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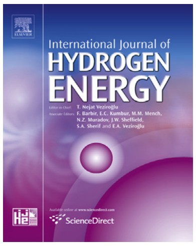

Kinetic mechanisms of hydriding and dehydriding reactions in La–Mg–Ni alloys investigated by the modified Chou model

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ABSTRACT

The phenomenon of volume change is very important in the hydriding and dehydriding reactions to clarify their kinetic mechanisms. However, few of the theoretical models take this factor into account in the study of kinetic mechanisms. In the present work, the modified Chou model with considering the volume change by Pilling-Bedworth Ratio (PBR) β is applied to interpret the kinetic mechanisms of hydriding and dehydriding reactions in La–Mg–Ni ternary hydrogen storage alloys. The calculation results agree well with the experimental data, indicating that the modified Chou model can well describe the kinetic behaviors of La–Mg–Ni alloys. Diffusion is determined to be the rate-controlling step of hydriding and dehydriding for the examples in this work. The activation energies are calculated to be 39.4 kJ/mol for hydriding reaction ($\beta = 1.29$) and 93.1 kJ/mol for dehydriding reaction ($\beta = 0.78$) of Mg–10.6La–3.5Ni nanoparticles at 453–623 K. For the hydrogen absorption kinetics of $La_2Mg_{16}Ni$ alloy under 0.5–3 MPa at 598 K, β is 1.25 and the equilibrium hydrogen pressure is calculated to be 0.332 MPa. For the hydrogen desorption kinetics of $Mg_x(LaNi_3)_{100-x}$ alloys at 623 K, the characteristic times increase in the order of $t_{c(x = 70,\ \beta = 0.79)} < t_{c(x = 60,\ \beta = 0.79)} < t_{c(x = 40,\ \beta = 0.97)} < t_{c(x = 50,\ \beta = 0.85)}$. The value of β is 0.77 and the hydrogen desorption rate of Mg–5La–10Ni alloy prepared by the ultrahigh pressure (UHP) method is faster than that of the alloy prepared by the as-cast method, whose characteristic times are 7428 s and 4651 s, respectively. Furthermore, the calculation accuracy can also be improved by the modified Chou model compared with the original Chou model after taking PBR into consideration.

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Introduction

The application of magnesium-based alloys as hydrogen storage materials is limited by the slow hydrogenation and dehydrogenation kinetics [1–4]. Ternary La–Mg–Ni hydrogen storage alloys have attracted much attention because the formation of LaH_3 and Mg_2NiH_4 can significantly improve the hydrogen storage properties by catalysis and destabilization effects [5–8]. Liang et al. [9] reported that Mg–30$LaNi_5$ alloy catalyzed by Mg_2Ni and LaH_3 can absorb 4.1 wt. % H_2 within 1000 s at 423 K. Li et al. [10] found that the $La_{1.5}Mg_{17}Ni_{0.5}$ alloy catalyzed by $LaNi_5$, LaH_3 and La is able to absorb 4.34 wt. % H_2 and desorbed 4.12 wt. % H_2 within 300 s at 523 K, which is over 30 times faster than that of La_2Mg_{17} alloy under the same conditions.

