

## KINETICS STUDY OF HYDROGEN STORAGE IN MECHANICALLY ALLOYED Mg ALLOYS

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### ABSTRACT

The present work is aimed to the study of the kinetic mechanisms of hydrogen storage and release in mechanically alloyed  $\text{Mg}_{97.4}\text{Fe}_{2.6}$  and  $\text{Mg}_{90}\text{Ni}_{10}$  powders, at three different temperatures (275, 300 and 350°C), and particle sizes in the range of 1-7  $\mu\text{m}$ . At each temperature, the powders were subjected to two complete cycles of hydriding and dehydriding by exposure to an atmosphere of hydrogen under alternate pressures of 3 and 0.01 MPa, respectively.

The experimental data of transformation fraction of hydrogen captured (or released) *versus* time were analyzed using the Johnson-Mehl-Avrami model (JMA). Fitting of the data to the JMA model was best performed using only one set of kinetic parameters ( $k$ ,  $n$ ).

The calculated values of the JMA exponent  $n$  are remarkably different among the two different alloyed powders. However, in most cases it is difficult to reconcile such calculated values of  $n$  with the physical mechanisms expected to operate during the hydriding and dehydriding processes in Mg alloys. Only with supporting microstructural observations of partially transformed samples it will be possible to demonstrate whether the description of transformation kinetics with a given model is fortuitous or true.

**Key words:** Mg alloys, hydrogen storage, hydriding kinetics

## 1. INTRODUCTION

The high cost and eventual depletion of fossil fuels, together with the environmental problems associated with their use, have given impetus to current interest in fuel cell technology. One of the mayor obstacles to implementing this technology resides in the development of suitable means of hydrogen storage. Light metal hydrides are attractive storage materials due to their relatively large gravimetric density of hydrogen stored. However, the kinetics and thermodynamics of hydriding (H) and dehydriding (D) processes should be improved. Among light metals, magnesium is a suitable candidate because of its moderate cost, abundance and a relatively high gravimetric density of 7.7 wt. % hydrogen [1]. Ball milling of magnesium with additions of transition metals are known to improve the kinetics and thermodynamics of hydrogen storage [2]. In this paper, we study the effect of the incorporation of Fe and Ni in a Mg matrix on the kinetics of H/D, at temperatures of 275, 300 and 350° C.

### 1.1 ANALYSIS OF H/D KINETICS

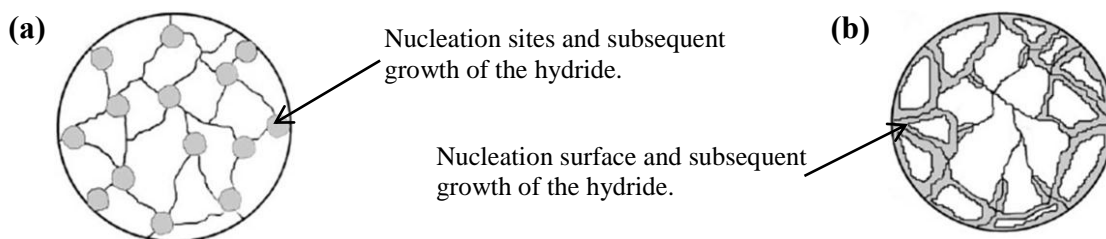
Two models are frequently used to analyze the kinetics of H/D of magnesium and its alloys [3]. One, the classic Johnson-Mehl-Avrami (JMA) model is commonly used to fit the experimental data in circumstances in which the formation and decomposition of the hydride is expected to occur randomly by nucleation and growth, as illustrated in Fig. 1a [4]. The JMA model equation is usually written as:

$$\alpha = 1 - e^{-(kt)^n} \quad (1)$$

where  $k$  and  $n$  are constants for a given temperature,  $\alpha$  is the weight fraction of transformed hydrogen (or hydride) and  $t$  is time. The value of  $n$  depends on the location of the new phase in the microstructure of the matrix and on the geometry and dimensions of growth [5]. In any case, the limiting step is the speed of the Mg/hydride interface, provided that bulk hydrogen diffusion is fast enough [3,4]. In the literature, the value of  $n$  is sometimes set to 2 or 3 as shown in equations 2 and 3, respectively [4]:

$$\text{JMA model with } n \text{ fixed} \quad kt = -\ln(1 - \alpha)^{\frac{1}{2}} \quad (2)$$

$$kt = -\ln(1 - \alpha)^{\frac{1}{3}} \quad (3)$$



**Figure 1.** Schematic picture of phase grow according to (a) JMA model and (b) CV model [4]

On the other hand, the volume contraction (CV) model [3,4] assumes that the nucleation process occurs early at the surface of the particles and growth of the new phase proceeds after formation of a thin transformation layer (Fig. 1b). Hence, the kinetics of transformation is dependent on the diffusion of  $H_2$  through this layer. This model is usually described by an equation of the type:

$$kt = 1 - (1 - \alpha)^{\frac{1}{n}} \quad (4)$$

The calculated values for  $n$ , for dehydriding experiments with Mg alloys, vary over a wide range, from 0.5 to 14 (Table 1); however, most reported values range from 1 to 3. In turn, for the corresponding hydriding experiments, the relatively few reported values are in the range of 0.5 to 3 (Table 2). The majority of the values included in Tables 1 and 2 were calculated using the JMA model.

## 2. EXPERIMENTAL PROCEDURES

Mechanically alloyed powders of nominal compositions (in at.%)  $Mg_{97.4}Fe_{2.6}$  and  $Mg_{90}Ni_{10}$  were produced as described in previous works [12]. In order to avoid combustion of the powders, they were slowly exposed to air (passivated) after the milling operation. In such condition, the powders were subjected to H/D treatments by direct exposure to hydrogen at different temperatures (in the range 250 – 350 °C) under a hydrogen gas pressure of 3MPa, as described in previous works [12]. The particle size of the as-milled powders was in the range of 1-7  $\mu m$ .

Table 1. Kinetic properties in the dehydriding process of Mg alloys

Material	T °C	Model	n	Comments
Mg [6]	300-400	JMA	1.5 - 2	Act
Mg+10 wt% V [7]	300-350	JMA	3	NR
Mg+10 wt% Y [7]	300-350	JMA	3	NR
Mg+10 wt% Zr [7]	300-350	JMA	3	NR
MgH <sub>2</sub> [8]	350	JMA	2.7	w/M, Act
MgH <sub>2</sub> [9]	360-400	JMA	2.3 - 4.4	S/M, MgO
MgH <sub>2</sub> [10]	150-225	JMA	0.33	
MgH <sub>2</sub> -1% C [8]	350	JMA	2.1	Act
MgH <sub>2</sub> -11% C [8]	350	JMA	2.0	Act
MgH <sub>2</sub> -Nb <sub>2</sub> O <sub>5</sub> [4]	300	CV-2D	2.0	
MgH <sub>2</sub> -17Mg-8MgO [11]	425-500	JMA	4	NIT, Act
MgH <sub>2</sub> -2 wt% Ni [9]	350-390	JMA	4.2 - 14.9	w/M, MgO

JMA = Johnson-Mehl-Avrami model; NR = not reported; E/A = exposed to air; Act = activation treatments; w/M = without milling; MgO = oxidation reported; CV-2D = CV model in 2 dimensions; NIT = non-isothermal tests

Table 2. Kinetic properties in the hydriding process of Mg alloys

Material	T °C	Model	n	Comments
Mg [6]	300-400	JMA	0.5 - 1	Act, high P <sub>H</sub>
Mg [11]	377-427	JMA	NR	Act. thin film
Mg [11]	341-368	JMA	NR	Act
MgH <sub>2</sub> -5% Ni [10]	150-350	JMA	0.33	
MgH <sub>2</sub> - Nb <sub>2</sub> O <sub>5</sub> [4]	300	CV 3D	2	
MgH <sub>2</sub> - 0.5% mol Nb <sub>2</sub> O <sub>5</sub> [4]	300	CV-3D	2 - 3	

