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Interaction of hydrogen with an Mg–Al alloy

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Abstract

The interaction of hydrogen with an Mg–Al alloy pre-exposed to air have been studied with in situ time resolved X-ray powder diffraction. Phase fractions as a function of time are derived from series of consecutive diffraction patterns allowing kinetic analysis. The apparent activation energy for dehydrogenation of the Mg–Al alloy is found to be 160 kJ/mol. This is not significantly higher than for pure and fully activated Mg. It is suggested that the addition of Al improves the resistance towards oxygen contamination.

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Keywords: Intermetallics; Hydrogen storage materials; Gas–solid reactions; X-ray diffraction

1. Introduction

Magnesium hydride has a high theoretical gravimetric hydrogen density (7.6 wt.%) but, suffers from several drawbacks e.g.: (i) thermodynamics dictate heating to above 280–300 °C for desorption of hydrogen from MgH_2, making it unsuitable for low-temperature applications, (ii) kinetics of hydrogenation/dehydrogenation may be regarded as slow and (iii) magnesium is very sensitive to gaseous impurities such as oxygen, creating an oxide shell retarding the kinetics. Thermodynamics and kinetics may be improved to some degree by alloying. The price being a reduced hydrogen capacity.

Alloying with Al have been reported to improve both thermodynamics [1,2] and kinetics [3]. From X-ray powder diffraction studies of the hydrogenated Mg–Al compound disproportionation into MgH_2 and Al could be concluded [1]. Desorption of hydrogen leads to complete reaction forming an Mg–Al compound, suggesting reversibility upon hydrogenation/dehydrogenation. These findings are in agreement with those of Bouaricha et al. [3]. Moreover, the addition of aluminum may add improved heat transfer properties to the hydride bed. This has prompted us to study the interaction of hydrogen with an Mg–Al alloy.

2. Experimental

The Mg–Al alloy subject to our investigations was prepared by arc melting approximately 5 g of a mixture of magnesium and aluminum according to the stoichiometry $Mg_{17}Al_{12}$ (γ-phase [4]) in an Edmund Buhler Arc Melting system. The magnesium (7.9 mm rod from Goodfellow) and aluminum (5–15 mm ingots from Sigma–Aldrich) used were 99.9% purity. The Mg–Al sample was melted repeatedly in an Argon atmosphere until the sample appeared homogeneous. Subsequently, the Mg–Al sample was ball milled for 10 min using WC balls.

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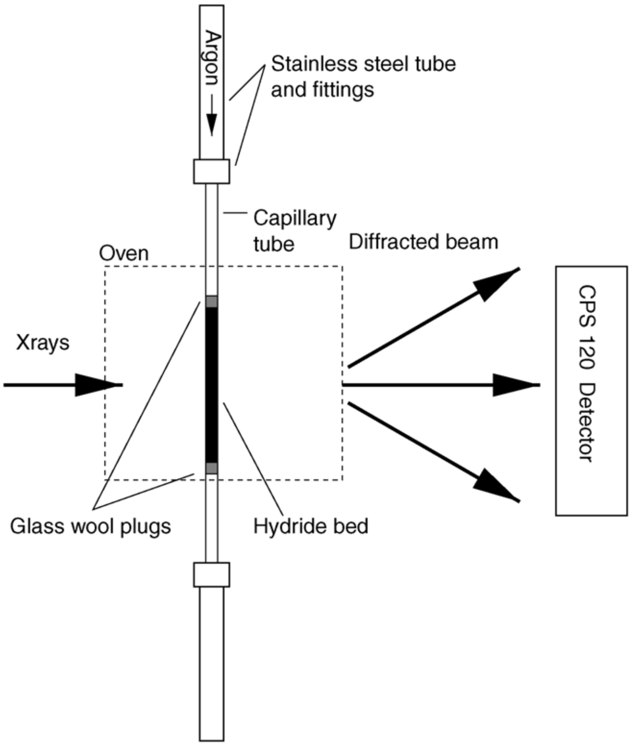

Fig. 1. Schematic drawing illustrating the experimental setup.

The ball milled sample of Mg–Al alloy was initially hydrogenated in a Sartorius high pressure balancing unit described in detail elsewhere [5]. The sample was hydrogenated by applying a hydrogen pressure (99.9997% purity from Air Liquide) of approximately 30 bar and a temperature of approximately 350 °C.

The X-ray instrument used for time resolved in situ X-ray powder diffraction (XRPD) was built around a Rigaku rotating anode (Cu $K\alpha_{12}$ radiation, $\lambda = 1.5418$ Å, 50 kV and 300 mA). The intensity of the diffracted beam was recorded with a curved position sensitive detector, INEL CPS 120, covering 120° in 2θ with a resolution of ca. 0.03°. The acquisition time per powder pattern was chosen to be 150 s. The in situ reactor cell is described in detail elsewhere [6]. The powder sample was loaded between plugs of quartz glass wool in a quartz capillary tube (0.7 mm o.d.) in order to fix the bed and allow a gas flow (Ar, 10 mL/min) through the sample during data acquisition as shown in Fig. 1. The samples were heated by a stream of hot nitrogen gas (20 °C/min) to a constant temperature in the range 350–400 °C and the dehydrogenation was followed under isothermal conditions.

3. Results and discussion

The XRPD of the as prepared ball milled sample is shown in Fig. 2. No metallic magnesium or aluminum was observed. The powder pattern shows relatively wide reflections and the peak positions correspond well with those observed for the γ-phase ($Mg_{17}Al_{12}$). However, content of the ϵ ($Mg_{42}Al_{58}$ [4]) and β-phase (Mg_2Al_3 [4]) can not be ruled out. Using the Scherrer equation the crystallite size is approximated to be 10 nm.

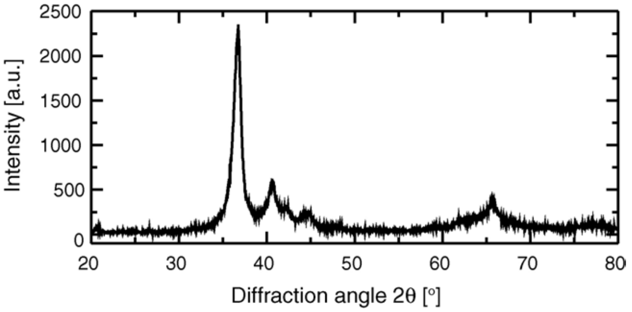

Fig. 2. XRPD of the as-prepared ball milled sample.

The initial hydrogenation of the ball milled Mg–Al alloy showed almost complete hydrogenation within approximately 17 h. The total hydrogen uptake was approximately 3.1 wt.% corresponding to an approximate stoichiometry of $Mg_{0.41}Al_{0.59}$ assuming hydrogenation of Mg only. This stoichiometry is close to both that of the β and the ϵ-phase. The hydrogen uptake is somewhat lower than expected from the initial stoichiometry. The Mg–Al alloy is transformed completely into MgH_2 and metallic Al cf. Fig. 3 at $t = 0$. The peak width is reduced probably due to sintering at the elevated temperature during hydrogenation and corresponds to a crystallite size of approximately 70 nm.

The decomposition of MgH_2 + Al studied with in situ time resolved XRPD is illustrated by 72 consecutive XRPD patterns in Fig. 3 showing the disappearance of the MgH_2 (1 1 0), (1 0 1), (2 2 0) and the Al (1 1 1) and (2 0 0) reflections and the corresponding appearance of several reflections in the range $2\theta = 35$–43 °C of an Mg–Al alloy. During the heating of the sample the MgH_2 and Al reflections shift towards lower 2θ values due to the thermal expansion of the crystal lattices.

