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Mg composites for hydrogen storage The dependence of hydriding properties on composition

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Abstract

Magnesium alloys show great potential as materials for gaseous hydrogen storage. However, their practical use is limited by poor hydrogen absorption and desorption kinetics. This problem can be resolved by mixing Mg alloys with other materials to form composites. We present an investigation of composites formed by mechanically milling La_2Mg_{17} with x wt.% $LaNi_5$ (x=0, 10, 20, 30, 40, 50, 60 wt.%). The rate of hydrogen absorption and desorption was measured for all of these compositions over a wide range of temperatures. These composites were then characterized using a set of reaction rate equations. The composite La_2Mg_{17}+40 wt.% $LaNi_5$ showed the best overall kinetics. At 250 °C it has an average absorption rate of 8.2 (wt.% min^{-1}) and a desorption rate of 1.0 (wt.% min^{-1}) with a final capacity of 3.7 wt.%. This is approximately 50 times faster than pure La_2Mg_{17} under the same conditions. ©1997 Elsevier Science S.A.

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1. Introduction

Magnesium and magnesium alloys have been investigated as hydrogen storage materials for several decades because they store far more hydrogen by weight than most of the other currently known metal hydrides. However, these materials are plagued by poor absorption/desorption rates and are too stable for most practical applications. This study addresses the first of these problems, that is; the improvement of the kinetics of hydrogen absorption and desorption.

It was previously shown that, when cycled under hydrogen at temperatures up to 300 °C, composites of La_2Mg_{17} mechanically milled with $LaNi_5$ disproportionate into La, Mg and Mg_2Ni and their hydrides [1]. The composition of the resulting composite is:

$$La_2Mg_{17} + xLaNi_5 \rightarrow aLa + bMg + cMg_2Ni \quad (1)$$

{where: $a=(40.2+0.32x)/d$, $b=(59.8-0.56x)/d$, $c=1.24x/d$, $d=100/(100+x)$}.

The ratio of Mg_2Ni to Mg increases as the initial quantity of $LaNi_5$ is increased. This results in a continuous decrease in hydrogen capacity and a catalytic improvement of kinetics up to a certain ratio of Mg_2Ni to Mg. We present an analysis of this dependence of hydrogen capacity and kinetics on the initial composition in the system $La_2Mg_{17}+x$ wt.% $LaNi_5$ (x=0, 10, 20, 30, 40, 50, 60 wt.%).

Today, most measurements of hydrogen absorption and desorption of composites are simply presented as plots of reacted fraction versus time. Yet, the need for a quantitative approach to evaluate composites for applications is compelling. In this light, we have used the empirical reaction rate equations proposed by Suda and Wang [5] to characterize the absorption and desorption measurements of this series of composites. From these equations we derive general rate constants for each composite at various temperatures.

Many empirical and physical models have been developed which may be used to describe the kinetics of hydride formation and decomposition [2–9]. Kinetics measurements of single phase, homogeneous and well defined powders in thermal equilibrium, when identified with one or another model, can point to the mechanisms controlling kinetics. Composites, however, can be very complex inhomogeneous mixtures composed of several different phases with a broad distribution of grain sizes. The rate limiting mechanisms may be different for each

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individual phase and may change with temperature. Thus the separation and determination of the mechanisms controlling the kinetics of each phase in such a composite proves to be extremely difficult. In the present case, rate equations will only be used to compare the relative reaction rates of a series of similar composites with the aim of determining the best overall composition.

2. Experimental details

Samples were prepared from La_2Mg_{17} and $LaNi_5$ produced by r.f. induction melting. The composites were milled for 30 min at 130 m sec^{-2} using a Fritsch "Pulverisette 7" planetary ball-mill producing powders with particle sizes on the order of 1–10 μm. All operations were performed in an Argon atmosphere. After milling, 0.6 g of sample powder was loaded into a 500 g stainless steel sample holder which was positioned inside a PID controlled furnace. The dimensions of the sample space inside of the cylindrical sample holder were: $l=35$ mm, $r=2$ mm. The samples were activated with 10 hydrogen absorption and desorption cycles at 300 °C. "Bulk Kinetics" measurements for hydrogen absorption and desorption were performed as follows: Absorption—by applying a single allotment of gas (5 ml at 50 bar) to fully hydride the sample in one step, Desorption—by desorbing a fully hydrided sample into a large volume at a low pressure (12500 ml at 1 mbar). The system volumes were all known, thus by recording the change in gas pressure the sample's hydrogen content versus time could be measured.