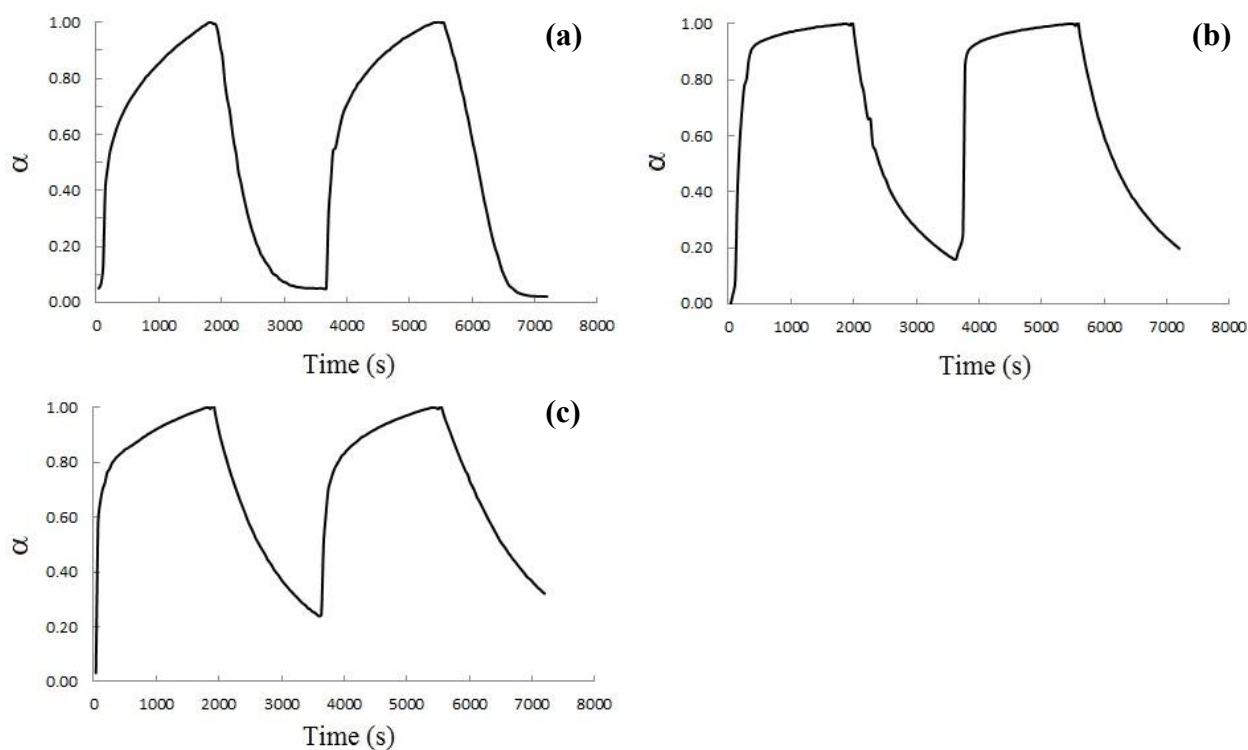
JMA = Johnson-Mehl-Avrami model; Act = activation treatments; P<sub>H</sub> = H<sub>2</sub> pressure; NR = not reported; CV-3D = CV model in 3 dimensions; CV-3DD = CV model in 3 dimensions controlled by diffusion.

### 3. RESULTS AND DISCUSSION

Figures 2 (a-c) shows H/D data for Mg<sub>97.4</sub>Fe<sub>2.6</sub> alloyed powders at different temperatures without prior activation. At 350°C (Fig. 2a), hydriding occurs rapidly, as it is typical for mechanically alloyed powders [4,10]. In this case, the maximum amount of hydrogen stored in the alloy is about 6 wt.%. The main reason for not reaching the theoretical capacity (7.6 wt.%) probably resides in the oxidation of magnesium in the process of passivation of the powders after mechanical alloying, as discussed in other works [7,9]. As a matter of fact, the x-ray diffraction patterns of our powder samples (not shown) commonly display some characteristic peaks from MgO, particularly after hydriding/dehydriding at temperatures of 300 °C or higher (see, for example, ref. [13]). Based on thermodynamics, MgO would not be expected to be reduced by

hydrogen gas under the conditions of our experiments. Nevertheless, dehydriding occurs less rapidly than hydriding, but still it is practically complete in 20 minutes.

At a temperature of 300°C (Fig. 2b), the hydriding process occurred initially faster than at 350°C, but with a sudden and drastic deceleration. The amount of hydrogen captured is of the order of 5 wt.% in 30 minutes. More importantly, the process of dehydriding did not release all the stored hydrogen, leaving a remanent of around 0.8 - 1.0 wt. % after 30 minutes. For the temperature of 275°C (Fig. 2c), the processes of H/D occur similarly to those observed at 300°C; however, in this case, there still remains an amount of hydrogen of the order of 1 - 1.5 wt.% after dehydriding for 30 minutes. The maximum amount of stored hydrogen during hydriding is about 4.5 wt.%, although it is clear that the period of 30 minutes was insufficient to complete the process.

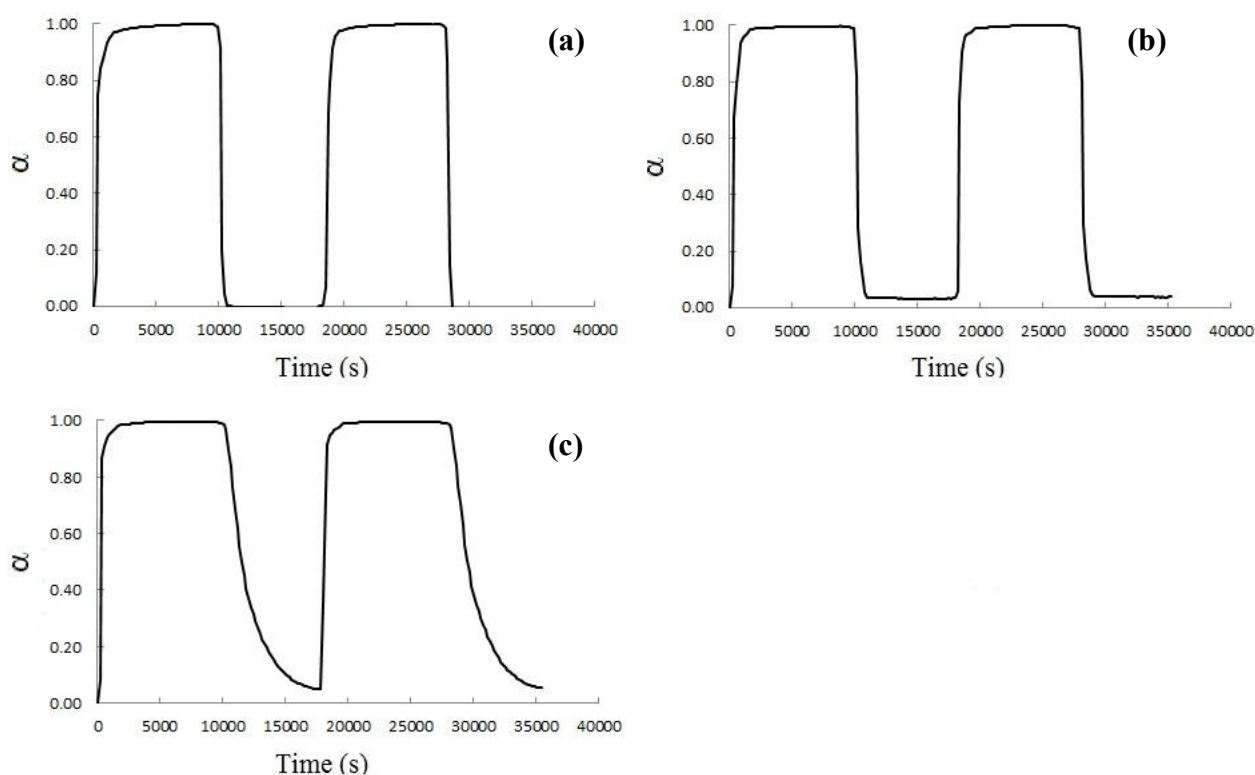


**Figure 2.** H/D cycles for  $\text{Mg}_{97.4}\text{Fe}_{2.6}$  alloyed powders at a  $\text{H}_2$  pressure of 3 MPa and temperatures of (a) 350°C, (b) 300°C and (c) 275°C



Figures 3 (a-c) shows the results of H/D tests performed on  $Mg_{90}Ni_{10}$  alloyed powders at 250, 300 and 350°C, respectively. In general, the data show that the H/D processes occur at rates faster than in the  $Mg_{97.4}Fe_{2.6}$  alloyed powders, but in contrast to the latter, the amount of stored hydrogen was about 5 wt.%, independently of the temperature.

