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Hydrogenation kinetics of ZK60 Mg alloy during solid–gas reaction milling in hydrogen

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ABSTRACT

The process of solid–gas reaction milling in hydrogen was applied to achieve the full hydrogenation of ZK60 Mg alloy by forming Mg hydride (MgH_2). The hydrogenation kinetics to form MgH_2 during reaction milling was experimentally investigated by in situ monitoring of the hydrogen absorbed by the alloy in the vial. The effect of milling parameters and hydrogen pressure on the hydrogenation kinetics was evaluated and the underlying mechanisms were discussed by referring to the mechanical energy input intensity, the vial temperature, and the Gibbs free energy change for the reaction. The kinetic equation, the rate constant, the reaction order exponent, and the activation energy for the hydrogenation reaction to form MgH_2 during reaction milling were obtained by fitting the experimental data with the Avrami–Erofeev theory.

1. Introduction

Magnesium alloys are becoming increasingly attractive in aerospace, automotive, materials handling, and portable electronic appliances, because of their low densities, excellent damping and electromagnetic shielding properties, etc. [1–3]. Nevertheless, Mg alloys in general suffer from relatively poor mechanical strength. In order to exploit the potential of Mg alloys for high performance structural applications, improvement of their mechanical strength is urgently demanded [4].

Grain refining is an effective way to improve the mechanical strength of metallic materials. In most cases, the yield stress, σ_y, can be related to the grain size, d, by the Hall–Petch expression $\sigma_y = \sigma_0 + k_y d^{-1/2}$, where σ_0 and k_y are positive constants for a specific material [5]. For Mg alloys, the strengthening due to grain refining can be very tempting because of the high k_y values [6,7]. For example, when the grain size is reduced to 100–200 nm, the $Mg_{97}Zn_1Y_2$ (atomic ratio) alloy presents a yield strength as high as 600 MPa [8].

Powder metallurgy (P/M) is a potential route to prepare nanocrystalline and ultrafine grained bulk alloys and components. For most Mg alloys, however, it is difficult to produce nanocrystalline powders for P/M use. To produce nanocrystalline Mg alloy powders for P/M use, we have developed the mechanically assisted hydriding–dehydriding process [9,10]. The key step of the process is to produce nano-structured hydrided alloy powders by mechanically assisted hydrogenation via reaction milling in hydrogen, so that a final nanostructure is developed after subsequent thermal dehydriding.

At present, there is no comprehensive knowledge on the kinetics of mechanically assisted hydriding of Mg and Mg alloys. In the present paper, we aim to model the hydrogenation kinetics of a ZK60 Mg alloy during solid–gas reaction milling in hydrogen by fitting the experimental investigation with the Avrami–Erofeev theory. Such work is certainly of significant importance both in scientific meaning and in engineering practice, because it helps not only to gain an insight into the solid–gas reaction kinetics and mechanism but also to achieve technologically process control and optimization.

2. Experimental

Commercially available ZK60 Mg alloy, with a purity of 99.5 wt% and a nominal composition of Mg–(5.5–6) wt%Zn–(0.4–0.5) wt%Zr, was used as the starting material. Before it was used for reaction milling in hydrogen, the alloy was crushed into coarse powders. The reaction milling was performed with the use of a planetary type QM-DY4 ball-mill supplied by Nanjing NanDa Instrument Plant. The ball to powder mass ratio was 60:1 or 120:1, the mill shaft rotation was 300 rpm or 400 rpm, and the hydrogen pressure for the reaction milling was 0.5 ± 0.03 MPa or 1 ± 0.03 MPa, respectively.

The charging of the vials was performed in a glove box filled with pure argon. Before milling, the charged vial was evacuated and flushed with high-purity hydrogen for at least once. Then, the vial was filled with hydrogen until the required pressure for reaction milling was achieved. When necessary, this procedure was repeated for operations to take sample powders or to replenish hydrogen in case that the pressure in the vial falls to the lower limit. During milling, the hydrogen pressure in the vial was in situ monitored by a pressure gauge with a measurement

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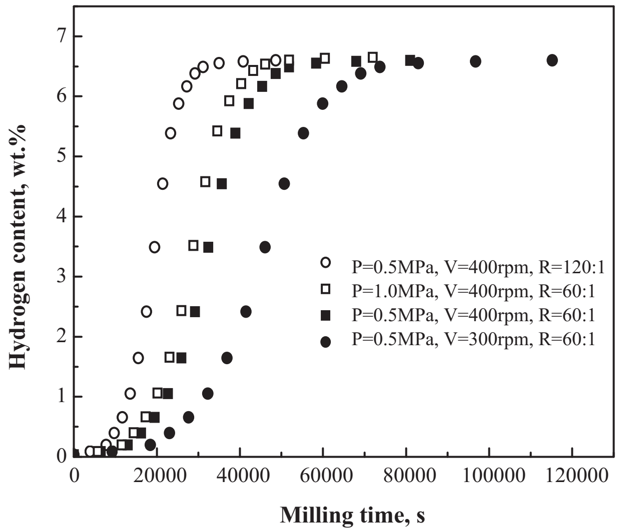

Fig. 1. Hydrogen absorption of ZK60 Mg alloy during reaction milling.

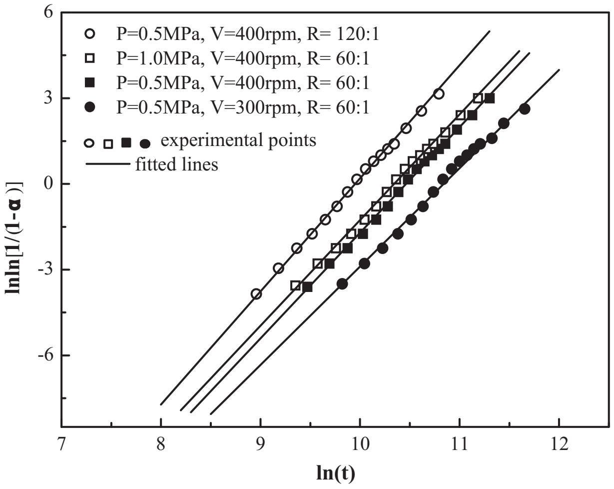

Fig. 2. Plots of $\ln \ln[1/(1-\alpha)]$ against $\ln(t)$ and the linear fitting.

accuracy of less than 0.2 kPa, and the hydrogen absorbed by the alloy was calculated referring to the vial pressure change.

3. Results and discussion

3.1. Experimental kinetic curves

Fig. 1 shows the hydrogen absorption of ZK60 magnesium alloy against milling time during reaction milling by using different hydrogen pressure (P), mill shaft rotation (V), and ball to powder mass ratio (R). It shows that the hydrogen absorption kinetic curves under different milling conditions are similar in shape or changing trend with milling time, attributed possibly to the same mechanism for hydrogenation of the alloy during reaction milling. The time needed for achieving hydrogen saturation in the alloy is dependent on the milling parameters used for the process. The hydrogenation is obviously accelerated with either a stronger milling intensity, i.e., a higher V and/or R, or a higher hydrogen pressure, since in the former case the intensity of the mechanical energy input for driving the reaction of "$Mg + H_2 \rightarrow MgH_2$" is increased, while in that latter case the Gibbs free energy change for the formation of MgH_2 by the above reaction is more negative as compared with the use of a relatively lower hydrogen pressure [11].

3.2. Fitting of experimental data with Avrami–Erofeev theory

For most solid–gas reactions, the reaction kinetics can be formulated by applying the Avrami–Erofeev theory [12,13]:

$$\alpha = 1 - \exp(-kt^n) \quad \text{or} \quad \ln\ \ln\left[\frac{1}{(1-\alpha)}\right] = \ln(k) + n\ln(t) \tag{1}$$

where k is the rate constant, which is related to the reaction temperature and activation energy, n is the reaction order exponent, which is dependent on the physical and chemical nature of the reactants, t is the reaction time, and α is the reaction fraction or transformed fraction at time t, respectively.

Assuming that the hydrogen absorbed by the alloy is exclusively to form MgH_2, and the total transformation of the Mg in the alloy to MgH_2 corresponds to the full hydriding or 100% of hydrogenation, then we can obtain the variation of hydrided fraction with milling time during reaction milling by using the experimental data in Fig. 1 to make plots of $\ln \ln[1/(1-\alpha)]$ against $\ln(t)$, as shown in Fig. 2.

Listed in Table 1 are the values of n and $\ln(k)$ by measuring the slope and intercept of the fitted lines in Fig. 2. By applying the values of n and $\ln(k)$ in Table 1 to Eq. (1), the kinetic equations corresponding to different milling conditions were obtained, as also shown in Table 1.