The study of kinetic mechanisms of the hydriding and dehydriding reactions in La–Mg–Ni hydrogen storage alloys are of importance from the viewpoint of practical application. In the last decades, many theoretical kinetic models have been applied to interpreting the kinetic mechanisms of hydriding and dehydriding reactions depending on the rate-controlling steps, such as Kolmogorov–Johnson–Mehl–Avrami (KJMA) model [11] and Chou model [12], etc. However, most of the kinetic models describing the kinetics of hydriding and dehydriding reactions do not take the volume change into account. It is known that hydrogen causes lattice expansion/shrinkage when hydrogen is absorbed/desorbed in/from the alloys' crystal lattice. For example, the volume expansion ratio during hydrogen absorption is 24% for $LaNi_5$ and 28–32% for Mg_2Ni [13]. The phenomenon of volume change is first observed by Pilling and Bedworth thus the researchers usually use the Pilling-Bedworth Ratio (PBR) to characterize the extent of volume change [14,15]. The volume change is usually accompanied with the stress and strain in the materials. When hydrogen atoms enter into an alloy's lattice, the lattice expansion induces significant micro-stress and leads to alloy pulverization [16]. The large strain energy induced with volume change of hydriding and dehydriding reactions may have a significant effect on hydrogen-metal interactions [17]. Zhdanov et al. [18] found that the strain would suppress the hydrogen desorption primarily during the initial stage from the fact that the hydrogen desorption rate is relatively slow for nanoparticles. The above studies provide clear evidence that the volume change between metal and hydride which causes micro-stress and strain in the alloys can have a non-negligible effect on the hydriding and dehydriding kinetics of hydrogen storage alloys. To our knowledge, the possible effect of volume change on the hydriding and dehydriding kinetics of La–Mg–Ni alloys has not been considered yet. Therefore, it is necessary to take the volume change into account when studying their kinetic mechanisms of hydriding and dehydriding reactions. In the previous work of Chou and co-workers [19], they proposed a modified Chou model by considering the effect of volume change on the kinetics of gas–solid reactions. In this model, solid particles are regarded as sphere balls, flat planes or fibers with the same density and size. When the gas–solid reaction happens, the product layers with a different density are formed outside of the particles and thickened with reaction time. Because hydriding and dehydriding of Mg-based alloys have been proved to meet these assumptions as typical gas–solid reactions [20–23], we believe that this model should be suitable for describing their hydrogen storage reactions.

In the present paper, we use the modified Chou model with considering PBR to study the kinetic mechanisms of hydriding and dehydriding reactions in La–Mg–Ni alloys to get physical meaningful results and describe the real reactions more precisely. It is expected that this Chou model with considering the volume change induced by hydrogen absorption and desorption would be suitable for the interpretation of the effect of temperature, hydrogen pressure, composition and prepare method on the kinetics of hydriding and dehydriding reactions in La–Mg–Ni alloys. Also, the comparison between the original Chou model without considering PBR and the modified Chou model is discussed in this paper.

Kinetic model

The concept of PBR was first proposed by Pilling and Bedworth in 1923 to express the difference between the volumes of matrix and oxide layer [13]. Chou et al. introduced this concept into their investigation on the influence of the density of oxide in oxidation kinetics on the basis of the original Chou model [19]. The PBR can be used to describe the magnitude and influence of stress in the hydride [13]. If the PBR is smaller than 1, the stress in the hydride is tensile. If the PBR is larger than 1, the stress in the hydride is compressive. Larger difference of PBR from 1 induces larger stress (compressive or tensile). This modified model is suitable for the reaction when the rate-controlling step is diffusion. It can be applied to three kinds of situation: sphere ball, flat thin plane and fiber [19]. Since most studies on hydrogenation and dehydrogenation are based on the ball-like particle materials, we adopt the situation of sphere ball. The equation with considering PBR for sphere balls can be expressed as:

$$F(\beta,\xi)=\int_0^{\xi}\frac{[\beta-(\beta-1)(1-\xi)]^{\frac{1}{3}}-(1-\xi)^{\frac{1}{3}}}{3(1-\xi)^{\frac{2}{3}}}d\xi=\frac{D_H^0 M k_0\left(\sqrt{P_{H_2}}-\sqrt{P_{H_2}^{eq}}\right)}{\rho r_0^2 exp\left(\frac{E_a}{RT}\right)}t, \quad (1)$$

where ξ is the reaction fraction, β is the Pilling-Bedworth ratio, D_H^0 is the diffusion coefficient of hydrogen, M is the molecule weight, k_0 is the Sievert's constant, P_{H_2} and $P_{H_2}^{eq}$ are the hydrogen concentration at the gas/hydride interface and hydride/metal interface respectively, ρ is the density, r is the radius of the particle from the center to the hydride layer, E_a is the activation energy and R is the gas constant. When the reaction is completely finished, i.e. $\xi = 1$, the needed time is called the characteristic time t_c. One may use this characteristic time to measure the kinetic property of a certain hydrogen storage alloy. With Eq. (1), one can calculate the experimental data in the following steps:

First, determine the value of β by calculate the volume change ratio during the hydrogenation/dehydrogenation. The value of β can be calculated by the following equation: