Effect of some partial substitutions in lanthanum–magnesium alloys on their hydriding kinetics

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The effect of the partial substitution of calcium for lanthanum, and nickel for magnesium, in the binary alloys La_2Mg_{17} and $LaMg_{12}$ on the hydriding kinetics of the alloys is studied. The activation energies of hydrogen chemisorption on the alloy surfaces and the diffusion of hydrogen through the hydride layer formed are determined. The data obtained on the character of changes due to the altered composition of the alloys are used for explaining the experimentally observed differences in some of their properties.

1. Introduction

In previous studies [1–4] it was established that partial substitution of calcium for lanthanum, and nickel for magnesium, in the hydrogen-storing alloys La_2Mg_{17} and $LaMg_{12}$ affects the absorption–desorption characteristics of the latter. Substitution leading to single-phase samples with the structure of the initial alloy has a strong influence on the rate of hydrogen desorption from the samples. This was ascribed to the change in area of the metal/metal hydride interface as a result of substitution.

It is known that the hydriding of metal alloys passes through the following stages: (i) hydrogen chemisorption on the alloy surface; (ii) dissociation of hydrogen molecules to atoms and ions; (iii) diffusion of hydrogen particles through the hydride layer being formed, and (iv) chemical reaction of the hydride/alloy interface. Hydrogen desorption is preceded by hydride dissociation, back diffusion and association of hydrogen particles to molecules.

In a series of investigations [5–9] it was shown that during hydriding of the alloys, various stages of the process can be rate-controlling, depending on the fraction-transformed function, F. For example, with La_2Mg_{17} and its calcium-substituted isostructural derivatives at low F values (below 0.4), hydrogen chemisorption on the surface of alloy particles is rate-controlling [9]. With advancing hydriding, hydrogen diffusion becomes rate-limiting, and when $F > 0.65$, the rate-controlling stage is the chemical reaction on the interface.

In a previous paper [2], it was assumed that the nonstoichiometric lanthanum hydride formed during the hydriding of the alloy La_2Mg_{17} plays an important role during the transfer of electrons needed for the formation of H^- hydride ions. If this assumption is correct, the decrease in lanthanum content during its partial replacement by calcium should lead to a decrease in number of the chemisorption centres and the coverage degree. Indeed, it was shown by

Khrussanova *et al.* [9] that with low values of the fraction-transformed function, the activation energy of chemisorption of the $La_{2-x}Ca_xMg_{17}$ alloys will be higher than that of the binary alloy La_2Mg_{17}. However, substitution also leads to enhanced dispersion and defect number in the alloys. This would affect the rate of hydrogen diffusion and favour hydrogen desorption, as is observed [2]. Desorption is also facilitated if magnesium in La_2Mg_{17} is partially replaced by nickel [1].

On the other hand, it was established [4] that partial substitution of calcium for lanthanum in the $LaMg_{12}$ alloys leads not to acceleration but to retardation of hydrogen desorption from the samples. The main reason for this phenomenon was assumed to be the observed second nondissociating hydride formed under the experimental conditions.

The purpose of the present paper was to determine some kinetic parameters of the hydriding processes and, on their basis, to estimate the correctness of the assumptions concerning the role of the partial substitution of nickel for magnesium in the La_2Mg_{17} alloy and calcium for lanthanum in the $LaMg_{12}$ alloy.

2. Kinetic equations

The activation energies of chemisorption and diffusion were determined using the equations proposed by Park and Lee [6] and Song and Lee [7] and based on the following suppositions: (i) the alloy consists of equal-sized spherical particles, (ii) the alloy particles are hydrogen-saturated before the hydride formation, and (iii) a quasi-steady state of the system corresponds to each stage of hydriding.

According to the above authors, in the case when hydrogen chemisorption on the surface of alloy particles is the rate-controlling stage of hydriding, the experimental data should satisfy the equation

$$F = A(P_0 - P_{eq})T^{-1/2}e^{-E_a/RT}t \qquad (1)$$

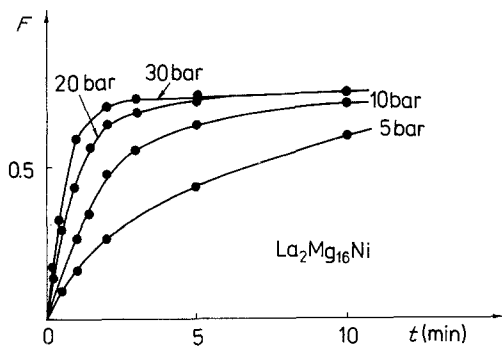where F is the fraction-transformed function and A is a constant whose value depends on the condensation