In Ref. [14], it has been reported that a reaction order exponent n equal to 3 accounts well for the conventional thermally driven hydriding reaction of Mg alloy with hydrogen. In the present study, the reaction order exponent, n, falls in the range of 3.44–3.95, as shown in Table 1. The higher n value in the present study may be attributed to the sustained formation of new solid–gas interfaces and lattice defects in Mg crystals during intensive milling. In addition, Table 1 also shows that both n and k increase with increasing milling intensity or hydrogen pressure. This can be interpreted by the fact that the increase in milling intensity means the more mechanical energy input per unit time to overcome the activation energy barrier for the reaction of "$Mg + H_2 \rightarrow MgH_2$", while a higher hydrogen pressure provides a stronger thermodynamic driving force, i.e., a more negative Gibbs free energy change, for the above reaction.

Fig. 3 shows the hydrogenation kinetic curves plotted by using the equations listed in Table 1. For comparison, the experimental data were presented as points. It is seen that the experimental points are well fitted with the theoretical curves, suggesting that the hydrogenation kinetics of the ZK60 Mg alloy during reaction milling in hydrogen can be well described by the Avrami–Erofeev theory.

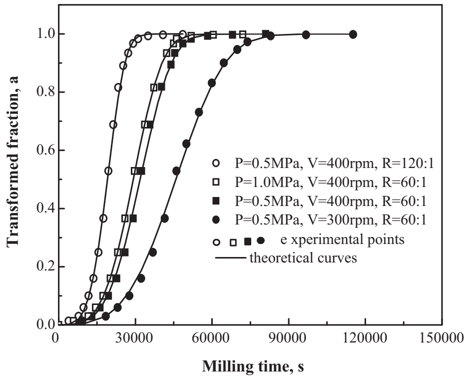

Fig. 3. Kinetic curves by fitting experimental data with Avrami–Erofeev theory.

Table 1
Values of n and $\ln(k)$ under different milling conditions.

Hydrogen pressure (P)	Mill rotation (V)	Ball to powder ratio (R)	n	$\ln(k)$	Kinetic equation $\alpha = 1 - \exp(-kt^n)$
0.5 MPa	400 rpm	120:1	3.95	−37.82	$\alpha = 1 - \exp(-3.76 \times 10^{-17} t^{3.95})$
1.0 MPa	400 rpm	60:1	3.70	−38.41	$\alpha = 1 - \exp(-2.08 \times 10^{-17} t^{3.70})$
0.5 MPa	400 rpm	60:1	3.69	−38.60	$\alpha = 1 - \exp(-1.72 \times 10^{-17} t^{3.69})$
0.5 MPa	300 rpm	60:1	3.44	−39.95	$\alpha = 1 - \exp(-4.46 \times 10^{-18} t^{3.44})$

3.3. Reaction activation energy

It is noted that the rate constant, k, in Eq. (1) can be related to the reaction temperature, T, and the activation energy, E, by the Arrhenius expression:

$$k = k_0 \ \exp\left(\frac{-E}{RT}\right) \quad \text{or} \quad \ln(k) = \ln(k_0)\frac{-E}{RT} \tag{2}$$

where k_0 is the pre-exponential constant term, and R is the gas constant. Since theoretically the value of k in Eq. (2) is dependent only on temperature for a certain chemical reaction, the variation of k with milling conditions shown in Table 1 suggests that the vial temperature during milling is also dependent on the milling conditions. Indeed, this has been confirmed by temperature measurements during milling (Fig. 4). From Fig. 4, it is seen that the vial temperature rises very fast in the initial milling stage, but soon becomes stabilized after milling for about 3600 s. The stabilized temperature is dependent on the milling intensity and hydrogen pressure. Increasing the milling intensity or the hydrogen pressure leads to a higher stabilized vial temperature

In order to figure out the activation energy, E, for the formation of MgH_2 during reaction milling of ZK60 Mg alloy in hydrogen, the values of $\ln(k)$ were plotted against $1/T$ (Fig. 5). Due to the linear relationship between $\ln(k)$ and $1/T$ in Eq. (2), it is clear that the slope of the fitted line in Fig. 5 represents $(-E/R)$. Based on the slope measurement and calculation, the value of E for the hydriding reaction of ZK60 Mg alloy by milling in hydrogen was estimated to be 49.8 kJ/mol.