A thermocouple was inserted into the middle of the sample to measure the temperature during absorption and desorption. The maximum temperature variation was less than 2% for all measurements with the exception of absorption measurements of the samples $x=40$ and 50 wt.% at 250 and 300 °C. Sample $x=40$ wt.% had a maximum temperature increase of 8% during an absorption measurement at 300 °C dropping to 2% in less than 10 s. The apparatus and the variations from isothermal conditions would not be adequate to study the mechanisms controlling kinetics. However, they are sufficient for this type of comparative study.

3. Results and discussion

Most of the reversible hydrogen capacity of these composites is due to the Mg and Mg_2Ni phases. Because the capacities of these two phases (7.7 and 3.6 wt.% respectively) are very different, the reversible capacity of the composite decreases with increasing Mg_2Ni (i.e. initial $LaNi_5$) content. This relationship is pictured in Fig. 1. On the other hand, the relative absorption and desorption rates increases with increasing Mg_2Ni content up to a certain point. Examples of typical absorption and desorption measurements are shown in Fig. 2. These show the very

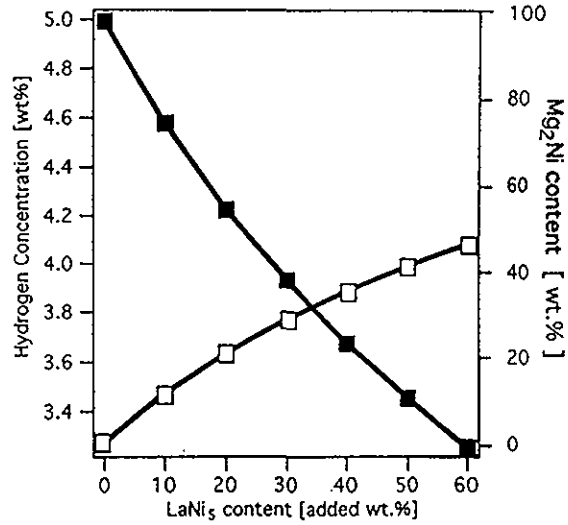


Fig. 1. Hydrogen capacity (■) versus $LaNi_5$ content for the composites $La_2Mg_{17}+x$ wt.% $LaNi_5$. Also shown is the Mg_2Ni content in wt.% (□).

different reaction rates of pure La_2Mg_{17} and $La_2Mg_{17}+40$ wt.% $LaNi_5$ at 200 °C. Fig. 3 shows calculated values of $t_{95\%}$ for the absorption and desorption of each sample at 200 °C. $t_{95\%}$ is the time required to reach 95% of the final capacity. It provides a measure of the relative kinetics of different samples independent of their hydrogen capacities. There is a minimum in the $t_{95\%}$ for both the absorption and desorption curves at $x=40$ wt.%. From Eq. (1) it can be seen that with increasing addition of $LaNi_5$ there is a resulting continuous increase in La and Mg_2Ni and a continuous decrease in Mg until $x=106$ wt.%, at which point all of the available Mg is used to form the Mg_2Ni phase. There is not a significant change in the make-up of the composite at $x=40$ wt.%. Thus, the minimum in $t_{95\%}$

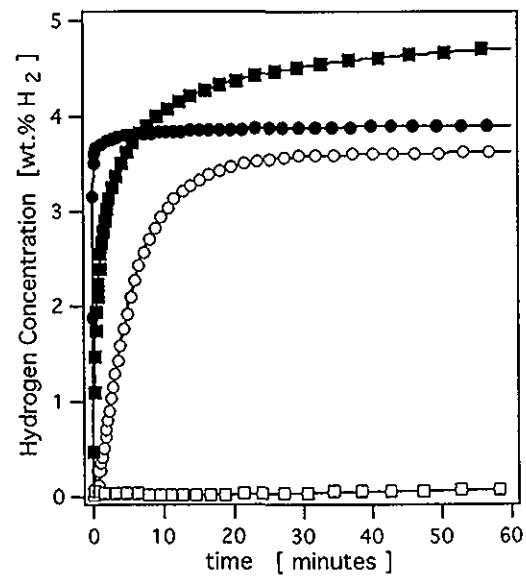


Fig. 2. Measured hydrogen reacted capacity versus time at 200 °C for the composites: La_2Mg_{17} (Absorption – ■ –; Desorption – □ –) and La_2Mg_{17} +40 wt.% $LaNi_5$ (Absorption – ● –; Desorption – ○ –).