Figure 1 F–t hydriding curves of the alloy $La_2Mg_{16}Ni$ at 598 K and different pressures.

coefficient, the molecular weight of the gas (hydrogen), the coverage degree of the surface and the particle radius; P_0 denotes the hydrogen pressure during hydriding; P_{eq} is the equilibrium pressure of hydrogen determined from the P–C–T curves; T is the temperature (K), E_a, the activation energy of chemisorption, R, the gas constant and t, the time.

The same authors are of the opinion that for the three–dimensional hydrogen diffusion the following dependence should be valid:

$$1 + 2(1 - F) - 3(1 - F)^{2/3} = K_d(P_0^{1/2} - P_{eq}^{1/2})t \quad (2)$$

where K_d is the coefficient of diffusion rate which depends on temperature alone.

The kinetic equation for the chemical reaction on the interface has the form

$$1 - (1 - F)^{1/3} = K(P_0^{1/2} - P_{eq}^{1/2})t \quad (3)$$

where K is a temperature-dependent constant.

3. Results and discussion

Figs 1 to 3 present the dependences $F = f(t)$ for the hydriding processes of the alloys $La_2Mg_{16}Ni$, $LaMg_{12}$ and $La_{0.9}Ca_{0.1}Mg_{12}$. These dependences are obtained using experimental data from previous investigations [1, 4]. Measurements of the absorbed amounts of hydrogen were performed at different pressures and a constant temperature $T = 598$ K maintained with an accuracy of ± 0.5 K by means of an electronic temperature controller. Each point of the curves in Figs 1 to 3 is a mean value resulting from the processing of the results of at least three measurements, the error amounting to 0.12%.

All curves have an initial linear part for which
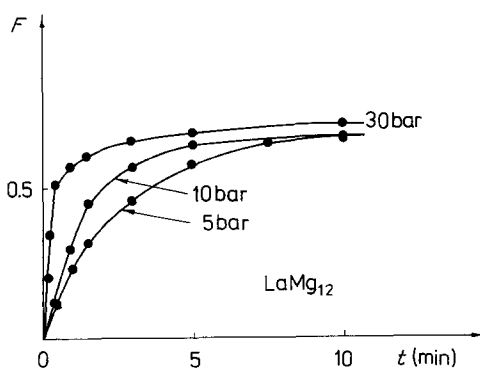
$$F = K_1 t \quad (4)$$

Figure 2 F–t hydriding curves of the alloy $LaMg_{12}$ at 598 K and different pressures.
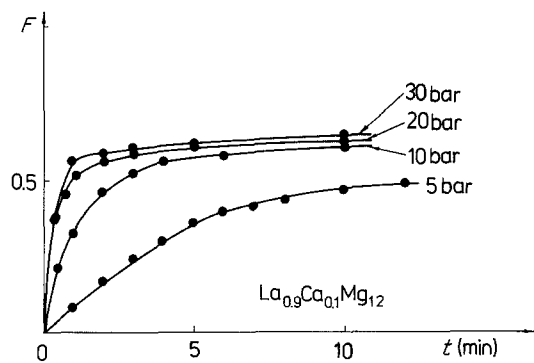

Figure 3 F–t hydriding curves of the alloy $La_{0.9}Ca_{0.1}Mg_{12}$ at 598 K and different pressures.

In this expression K_1 is a function of temperature and pressure.

For each hydriding pressure, P_0, the dependence

$$K_1 = K_1'(P_0 - P_{eq})$$

is valid. Here, the constant K_1' is a function of temperature only. Upon inserting the above expression in Equation 4, one obtains

$$F = K_1'(P_0 - P_{eq})t \quad (5)$$

Comparison between Equations 5 and 1 leads to

$$K_1' = AT^{-1/2} e^{-E_a/RT}$$

Fig. 4 shows the correlations between $\ln(K_1'T^{1/2})$ and $1/T$ for $La_2Mg_{16}Ni$, $LaMg_{12}$ and $La_{0.9}Ca_{0.1}Mg_{12}$. From the slope of the straight lines obtained one can determine the corresponding activation energies of hydrogen chemisorption, E_a.