It has been reported that, for the thermally driven hydrogenation of conventional Mg and Mg alloys, the activation energy is around 90 kJ/mol [14]. However, for nanostructured Mg and Mg alloys prepared by ball milling, the activation energy can be reduced significantly because there are much more grain boundaries and crystal defects which result in the raising of the average atomic energy level. For example, in Ref. [15], the activation energy for thermally driven hydriding of nanocrystalline Mg was reported to be 52.91 kJ/mol. In the present study, the activation energy was found to be 49.8 kJ/mol, which is a bit little lower than that reported in Ref. [15]. This may be attributed to fact that the MgH_2 phases formed on the Mg particles tend to peel off or break down in situ during reaction milling [10,16], which contributes to the further raising of the average atomic energy level because as a whole the ratio of the surface Mg atoms is enhanced significantly for this mechanically driven hydrogenation process. Also, it is possible that the alloying elements Zr and Zn in ZK60 Mg alloy may be partially responsible for the lower activation energy, and this needs to be further investigated in our future work.

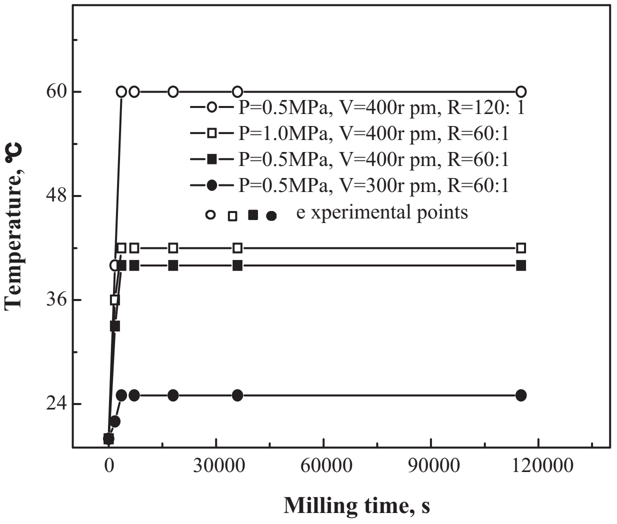

Fig. 4. Vial temperature change during milling under different conditions.

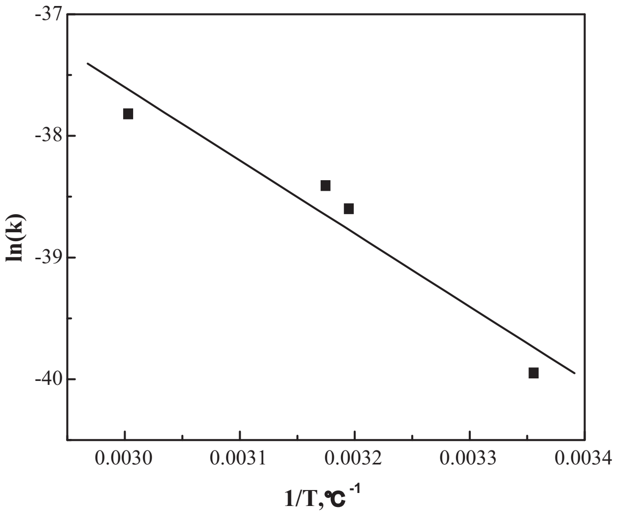

Fig. 5. Plot of $\ln(k)$ against $1/T$ and the linear fitting.

4. Conclusions

(1) The kinetics of the mechanically driven hydrogenation of ZK60 Mg alloy by solid–gas reaction milling in hydrogen can be well described by using the Avrami–Erofeev theory, with the reaction fraction, α, formulated as $\alpha = 1 - \exp(-kt^n)$.
(2) The reaction order exponent, n, for the hydrogenation by reaction milling in hydrogen is higher than that for the conventional thermally-driven process, and it is dependent on the milling conditions. The higher the milling intensity or hydrogen pressure, the higher the reaction order exponent n. In the present study, the value of n falls in the range of 3.44–3.95.
(3) The activation energy for the hydrogenation of ZK60 Mg alloy by reaction milling in hydrogen under conditions in the present study is found to be 49.8 kJ/mol, which is much lower compared to the value of around 90 kJ/mol reported for the thermally driven hydrogenation of conventional Mg and Mg alloys.

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