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Hydrogen sorption kinetics of La–Ni–Sn storage alloys

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ABSTRACT

In this work we identify the limiting mechanism in the hydrogen absorption reaction of $LaNi_{5-x}Sn_x$ alloys. For this purpose the absorption reaction was modeled as a process involving several partial reactions occurring sequentially. The analysis was performed by comparing the experimental data with the descriptions derived from four different kinetic expressions, each considering that there is only one mechanism governing the hydrogen absorption reaction while the other steps occur near equilibrium conditions. Kinetic curves corresponding to the binary alloy $LaNi_5$ and to the substituted alloys $LaNi_{4.73}Sn_{0.27}$ and $LaNi_{4.55}Sn_{0.45}$ were measured using the Sieverts volumetric technique. Experiments were carried out over a temperature range from 300 K to 348 K and under different hydrogen pressures. In all cases, the best fit to the experimental data was achieved by applying an expression that assumes the limiting step of the overall reaction is the diffusion of hydrogen atoms through the hydride layer.

1. Introduction

The study of the hydrogen sorption reaction in hydride forming materials plays a key role in the design of storage and purification devices and heat-pump applications. Metal hydrides belonging to the AB₅ family have been widely studied because of their good reaction kinetics at room temperature, high cycling stability and good volumetric capacities. Partial substitutions of elements on the A and B sites allow the design of alloys that fulfil pressure and temperature requirements demanded by specific applications. As a consequence, these systems are used throughout a wide range of applications including hydrogen storage, compression, purification and rechargeable batteries [1,2]. In order to optimize devices design and to adequately model their performance it is necessary to fully characterize the alloy hydrogen reaction kinetics in the ranges of pressure and temperature that result of interest for specific operational conditions.

Many efforts have been made to study the underlying mechanisms of the reaction kinetics of AB₅ hydride forming alloys. In particular, several studies have focused in determining the kinetic mechanism governing the hydrogen absorption reaction. In this direction, hydrogen absorption curves corresponding to the LaNi₅, LmNi₄.₉₁Sn₀.₁₅ and LaNi₄.₇Al₀.₃ intermetallics have been modeled using the Johnson–Mehl–Avrami (JMA) and the Jander diffusion models [3]. JMA comprises both diffusion and nucleation and growth

as the limiting steps, while the Jander model only takes diffusion into account. The results indicated that the latter model was the best option for describing the process in all cases [3]. Payá and co-workers have also analyzed the mechanisms controlling the kinetics of absorption for LaNi₅ using JMA and the Crank–Nicholson diffusive model [4]. They found that both mechanisms were necessary to describe the reaction kinetics. While the initial 65% of the complete hydriding reaction fitted according to JMA, the final 35% was better described by the diffusive model. A different approach was taken by Dhaou et al. for the study of the reaction kinetics of LaNi₅, LaNi₄.₈₅Al₀.₁₅ and LaNi₄.₇₅Fe₀.₂₅ alloys [5]. According to these authors, after trying different possibilities they concluded that no existing kinetic model was satisfactory and instead preferred to derive empirical equations to describe the experimental data.

In order to gain more insight on the reaction mechanisms, Martin et al. have pointed out that neither the first-order reaction kinetics nor JMA equations are suited for describing the physics of the kinetics in metal-hydrogen systems [6]. Instead, they proposed a more detailed description in which the reaction follows five sequential steps and developed the corresponding mathematical descriptions. Each description assumes that only one step would limit the reaction. By applying this approach to LaNi₄.₇Al₀.₃ experimental results, they determined that the absorption reaction was controlled by surface chemisorption, whereas for the desorption process diffusion was found to be the limiting step. Fernández et al. applied the same model for the analysis of MmNi₄.₇Al₀.₃ hydrogen absorption kinetic [7]. They concluded that in the case of intentionally oxidized samples the reaction was dominated by surface processes, while for untreated and Pd-covered samples the kinetics was limited by diffusion. In a similar study [8], a combined model including all the partial reactions occurring during hydrogen absorption was developed. Furthermore, the model considered the case of transitional situations. The application of the model to the experimental kinetic curves of LaNi₅ showed good agreement with a reaction governed by a transition regime between diffusive and surface penetration mechanisms.