The phase fraction of MgH_2 have been calculated from the in situ XRPD data by numerically integrating the (1 1 0) reflection of MgH_2. Dehydrogenation curves i.e. phase fraction of MgH_2 versus time have been constructed for all experiments using normalized integrated intensities. The results are shown in Fig. 4. All dehydrogenation curves show a sigmoidal shape and faster dehydrogenation with higher temperatures, although, the shape of the dehydrogenation curve at 390 °C seems to deviate slightly from the others.

A Johnson–Mehl–Avrami (JMA) type nucleation and growth rate equation has been fitted to the dehydrogenation curves in Fig. 4

$$\alpha(t) = \exp\left(-(kt)^n\right) \tag{1}$$

where $\alpha(t)$ is the time-dependent phase fraction. Assuming an Arrhenius expression for the rate constant k cf. Eq. (2)

$$k = A \exp\left(-\frac{E_A}{RT}\right) \tag{2}$$

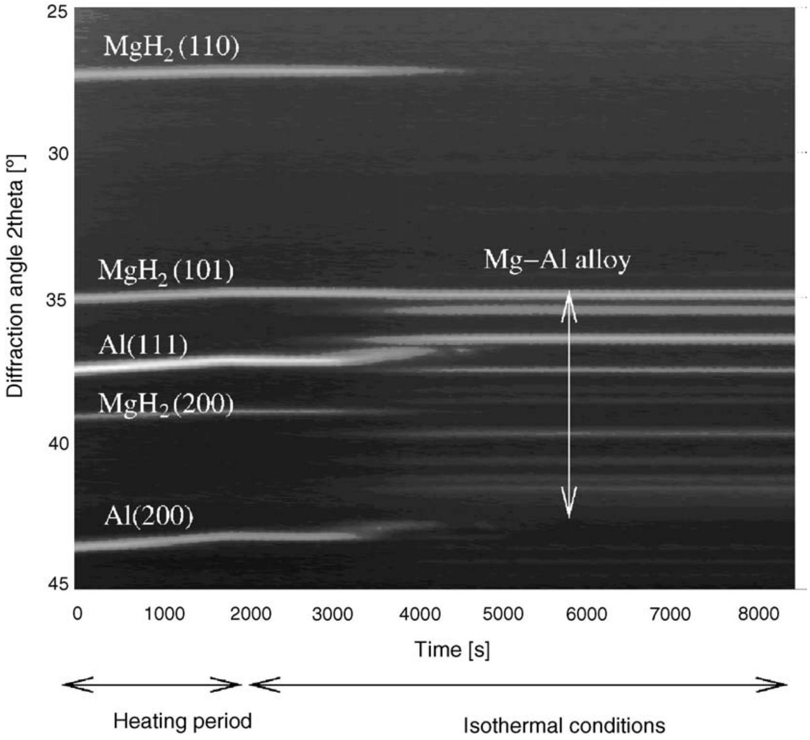

Fig. 3. Time resolved in situ XRPD of the dehydrogenation of MgH_2 + Al. The graphic consists of 72 consecutive diffraction patterns stacked chronologically from left to right. Bright areas correspond to a high detector count rate (reflections), whereas dark areas correspond to low detector count rates (background). The isothermal reaction temperature is $T = 400\,^\circ\mathrm{C}$ and acquisition time is $t = 150$ s.