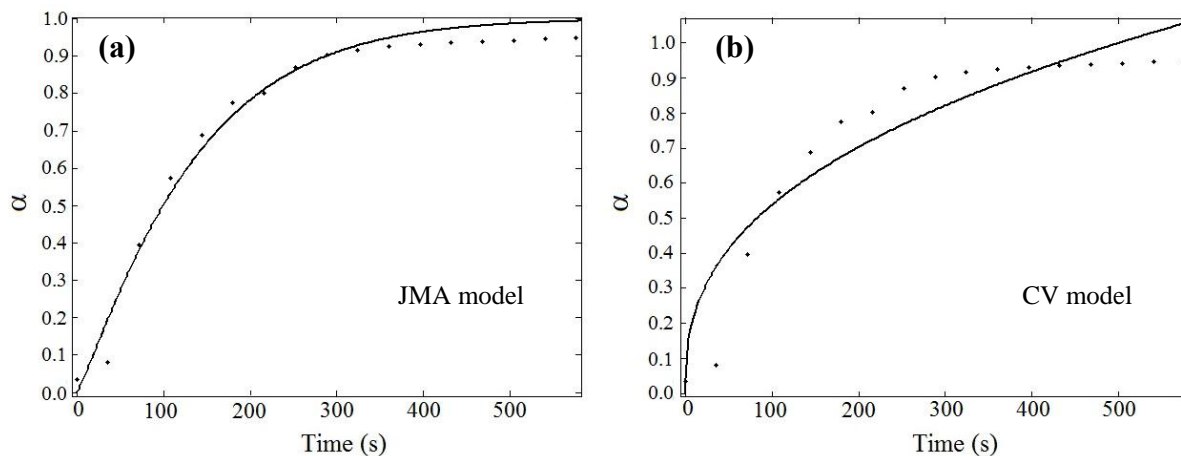
The process of dehydriding at 300 and 350°C occurred rather suddenly (Figs. 3a,b), while at 250°C occurred somewhat more slowly (Figure 3c). The amount of hydrogen remaining in the alloy after 150 minutes was 0.1 wt.% or less.



**Figure 3.** H/D cycles for  $Mg_{90}Ni_{10}$  alloyed powders at a  $H_2$  pressure of 3 MPa and temperatures of (a) 350 ° C, (b) 300 ° C and (c) 275 ° C.

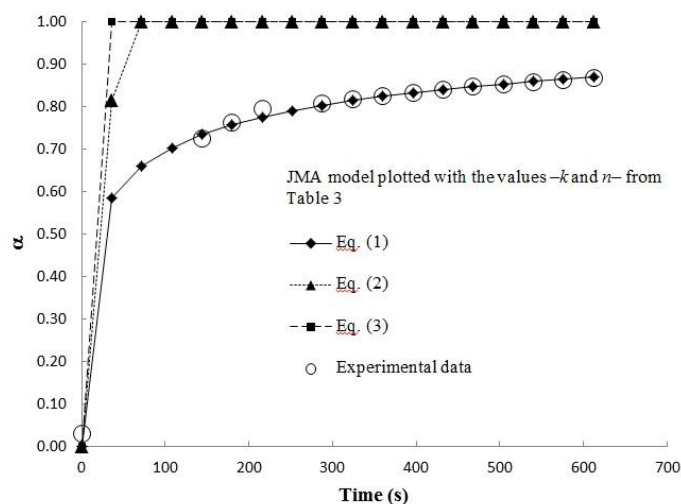
Attempts to fit the experimental data to the CV model usually failed (Fig. 4). Consequently, in the following only the JMA model was used to fit the experimental data.

Initially, the experimental data was corrected for an effective "zero time". Additionally, if an irregular fluctuation in the data occurred at the beginning of a H/D process, such data were not included in the calculation, considering that the experimental system was in a transient state.



**Figure 4.** Fit for first hydriding from sample  $\text{Mg}_{97.4}\text{Fe}_{2.6}$  at  $300^\circ\text{C}$  with: (a) JMA model and (b) CV model.

To illustrate the details of the fitting procedure of experimental data to the JMA model, Fig. 5 graphically shows the best fits using equations (1) to (3) for the first hydriding operation at  $275^\circ\text{C}$  for sample  $\text{Mg}_{97.4}\text{Fe}_{2.6}$ . It can be seen in Table 3 that fitting without restrictions on the value of  $n$



**Figure 5.** Comparison of the different JMA equations as they fit the experimental data for the first hydriding process of  $\text{Mg}_{97.4}\text{Fe}_{2.6}$  at  $275^\circ\text{C}$ .

produced a high correlation coefficient, while the fittings using a default value of  $n$  (2 and 3) did not fare as well even when the data was fitted to two different  $k$  values (assuming some change in the kinetic conditions during the hydriding stage). It is clear that the fit made with equation (1) is the one that best represents the experimental trend in this example. This was also the case in practically all instances of the H/D data shown before for  $\text{Mg}_{97.4}\text{Fe}_{2.6}$  and  $\text{Mg}_{90}\text{Fe}_{10}$  samples. It should be mentioned that the practice to fix the value of  $n$  has occurred in several instances in the published literature, in many cases without any verifiable justification.

