

Kinetic analysis of Mg–8 mol%LaNi_{0.5} composite

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Abstract

The aim of this paper is to apply a new kinetic model in order to investigate kinetic mechanism of the hydriding kinetics at 553 K and hydrogen pressure range from 0.256 to 0.992 MPa in the two-phase (α – β) region of the Mg–8 mol%LaNi_{0.5} composition prepared by different methods. Much attention was put on the influence of the fabrication technique and the initial hydrogen pressure on hydriding kinetics of Mg–8 mol%LaNi_{0.5} composite. This model has been validated by comparison of our calculation results with experimental data. The hydriding kinetic mechanism of Mg–8 mol%LaNi_{0.5} was determined and the rate-limited step in the two-phase (α – β) region is hydrogen diffusion in the β phase.

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1. Introduction

The introduction of hydrogen as a major global energy carrier depends on solving a number of fundamental and technical problems. Perhaps, the largest challenge today is to find hydrogen storage solutions that at the same time are safe, compact, light, reversible and cheap. One of the 2010 technical targets of the US-DOE for on-board hydrogen storage is to overcome a “commercialization barrier” of about 6 mass%H a storage material should contain [1]. A key issue is to seek a new material that can fulfill the current requirements for the desired application with respect to both capacity and kinetics. Magnesium and its derived alloys are looked upon as promising candidates for hydrogen storage due to their high theoretical storage capacity (7.6 mass%H for MgH₂), light weight and low cost. However, high operating temperatures and poor kinetics prevent them from practical application. Much research has been carried out to improve the kinetic properties of Mg-based alloys. The main approaches include: (1) adding alloying elements [2]; (2) modifying the surface of alloys [3]; (3) using novel methods, such

as hydriding combustion synthesis (HCS) [4] and mechanical alloying (MA) [5]; (4) forming composites with other hydrogen storage alloys [6].

It is important to clarify the kinetic mechanism of hydrogen absorption/desorption (A/D) in metal hydrides for improving their kinetic properties with pertinence. Usually, the reaction mechanism can be analyzed by comparing the observed hydriding rate curves with the rate equations derived from different processes, such as nucleation and growth process, auto-catalytic reactions, phase-boundary-controlled reactions and so on. Some rate equations proposed in the literatures [7–9] have been used to treat the experimental data, but the fittings were very unsatisfactory. From published literatures, most researchers paid their attention to the influence of the temperature on the hydriding/dehydriding (H/D) kinetic mechanisms [10–12], a little work on the effect of the pressure on the kinetic mechanism of the hydrogen storage alloys was carried out [13,14]. In fact, there are many factors to impact the kinetic properties of hydrogen storage materials, such as temperature, pressure, the size of the particle, the thermal conductivity of the reactor, the properties of surface and so on.

In our previous research [15], it was found that Mg–8 mol%LaNi_{0.5} possesses a large hydrogen storage capacity with excellent kinetic property. It is well known that the two-phase (α – β) region is of importance for the hydrogen storage

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alloy. In this paper we will pay more attention to the influence of hydrogen pressure on this region of Mg–8 mol%LaNi_{0.5} composite and the impact of the different fabrication techniques.

2. Kinetic theoretical analysis

There are some difficulties in the hydrogenation kinetics including experimental study and theoretical analysis because the hydrogen A/D is very complicated. If one treats each step rigorously, that will lead to solve a group of differential equations or integral equations. The situation now is that some treatments are so complicated that cannot offer an explicit analytic expression and cannot give an intuitionistic quantitative discussion. From the point of view of practical application it is desired to have a simpler and physical meaningful explicit analytic expression, which is convenient for use and can still give a good prediction under an acceptable simplified assumption. In order to solve the problem above mentioned Chou et al. [16] proposed a new model to predict and analyze the kinetics on the hydrogen A/D in alloy powder based on a reasonable simplified assumption that the hydrogen diffusion in hydride phase is slowest in all hydriding processes and that might not sacrifice too much calculation accuracy.