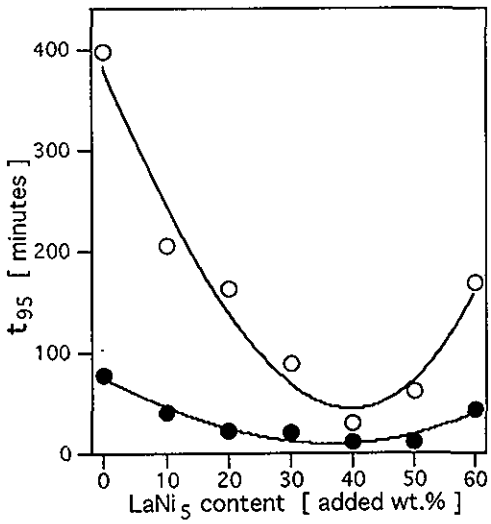


Fig. 3. Absorption (●) and desorption (○) t_{95} versus $LaNi_5$ content for the composites $La_2Mg_{17}+x$ wt.% $LaNi_5$ at 200 °C. t_{95} is the time to reach 95% of full capacity.

cannot be accounted for by one phase alone. In this case it points to a catalytic interaction between two or all of the phases. Indeed, it has been proposed that Mg_2Ni acts to catalyze the disassociative reaction of H_2 [10–12].

The normalized rate $t_{95\%}$ is also an average rate. It does not take the shape of the measured curve into account. This can be misleading as is shown schematically in Fig. 4. All of the curves in this figure have the same $t_{95\%}$. For this reason we have fitted the measured kinetics curves with a set of empirical rate equations, where the rate constant determined from the fit describes the shape of the measured curve. The equations we used were those proposed by Wang and Suda [5] for reactions in the $\alpha+\beta$ phase domain:

$$\text{Hydriding: } dC/dt = k_h F_h(P, C) \text{ and } k_h = Ae^{-Eh/RT} \quad (2)$$

where $F_h(P, C)=(P/P_{ch})^a[1-(P_f/P)^a(C/C_f)^b]$

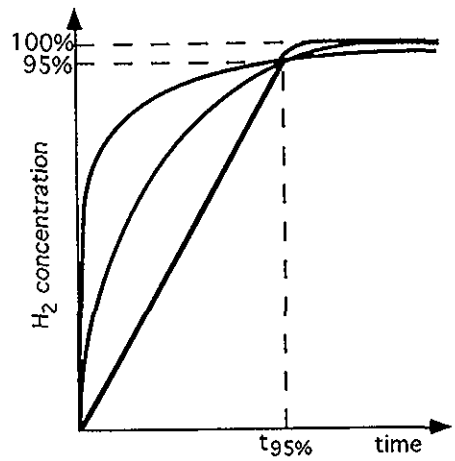


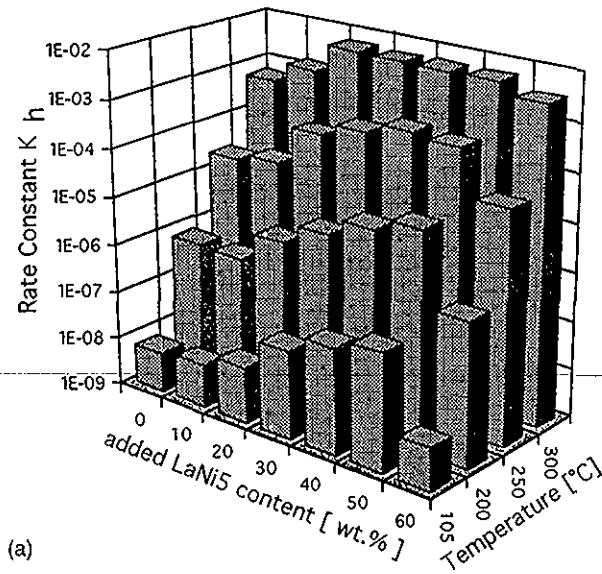
Fig. 4. Schematic representation of concentration versus time curves of different shapes which all have the same t_{95}.