where A is a pre-exponential factor, E_A the apparent activation energy and R is the universal gas constant, we can extract the apparent activation energy by plotting $\ln k$ versus $1/T$ cf. Fig. 5 and find E_A/R as the slope. As shown in the figure the data points fit the Arrhenius expression Eq. (2) fairly well. The apparent activation energy is found to be 160 kJ/mol H_2. This value is very close to the activation barrier of 160–166 kJ/mol H_2 for the dehydrogenation of pure magnesium hydride recently found by Fernandez and Sanchez [7,8]. The sample in this investigation differs from the one investigated by Fernandez and Sanchez not only in composition but also in pretreatment. Special precautions were taken not to oxidize the sample in Ref. [7,8] prior to kinetic measurements and the sample was also fully activated by several adsorption/desorption cycles before measurements. In this investigation the sample has been exposed to air both before the initial hydrogenation and before the time resolved XRPD study. Recently, we investigated the dehydrogenation of pure magnesium [9] with the same setup used here and with the same pretreatment procedure. We found a substantial increase in the apparent activation enthalpy of dehydrogenation to approximately 250–300 kJ/mol (probably due to oxygen contamination/magnesium oxide formation). This comparison suggests that alloying with Al creates a compound less sensitive towards oxygen contamination which requires little if any pretreatment in order to activate the sample. No crystalline magnesium oxide is observed neither in the as-prepared ball milled sample nor in the hydrogenated/dehydrogenated sample. However, oxygen was detected using Energy Dispersive X-ray Spectroscopy suggesting the presence of an X-ray amorphous oxide. This is consistent with the observations of Scotto-Sheriff et al. [10]. Compared to a crystalline oxide layer, the presence of an amorphous oxide layer is likely to offer improved hydrogen diffusion [11,12].

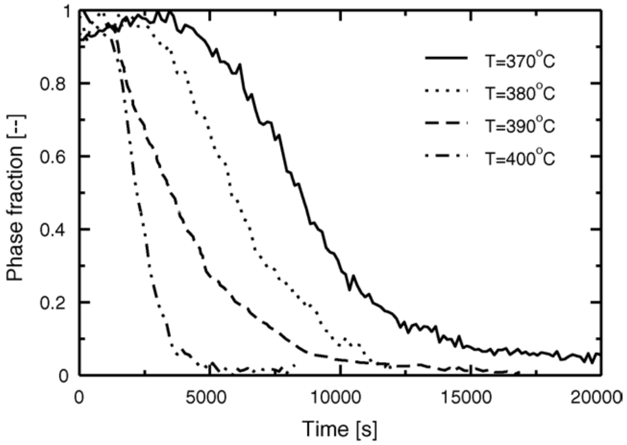

Fig. 4. Experimental dehydrogenation curves for pure MgH_2 in MgH_2 + Al determined by integrated intensity of the MgH_2 (1 1 0) reflection from time resolved in situ XRPD data.

There may be other kinetic improvements associated with alloying Mg with Al. The grain boundaries between MgH_2/Al/Mg–Al may provide favorable diffusion paths as proposed for Mg/Mg_2Cu [13].

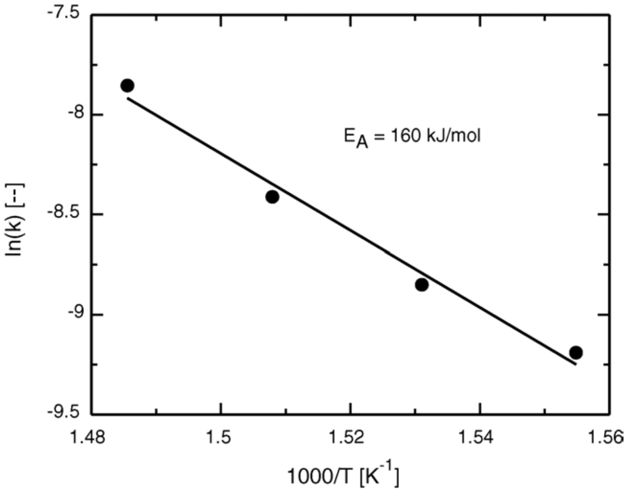

Fig. 5. Arrhenius plot of the logarithmic rate constant (derived from fitting the dehydrogenation data from time resolved in situ XRPD) vs. reciprocal temperature for the dehydrogenation of MgH_2 + Al.

4. Conclusion

The interaction of hydrogen with an Mg–Al alloy has been studied by in situ time resolved X-ray powder diffraction. The activation energy of dehydrogenation is found to be 160 kJ/mol. Further, we suggest that Mg–Al is less sensitive than Mg to oxygen contamination.

Acknowledgments

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