In the previous series of papers [17,18], we have successfully studied the effect of temperature on the hydrogen A/D for various kinds of hydrogen storage materials by using our model. From now on we would like to focus our sight on the influence of pressure on the hydrogen A/D kinetics. According to the model, the reacted fraction ξ for hydride reaction can be expressed as [16]

$$\xi = 1 - \left\{ 1 - [1 - (1 - \phi)^{1/3}] \sqrt{\frac{t}{t_{\xi=\phi}}} \right\}^3 \quad (1)$$

where ϕ represents the fixed hydriding reacted fraction in given time and $t_{\xi=\phi}$ is called the characteristic A/D time that is a very important physical quantity. The less the $t_{\xi=\phi}$, the faster the A/D reaction. This quantity indicates the H/D ability of hydrogen storage materials. One may use this quantity as an index to compare different kinds of hydrogen storage materials. This quantity can be expressed as

$$t_{\xi=\phi}(T) = - \frac{[1 - (1 - \phi)^{1/3}]^2}{2(C''_{\text{H}}^{\beta} - C''_{\text{H}}^{\alpha})D_{\text{H}}^0 \exp(-\Delta\varepsilon/RT)/R_0^2 v_{\text{m}}} \quad (2)$$

where C''_{H}^{β} and C''_{H}^{α} are the concentration of hydrogen in the β phase at the gas/ β and α/β side, respectively, D_{H}^0 the constant related diffusion coefficient of hydrogen and v_{m} is the coefficient depending on substance and reaction. R_0 is the radius of the particle, R and T the gas constant and absolute temperature with K , t the time in second and $\Delta\varepsilon$ is the activation energy of absorbing hydrogen.

The above formula for calculating different ξ corresponds to different temperatures as the pressure is fixed. On the other hand, if the temperature is fixed but the pressure is changeable,

the $t_{\xi=\phi}$ then will be expressed as

$$t_{\xi=\phi}(P) = \frac{[1 - (1 - \phi)^{1/3}]^2}{2D_{\text{H}}^{\beta} C''_{\text{H}}^{\beta} ((K/C''_{\text{H}}^{\beta})\sqrt{P_{\text{H}_2}} - 1)/R_0^2 v_{\text{m}}} \quad (3)$$

where K is the equilibrium constant and P_{H_2} is the partial pressure of hydrogen in gas phase.

The reacted fraction of hydride can now be expressed as

$$\xi = 1 - \left\{ 1 - [1 - (1 - \phi)^{1/3}] \left(\frac{(K/C''_{\text{H}}^{\beta})\sqrt{P_{\text{H}_2}} - 1}{(K/C''_{\text{H}}^{\beta})\sqrt{P_{\text{H}_2}^0} - 1} \right)^{1/2} \sqrt{\frac{t}{t_{\xi=\phi}(P_{\text{H}_2}^0)}} \right\}^3 \quad (4)$$

This is the formula describing the influence of pressure on the reacted fraction of hydride.

3. Comparisons between experimental values and predicted calculation

In order to verify the reliability of the formula, its application to the Mg–8 mol%LaNi_{0.5} composite was studied. The hydrogenation properties of the composition were investigated in our previous works [15,19], in which no other kinetic mechanism was reported. In this paper our attention was put on not only the rationality of our model but also the kinetic mechanism of the Mg–8 mol%LaNi_{0.5} composite.

The samples in this study were obtained by hydrogen combustion synthesis and mechanical alloying from commercial pure Mg (purity > 99.8), Ni (purity > 99.9) and La (purity > 99.9), the preparing procedures of Mg–8 mol%LaNi_{0.5} composite made by different fabrication techniques were described elsewhere in details [15,19]. In this work samples were prepared by different fabrication techniques with the same nominal composition, respectively (sample 1 for HCS and sample 2 for MA). The H/D characteristics of the materials were determined by an isovolumetric method without any activation treatment. The reactor enables both isothermal measurements and unimpeded hydrogen flow rate. Mg–8 mol%LaNi_{0.5} powder weighing 0.5 g was placed on the bottom of the reactor and its thickness was less than 0.5 mm to reduce the generation of the reaction heat, and this method is effective to obtain isothermal or near isothermal conditions. The temperature was controlled within ± 1 K. A pair of thermocouple with 0.85 mm diameter was used to measure the temperature accurately. After establishing isothermal conditions, the samples were heated under vacuum to the desired temperature and evacuated again. The kinetic rate of the hydrogen A/D reaction of Mg–8 mol%LaNi_{0.5} was measured using a specially developed reactor during the initial hydrogen pressure changed between the initial hydrogen pressure of 0.256 and 0.992 MPa under the approximately isothermal condition. The changes of H₂ pressure were measured to their hydrogen absorption from the hydrogen storage

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