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# Phase field modeling of hydrogen transport and reaction in metal hydrides

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## ABSTRACT

The reaction of hydrogen with metals to form metal hydrides has numerous potential energy storage and management applications. The metal hydrogen system has a high volumetric energy density and is often reversible with a high cycle life. However, improving the often poor gravimetric performance of such systems through the use of lightweight metals usually comes at the cost of reduced reaction rates or the requirement of pressure and temperature conditions far from the desired operating conditions. Most studies of reaction kinetics of such systems focus on fitting low-dimensional kinetic models to measured rates and inferring the rate-limiting process based on the quality of the fit.

This work develops a methodology for describing these reactions using a multi-process model of the physical transport and energy state transitions of interstitial hydrogen atoms within a metal lattice. In its nondimensional form, this model is applicable to arbitrary geometries and dimensions using four nondimensional kinetic parameters based on the physical transport mechanisms present in the system.

The proposed model is then used for  $\text{LaNi}_5$  and  $\text{TiCrMn}$  to examine how the nucleation pattern, kinetic parameters, and particle aspect ratio affect the time of formation of a closed hydride layer and the apparent measured kinetics. The analysis is applied to both hydriding and dehydriding processes to show how different kinetic limitation mechanisms can manifest when considering the reciprocal reaction.

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## 1. Introduction

Characterization of the kinetics of metal hydride formation and decomposition is valuable for both system modeling (hydrogen storage, heat management, battery, propulsion) and for identifying and focusing research on improving the kinetics. An improved understanding of a material's intrinsic kinetic properties can be obtained by quantifying the roles different concurrent processes have on the overall rate of

hydrogen absorption and desorption. Furthermore, a model of the physical progression of the hydride phase which simultaneously accounts for the key rate limiting processes provides the ability to predict how modifications to microstructure can affect overall material kinetics.

The main physical phenomena which occur in the hydride formation process are: physisorption and chemisorption at the metal surface, growth of nucleated hydride sites until impingement, diffusion of hydrogen through the hydride

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layer inward to the phase boundary, and continued phase transformation (hydride growth) at the boundary. Most of these processes depend on either the available surface area or diffusion length scales through the particle. The simplest and most commonly used type of solid state kinetic model assumes that only a single process is involved through the entire reaction and that the geometry on which it acts is simple enough to be represented by a 0D or 1D object. Results using this method have produced large variations in reported kinetic parameters, and this is a subject of ongoing research and current publication [1–7].

There are two main methods used for interpretation of metal hydride kinetic parameters. The first is to assume a single process is rate limiting, and attempt to fit its expression to the data to determine a reaction rate (usually derived for a spherical particle when the process is dependent on domain length scales). Typically, a variety of process equations are compared with the data and the one with the best fit is considered to be the rate limiting process [8–16]. The second method is to assume there are a set of reactions occurring in series in a 1D framework and model this on a simple geometry (usually a plate or sphere). This method adds one or more fitting parameters at each step and fits the entire model to a data set. This procedure greatly increases the number of total fitting parameters compared with the first method [1,2,17–19], since each sub-model requires several inputs in addition to the inputs to determine when the reaction transitions from one mechanism to the next. The unfortunate consequence of the multiple inputs is that such models are often no more useful than simpler curve fits with an arbitrary number of  $n$ th order reactions from the standpoint of discerning which physical process is dominant.

The main objectives of this study are to derive a physically based phase field model for microstructure evolution in metal hydrides and use that model to examine the effect of geometry and kinetic coefficients on apparent kinetics and transitions between rate-limiting processes. First, we present a phase field model for metal hydride formation which is based on the interstitial sublattice regular solution model. The appropriate parameters for this model are measured for  $\text{LaNi}_5$  and  $\text{TiCrMn}$  using a high pressure Sievert system. Second, we compare multidimensional results from the phase field model with observed kinetic behavior in both candidate hydrides and illustrate key characteristics of the reactions.

## 2. Experimental methods

A Sievert system was used for this work to measure hydrogen sorption in materials at pressures up to 700 bar. This system, described in more detail in a prior publication, was used to measure the kinetic and thermodynamic properties of  $\text{TiCrMn}$  and  $\text{LaNi}_5$  [20]. The accuracy of the system has been verified through careful calibration and uncertainty analysis, coupled with calibration tests of well-characterized materials of both high and low densities [21].

There are two common techniques for measuring gas absorption kinetics using a volumetric apparatus: full reaction kinetics and incremental kinetics. In the first technique, a sufficiently high pressure is applied to the metal hydride to

allow the entire reaction to occur while attempting to minimize the temporal change in the surrounding gas pressure in order to maintain a pseudo-constant driving force. In the second, hydrogen is added to the system in steps and sufficient time is given to reach equilibrium at each step.

The most common method for analyzing the results of such measurements involves comparing the measured data with a set of possible reaction models and determining the reaction rate constant from the best fitting model [8–16]. This method, however, does not offer any distinction between the full reaction and incremental reaction described previously, and thus if used for incremental kinetics cannot be thought of as an independent determination of a single rate parameter, but rather a curve fit to an agglomeration of processes.

Two metal hydrides were used as case studies for this model:  $\text{TiCrMn}$  and  $\text{LaNi}_5$ .

The  $\text{TiCrMn}$  used for this work was obtained from Great Western Technologies in Warren, MI. It was tested by the manufacturer prior to delivery as having a composition of  $\text{Ti}_{1.01}\text{Cr}_{1.06}\text{Mn}_{1.00}$ , but is referred to herein as  $\text{TiCrMn}$  for brevity. This alloy was activated by four cycles of hydrogenation at 200 bar and 80 K followed by dehydrogenation at 373 K under vacuum.

In its fully hydrided state,  $\text{LaNi}_5$  has a hydrogen capacity of 1.4 wt.%. The  $\text{LaNi}_5$  used for these tests was obtained from Sigma Aldrich (Part # 685933) and was activated by five hydriding–dehydriding cycles prior to testing. Each cycle consisted of reaction with hydrogen at 283 K and 50 bar followed by dehydrogenation at 323 K under vacuum.

## 3. Phase field model

### 3.1. Free energy expression

A phase field model was developed to investigate the interplay between the different rate limiting processes involved in metal hydride phase transformation kinetics. The model can easily be extended to higher dimensions and is based on the regular solution model for free energy of the metal–hydrogen system. To represent the free energy of a solution of H atoms in a metal host which can be of two distinct phases we use the two-lattice method described by Oates and Hillert [22,23]. In this approach, the hydrogen and vacancies form a mixture on a sublattice and the metal atoms occupy the host lattice. In this system, the phase of the host lattice ( $\alpha$  or  $\beta$ ) influences the interaction energy parameters of the hydrogen/vacancy mixture on the sublattice. However, atoms are not permitted to switch lattices, so a hydrogen atom or vacancy cannot occupy a metal atom's lattice position and vice versa.

This is subtly different from the systems modeled by most phase field solutions for binary alloys, where both species can occupy the same sites. This difference results in a different expression for configurational entropy, and necessitates determination of energy parameters for the sublattice in each host phase. In this formulation, the regular solution is not of a mixture between hydrogen and metal, but rather a mixture of hydrogen and vacancies in the metal sublattice.

The regular solution free energy is expressed as a function of phase,  $\phi$ , and interstitial concentration,  $y$ , as

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