Table 3. Calculated values of  $n$  and  $k$  for the first hydriding operation of sample  $\text{Mg}_{97.4}\text{Fe}_{2.6}$  at 275 °C

Equation	$n$	$k$	$R^2$
1	0.2965	0.3032	0.9982
2	2	0.0004 0.0013	0.9944 0.5779
3	3	0.0003 0.0010	0.9940 0.5278

The procedure described previously was applied to all the experiments from the two different alloyed powders. Table 4 displays the calculated values of  $n$  and  $k$ . The values of  $n$  calculated for hydriding operations of the  $\text{Mg}_{97.4}\text{Fe}_{2.6}$  powders are in the range of 0.21 to 1.13. In turn, for dehydriding processes  $n$  varies from 0.73 to 2.15. The corresponding values for the  $\text{Mg}_{90}\text{Ni}_{10}$  samples are in the range of 1.52 to 3.05, and 1.17 to 2.77, for hydriding and dehydriding operations, respectively. Clearly, the calculated values of  $n$  are significantly larger for the  $\text{Mg}_{90}\text{Ni}_{10}$  samples for both H and D processes. Also, the latter material mostly displays an increasing tendency in the  $n$  values with higher temperatures, while the  $\text{Mg}_{97.4}\text{Fe}_{2.6}$  powders show no defined tendency at all.

The value of  $n$  in the JMA model can be associated to kinetic and geometric effects of the transformation [5]. For example, a value of  $n \approx 1$  is theoretically associated with conditions of diffusion controlled growth together with grain boundary nucleation after saturation or the growth of long needles or plates, while a value  $n \approx 3$  corresponds to conditions of site saturation (zero nucleation rate) after a “short” period of random nucleation (and diffusion controlled growth). However, the correspondence between the values of  $n$  and such kinetic and geometric



Table 4.  $n$  and  $k$  values calculated for H/D processes using the JMA model

Process	$k$ ( $s^{-1}$ )			$n$		
	275°C	300°C	350°C	275°C	300°C	350°C
$Mg_{97.4}Fe_{2.6}$						
1st H	$3.23 \times 10^{-3}$	$1.28 \times 10^{-2}$	$4.40 \times 10^{-4}$	0.30	1.13	0.75
1st D	$1.18 \times 10^{-3}$	$1.32 \times 10^{-4}$	$1.37 \times 10^{-2}$	1.05	0.73	1.47
2nd H	$6.29 \times 10^{-3}$	$2.86 \times 10^{-2}$	$1.78 \times 10^{-4}$	0.42	0.21	0.65
2nd D	$2.23 \times 10^{-3}$	$2.09 \times 10^{-4}$	$4.61 \times 10^{-2}$	1.20	0.80	2.15
$Mg_{90}Ni_{10}$						
	250°C	300°C	350°C	250°C	300°C	350°C
1st H	$3.27 \times 10^{-3}$	$2.48 \times 10^{-3}$	$2.81 \times 10^{-3}$	3.05	1.91	2.19
1st D	$2.40 \times 10^{-3}$	$1.80 \times 10^{-3}$	$1.91 \times 10^{-3}$	1.28	2.61	2.77
2nd H	$3.35 \times 10^{-3}$	$1.87 \times 10^{-3}$	$1.25 \times 10^{-3}$	1.52	2.77	2.61
2nd D	$4.23 \times 10^{-4}$	$2.73 \times 10^{-3}$	NC	1.17	1.63	NC

NC = Not calculated (due to problems with system stability).

factors is derived with the assumptions of a uniform (transforming) particle size and initiation time (time “zero”). In fact, Mintz and Zeiri [14] indicate that departure from these ideal conditions can lead to experimental  $\alpha$  versus  $t$  curves with a good fit to the JMA model even though the actual transformation mechanism corresponds to, for example, the CV model. The only way to assert that the agreement between experimental  $\alpha$  versus  $t$  data and the JMA model is not coincidental requires microstructural observations of partially transformed samples to determine how the new phase (in our case,  $MgH_2$  or pure Mg, on H and D processes, respectively) nucleates and grows during transformation under given experimental conditions of hydrogen pressure and temperature.

