 0.1, 0.2, 0.3$ and 0.4) alloys. Inset: variation of lattice constant with increasing Mm concentration.

3.2. Activation

Preliminary activation of hydrogen storage alloys is needed for their normal hydrogen absorption and desorption. Full activation consists of several repeated hydriding–dehydriding cycles. It is usually achieved through the following steps: (1) exposure to hydrogen (for absorbing hydrogen), (2) heating at high temperature in vacuum (for desorbing hydrogen), (3) a series of absorption and desorption cycles. The activation curves of $Ho_{1-x}Mm_xCo_2$-H for $x = 0.2$ and 0.4 are shown in Fig. 2. These kinetic curves clearly demonstrate that the changes observed with successive hydriding–dehydriding cycles. In the initial stage, an incubation period is followed by an accelerating stage, both of which become shorter as the number of cycles increases. The initial stage of the reaction can be roughly divided into two parts: first, hydrogen is dissolved in the near surface region, reaction rate starts out slowly and hydride nucleation commences. During this part, the amount of hydrogen concentration in the alloy is relatively small. The second part reflects the growth of hydride nuclei and the formation of the hydride layer. In hydriding kinetics it is frequently observed that there is a sensible induction period until the reaction commences [15,16]. This appears to be generally due to surface oxides (or sulfides, nitrides, etc.) or to adsorbed gas, which inhibits hydriding until this layer is ruptured, reduced