With the advance in hydriding of the alloys, i.e. with increasing F, hydrogen diffusion becomes the rate-controlling stage of the process and the experimental data satisfy Equation 2. The experimental points in coordinates $1 + 2(1 - F) - 3(1 - F)^{2/3}$ and t lie on a straight line as can be seen in Fig. 5. From the slope of these straight lines one can determine the temperature-dependent diffusion coefficient, K_d, and use its values for plotting the $\ln K_d = f(1/T)$ dependences for the three alloys. These dependences are shown in Fig. 6. They also represent straight lines and from their slope one can find the activation energies of hydrogen diffusion, E_d, through the hydride layer formed on the surface of the alloys $La_2Mg_{16}Ni$, $LaMg_{12}$ and $La_{0.9}Ca_{0.1}Mg_{12}$. These values and the
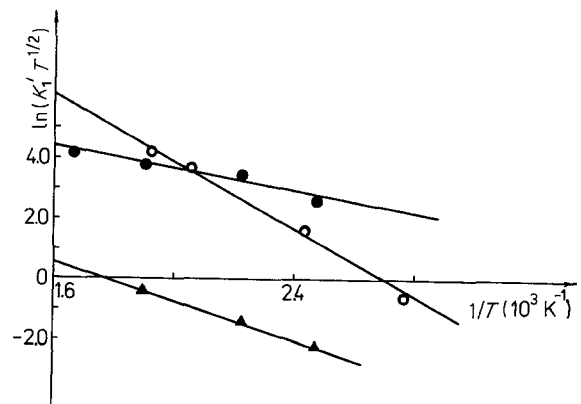
Figure 4 $\ln(K_1'T^{1/2}) - 1/T$ dependences for the alloys $La_2Mg_{16}Ni$, $LaMg_{12}$ and $La_{0.9}Ca_{0.1}Mg_{12}$.

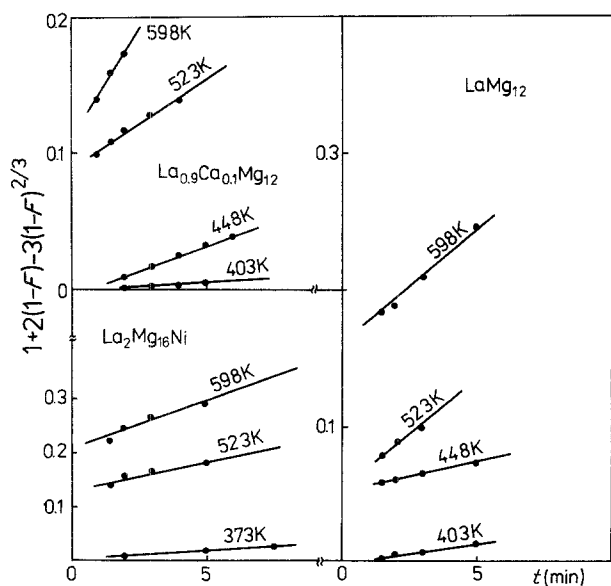*Figure 5* $1 + 2(1 - F) - 3(1 - F)^{2/3} = f(t)$ dependences for the alloys $La_2Mg_{16}Ni$, $LaMg_{12}$ and $La_{0.9}Ca_{0.1}Mg_{12}$.

TABLE I Activation energy of hydrogen chemisorption and diffusion during the hydriding of some binary and substituted lanthanum–magnesium alloys.

No.	Alloy	E_a (kJ mol^{-1})	E_d (kJ mol^{-1})	Reference
1	La_2Mg_{17}	16.6	26.2	[9]
2	$La_2Mg_{16}Ni$	47.9	17.0	present work
3	$La_{1.8}Ca_{0.2}Mg_{17}$	24.9	22.4	[9]
4	$LaMg_{12}$	15.8	23.2	present work
5	$La_{0.9}Ca_{0.1}Mg_{12}$	28.8	34.0	present work

activation energy of chemisorption for the three alloys are given in Table I. For the sake of comparison, data on E_a and E_d for the La_2Mg_{17} and $La_{1.8}Ca_{0.2}Mg_{17}$ alloys from a previous paper [9] are also included in further discussion.

The data in Table I show that partial substitution of calcium for lanthanum or nickel for magnesium in the La_2Mg_{17} alloy leads to an increase in E_a and a decrease in E_d. The increase of the activation energy of hydrogen chemisorption could be attributed to a change in number of the centres of hydrogen adsorption, which affects the coverage-dependent constant A in Equation 1. Because the nonstoichiometric lanthanum hydride formed is the main source of electrons for the formation of H^- hydride ions, the decrease in percentage of lanthanum in the substituted alloys reduces the possibility of the appearance of hydride ions.