$$\text{Dehydriding: } dC/dt = k_d F_d(P, C) \text{ and } k_d = A'e^{-Ed/RT} \quad (3)$$

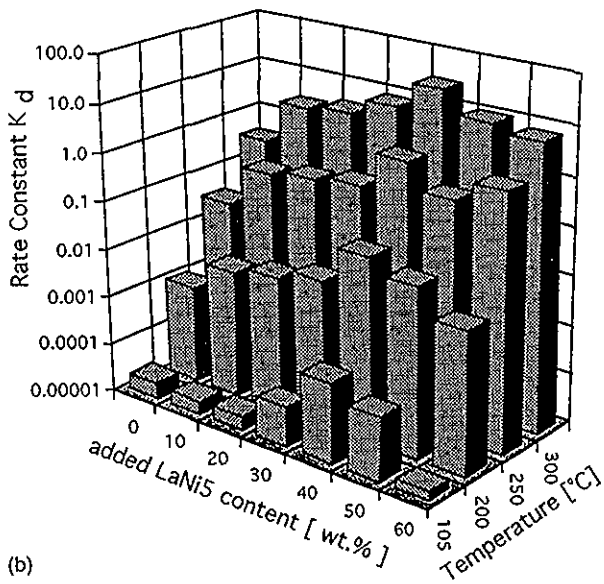
where $F_d(P, C)=(C^b/P_{cd}^a)[1-(P/P_f)^a(C_f/C)^b]$.

P: pressure at time t; P_f: equilibrium hydrogen pressure; P_{ch}: hydriding plateau pressure; P_{cd}: dehydriding plateau pressure; C: hydrogen concentration at time t; C_f: final hydrogen concentration; k_h: hydriding rate constant; k_d: dehydriding rate constant; E_h: hydriding activation energy; E_d: dehydriding activation energy; t: time; T: temperature; A and A': constants; R: universal gas constant; a and b: order coefficients—(best fit found for Absorption: $a=2$, $b=1$; Desorption: $a=1$, $b=1$).

Using these equations, the rate constants k_h and k_d were



(a)



(b)

Fig. 5. Rate constants versus Temperature for the composites $La_2Mg_{17}+x$ wt.% $LaNi_5$ ($x=0$, 10, 20, 30, 40, 50, 60 wt.%). a) Absorption and b) Desorption.

determined from the best linear fits to plots of dC/dt versus $F(P, C)$. The rate constants are global in the sense that they are composed of the sum of the reaction behaviors of all the component phases which absorb or desorb hydrogen simultaneously during a measurement. These rate constants are plotted versus Temperature in Fig. 5. It is apparent from these plots that relative kinetics increases with $LaNi_5$ content up to $x=40\ldots50$ wt.%. Plotting the log of the rate constants versus 1000/Temperature the measurements above 150 °C show roughly an Arrhenius like behavior (Fig. 6).

Below 200 °C the kinetics data was not well modeled by the reaction rate equations (Eqs. (2) and (3)). Two distinct domains appeared (Fig. 7). It is likely that this is due to the two major phases, Mg and Mg_2Ni, having substantially different kinetics at lower temperatures. It is also possible that a change occurs in the rate controlling mechanism of one or both of these phases. It appears that, for part of the absorption at 150 °C, a linear relationship exists between $\log(dC/dt)$ and $F(C, P)$ which is a $C \cong \log(t)$ behavior. This relationship was observed previously for the Mg_2Ni system [13].