Using a similar approach, Smith and Goudy [9] applied the Shrinking Core Model (SCM) [10] for diffusion and chemical reaction controlling steps to study the dehydriding kinetics of the LaNi₅₋ₓCoₓ-H system. Results indicated that for LaNi₅ diffusion was the controlling step, while for LaNi₄Co, LaNi₃Co₂ and LaNi₂Co₃ the process was controlled by chemical reaction at the hydride-fresh material interface. In Ref. [11] the absorption kinetics of the LaNi₅₋ₓAlₓ (0 ≤ x ≤ 1.0) system was studied by applying the kinetic models proposed by Chou [12]. In the cases of LaNi₅ and LaNi₄.₇Al₀.₃ the controlling mechanism was diffusion, while for LaNi₄Al the best fit to the experimental data resulted from considering the surface penetration mechanism as the controlling step. In the case of LaNi₅, it was also found that the limiting step changed from diffusion to surface penetration when subjected to different pressures [11].

Considering all previous references it is clear that there is no prevalent model for analyzing hydrogen sorption kinetic results in AB₅ alloys. The main findings could be loosely summarized by saying that hydrogen absorption processes are dominated by diffusion mechanisms for LaNi₅ and related alloys with low Ni substitutions. However, for higher Ni replacement by other elements or under pressure changes, the absorption process can be governed by surface reactions.

Among AB₅ systems, LaNi₅₋ₓSnₓ alloys appear as a candidate for low pressure static applications. Although the thermodynamics, structure and microstructure of these compounds are well characterized in the literature [13–22], their reaction kinetics have not been extensively studied. Sato et al. studied the desorption kinetics of LaNi₄.₈Sn₀.₃ and estimated model coefficients by assuming diffusion as the limiting step [23]. Laurencelle et al. [19] presented an experimental kinetic study of LaNi₄.₈Sn₀.₂ and analyzed their results on the basis of a shrinking plate model characterized by an exponential dependence of the type $x_r = (1 - e^{-kt})$. In a recent work, we followed this approach in order to compare Laurencelle results with newly obtained data for several LaNi₅₋ₓSnₓ alloys [22]. The main finding was that Sn addition to LaNi₅ decreased the observed hydrogen absorption time. On one hand, those measurements were performed under the same external pressure conditions for different materials and driving force differences were not taken into account. On the other hand, the kind of approach used did not allow for an identification of the limiting mechanisms for the absorption process.

The purpose of the present paper is to identify the mechanisms governing the hydrogen absorption kinetics of LaNi₅₋ₓSnₓ compounds. We consider composition, temperature and external pressure variations in ranges of interest for hydrogen capture and purification applications. Analysis of the reaction of H₂ uptake is performed by comparing the experimental data with the different model descriptions.

2. Reaction model

2.1. Reaction stages

The hydrogen absorption process for an AB₅ alloy can be divided into several relevant stages [8]:

  i. Hydrogen molecule in the gas moves to the surface of the intermetallic particle
  ii. Hydrogen molecule is physisorbed at the solid surface of the particle
  iii. Hydrogen molecule dissociates and hydrogen atoms are chemisorbed at the surface of the particle
  iv. Hydrogen atoms penetrate through the surface of the particle
  v. Hydrogen atoms diffuse through the hydride to the interface hydride/intermetallic
  vi. Hydrogen atoms react with the intermetallic forming new hydride as product
  vii. Hydrogen atoms diffuse through the α-metal phase

Stages i, ii and vii are usually not considered because, under normal operational conditions, they occur very quickly. For that reason, focus will be put on the other four processes, with the aim of determining which of them acts as the limiting stage in the hydrogen absorption reaction of the materials