The increase in activation energy of hydrogen chemisorption with the partial replacement of lanthanum by calcium in the $LaMg_{12}$ alloys can be explained in a similar way. However, substitutions in La_2Mg_{17} facilitate diffusion whereas in the case of $LaMg_{12}$ the opposite situation is observed: the E_d value for

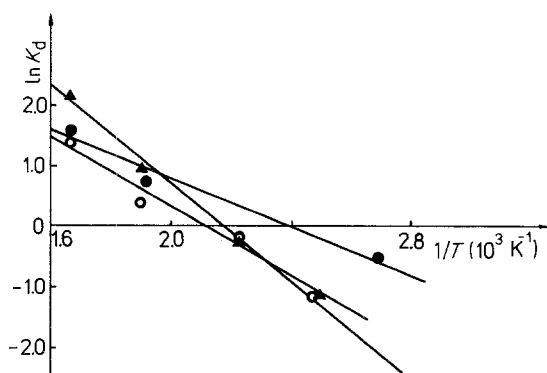$La_{0.9}Ca_{0.1}Mg_{12}$ is higher than that for the binary alloy. This is probably due to the formation of a second nondissociating hydride, LaH_2, during hydriding of the substituted alloy [4]. That additional hydride represents one more difficulty in the materialization of hydrogen diffusion.

During the hydriding of the binary La_2Mg_{17} and $LaMg_{12}$ alloys, only one nondissociating hydride, LaH_x ($x \approx 3$), is formed under the experimental conditions given by Khrussanova et al. [1] and Pezat et al. [4]. The hydriding in this case can be presented by the following equations:

$$La_2Mg_{17} + 20H_2 \longrightarrow 2LaH_3 + 17MgH_2$$

and

$$LaMg_{12} + 13.5H_2 \longrightarrow LaH_3 + 12MgH_2$$
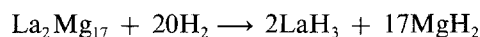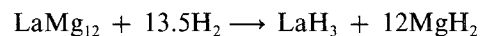
A simple calculation shows that with these reactions proceeding to completion, LaH_3 constitutes 39% of the total mass of the hydriding products of La_2Mg_{17} and about 31% of those of $LaMg_{12}$. The higher concentration of a nondissociating hydride in the first case is probably the reason for the higher value of the activation energy of hydrogen diffusion. This assumption is indirectly confirmed by experimental data on the desorption from the two hydrided alloys, which show hydrogen to be more easily desorbed from $LaMg_{12}$ than from La_2Mg_{17} [1, 4]. Evidently, the presence of a smaller amount of nondissociating hydride facilitates hydrogen back diffusion.

The accelerated hydrogen desorption from the alloy $LaMg_{12}$ compared to that from La_2Mg_{17} may also be due to another reason. Because of the higher magnesium concentration in $LaMg_{12}$, the initial hydriding stage in this alloy is associated with the appearance of a larger number of magnesium hydride nuclei. We have established [10] that after hydriding under different pressures, the samples desorb hydrogen with different rates. The more the hydriding pressure differs from the equilibrium, i.e. the larger the number of magnesium hydride nuclei, the higher the desorption rate due to the increased interface. On the basis of the foregoing, if a definite number of absorption–desorption cycles are carried out with the two alloys under the same conditions, the alloy richer in magnesium should show a higher dispersion degree. As is evident from the electron micrographs in Fig. 7, this is really observed.