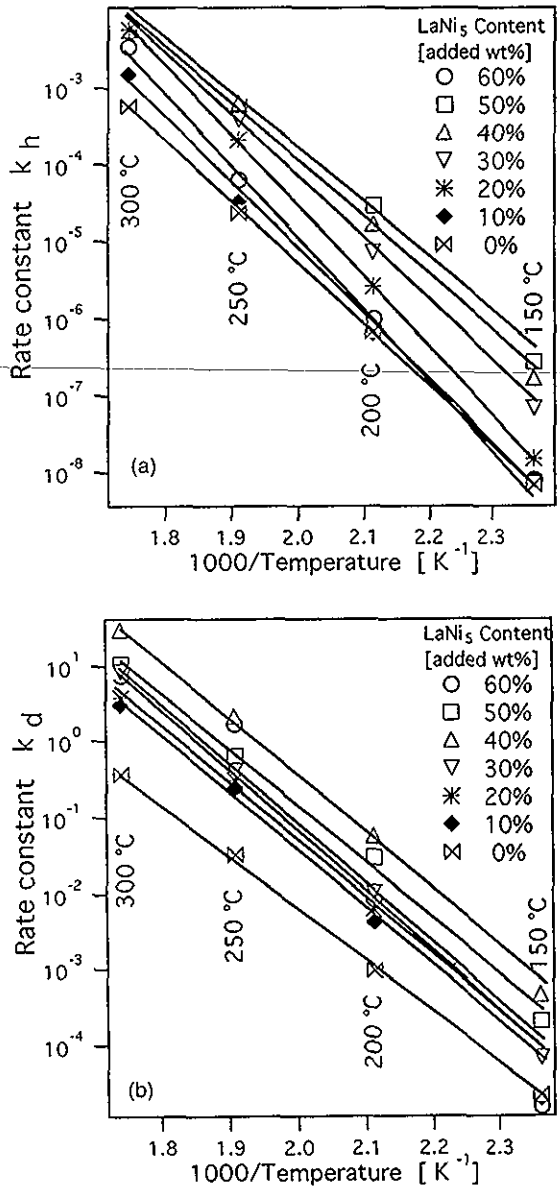


Fig. 6. Arrhenius plots: $\log(k)$ versus $1/T$ for the composites $La_2Mg_{17}+x$ wt.% $LaNi_5$ ($x=0$, 10, 20, 30, 40, 50, 60 wt.%). a) Absorption and b) Desorption.

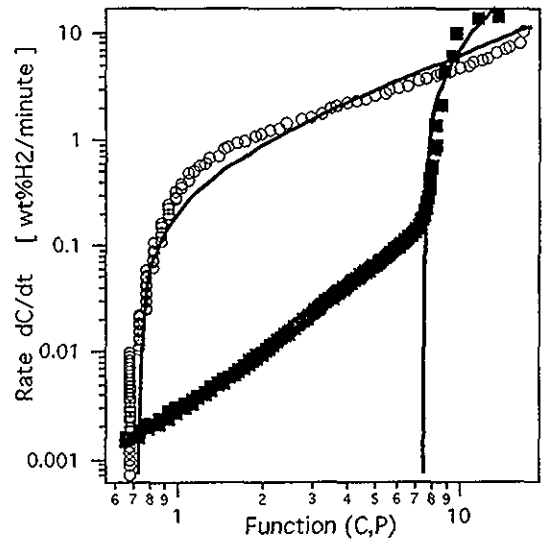


Fig. 7. Rate dC/dt versus $F(P, C)$ (Eq. (2)) for the composite La_2Mg_{17} +40 wt.% $LaNi_5$. Absorptions at 300 °C (○) and 150 °C. (■) and linear fits (———) are shown.

Normalized concentrations (reacted fractions) were used to calculate rate constants rather than the true concentrations to allow a comparison of the relative kinetics between the different composites. For applications, it is the "true" absorption and desorption rates which are important. Since capacity decreases as the kinetics are improved, it is necessary to know the system requirements before an appropriate composition can be chosen for a given application.

4. Conclusion

Composites produced by mechanically milling La_2Mg_{17} with $LaNi_5$ have a lower hydrogen capacity than pure La_2Mg_{17} but superior hydriding kinetics. Relative absorption and desorption kinetics improve with the addition of $LaNi_5$ up to 40 wt.%. In addition, the rate of hydrogen absorption and desorption of this composite is greater than an order of magnitude faster than that of pure Mg_2Ni [14–17] with the added advantage of having only 1/3 the Ni content (wt.).

The composition dependent increase in kinetics indicates that a catalytic process is involved. Empirical rate equations have been used to derive rate constants for a series of kinetics measurements. The rate constants show maximum

relative absorption and desorption rates for the composite with 40 wt% added $LaNi_5$. Below 200 °C the measurements are not adequately represented by these equations, indicating that the absorption and desorption rates of the two major phases (Mg and Mg_2Ni) may be substantially different and that there may be a transition in the rate limiting mechanisms. This system presents a good case study for advancing the fundamental understanding of composites and aiding in their development for applications.

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