In the case of our nanostructured powders the observation of their transformation at different stages of completion involves several obstacles. For one, the H and D processes may occur very rapidly. In some of the data shown in Figs. 2 and 3, it is evident that about 80 % of the transformation has occurred in a few minutes. Considering that the powders had an average size usually lower than 1  $\mu m$ , but were forming agglomerates of 10-20  $\mu m$  in size [12], it would be challenging to prepare suitable cross sections of such specimens. Nevertheless, this work is currently in progress within our research group.

Mintz and Zeiri [14] also indicate that the calculation of apparent activation energies for H/D processes may yield significant information even when the exact transformation mechanism is not clearly established. This is conventionally done by assuming an Arrhenius type dependence of the kinetic parameters, but without recurring to a specific transformation model. In that case, taking  $t_{50}$  as the time to reach 50 % of the transformation (any other transformation fraction could also be used), it can be shown that the following relation holds:

$$\frac{d \ln t_{50}}{d\left(\frac{1}{T}\right)} = \frac{Q_{50}}{R} \quad (5)$$

where  $R$  is the gas constant and  $Q_{50}$  denotes the apparent activation energy of the process, which may be a function of the transformation fraction  $\alpha$ . Application of this procedure to the data from the mechanically alloyed powders used in the present work yields the results that are shown in Table 5:

Table 5. Activation energy values for  $Mg_{97.4}Fe_{2.6}$  and  $Mg_{90}Ni_{10}$

Processes	$Q_{50}$ (kJ/mol)	
	$Mg_{97.4}Fe_{2.6}$	$Mg_{90}Ni_{10}$
1st H	101	7
1st D	98	30
2nd H	23	49
2nd D	19	No enough data

It should be mentioned that the data for the second H/D process did not fit well the assumed linear relationship between  $\ln t_{50}$  and  $1/T$ .

The above values for  $Mg_{97.4}Fe_{2.6}$  powders are in the range of values reported by Jensen et al. [9] for hydriding processes, but too small compared to other results for dehydriding experiments. The case of  $Mg_{90}Ni_{10}$  powders is even more biased towards lower values of the activation energy.

Overall, the analysis of the experimental data for  $Mg_{97.4}Fe_{2.6}$  and  $Mg_{90}Ni_{10}$  powders indeed points out to rather different controlling mechanisms of the H/D behavior in both materials. However, using only the goodness of fit of the data to models of the amount of transformation with time, it is not possible to unambiguously determine what mechanisms are actually operating unless the kinetic analysis is supported by microstructural observations of partially transformed samples. In

principle, the use of JMA type models implies that diffusion of hydrogen gas to (or away from) the specimen surface is very fast compared to other kinetic processes (which may be reasonably to assume in most H/D experiments), but the effect of powder agglomeration has not been explicitly analyzed (and it is most probable that the state of agglomeration changes with number of applied H/D cycles, especially at the very first cycles). Depending on the compactness of the agglomerates, one could envision extreme situations in which either the (very compact) agglomerate behaves as one single particle and an outer transformed layer forms at the beginning of the transformation (CV model) or the (very loose) agglomerate undergoes a transformation which resembles a sort of random nucleation and growth (JMA) process but. In any case, because of the small *true particle size*, the kinetics of transformation at each particle is overshadowed by the kinetics of the agglomerate.

#### 4. CONCLUSIONS

Analysis of the kinetics of hydriding/dehydriding of mechanically alloyed powders of nominal compositions  $\text{Mg}_{97.4}\text{Fe}_{2.6}$  and  $\text{Mg}_{90}\text{Ni}_{10}$ , was performed using the JMA model at temperatures in the range of 250- 350°C. The data could be fitted reasonably well without restrictions on the calculated  $n$  and  $k$  values, with values of  $n$  in the range of 0.3 to 3.05 and 0.73 to 2.77 for hydriding and dehydriding processes, respectively. However, the calculated values of  $n$  vary over too wide a range to be compatible with the physical mechanisms expected to operate during the hydriding and dehydriding processes in Mg alloys. It is argued that it may happen that the kinetics of transformation of *particle agglomerates* yields an overall transformation curve which fits the behavior predicted by a JMA-type model, even though the physical mechanisms under operation are different from those assumed by the random nucleation and growth models.

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