The initial $LaMg_{12}$ has larger particles than the initial La_2Mg_{17}. In both cases the particle size gradually decreases with successive hydriding–dehydriding and after a certain number of cycles it remains almost
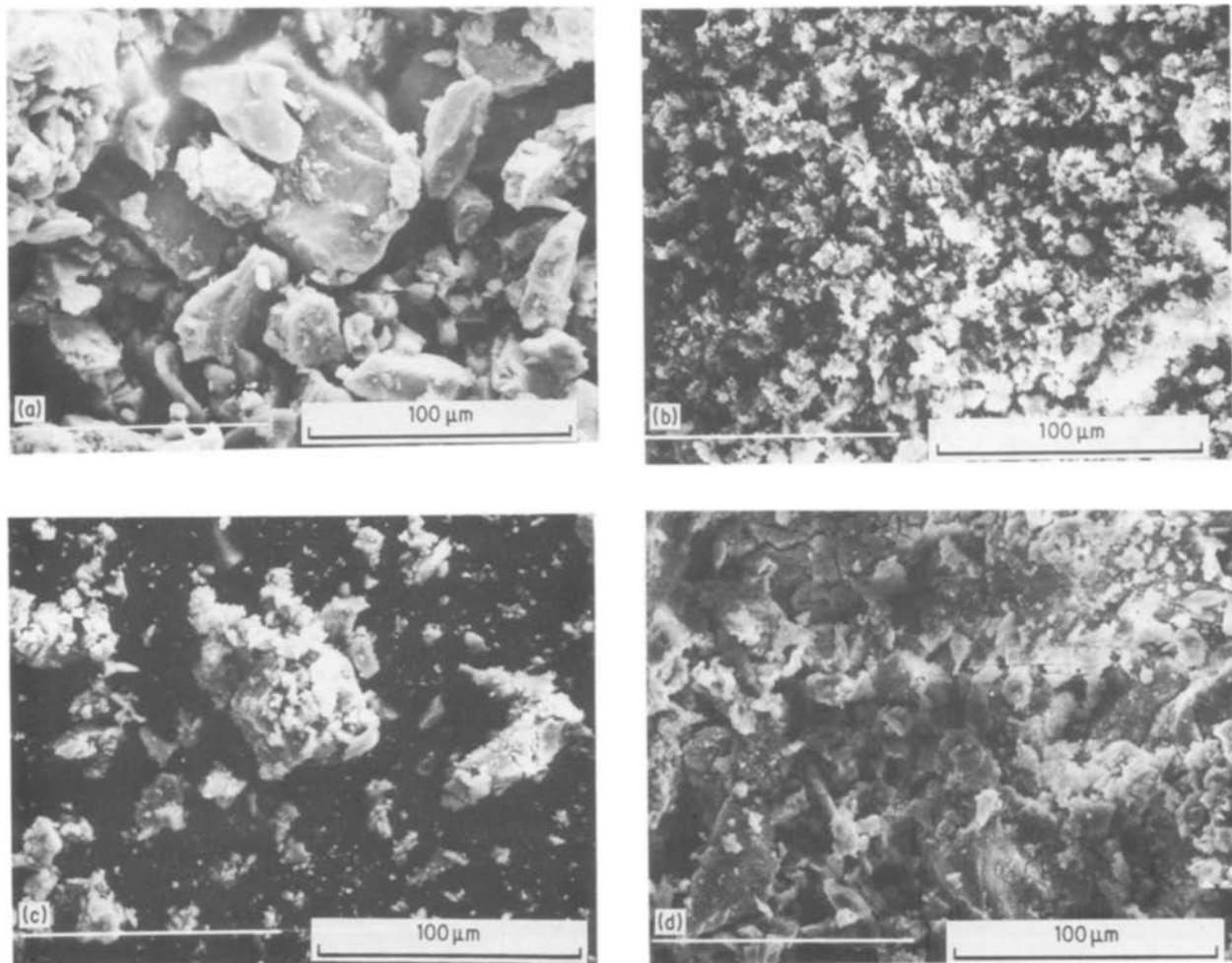

Figure 6 Ln $K_d = f(1/T)$ dependences for the alloys $La_2Mg_{16}Ni$, $LaMg_{12}$ and $La_{0.9}Ca_{0.1}Mg_{12}$.

Figure 7 Electron micrographs of alloys LaMg$_{12}$ and La$_2$Mg$_{17}$. (a) Initial LaMg$_{12}$, (b) LaMg$_{12}$ after 50 absorption–desorption cycles, (c) initial La$_2$Mg$_{17}$, (d) La$_2$Mg$_{17}$ after 50 hydrogen absorption–desorption cycles.

constant. Comparison of Figs 7b and d shows that the final effect is much more pronounced with LaMg$_{12}$ particles.

4. Conclusion

Partial substitution of calcium for lanthanum and nickel for magnesium in binary La$_2$Mg$_{17}$ and LaMg$_{12}$ alloys changes their hydriding kinetics and the activation energies of hydrogen chemisorption and diffusion, respectively. The character of these changes allows the formulation of some plausible explanations of the differences in some properties experimentally observed with both binary lanthanum–magnesium alloys and some of their isostructural derivatives obtained by partial substitution of the two metals.

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