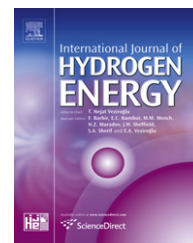


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# A study of phase transformations during the development of pressure-composition-isotherms for electrodeposited Mg–Al alloys

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## ABSTRACT

The evolution of microstructure during the pressure-composition-temperature (PCT) test at 350 °C for Mg-10at%Al and Mg-4at% alloy powders fabricated by electrodeposition as well as pure Mg powder were studied. The results of this study show that the starting microstructure of the Mg-10at%Al alloy powders consist mainly of the hcp-Mg phase. However, due to the rejection of Al by the MgH<sub>2</sub> phase, a considerable amount of the Mg<sub>17</sub>Al<sub>12</sub> phase forms upon the initial hydrogenation stage. Consequently, this powder exhibits three transformational steps with the final microstructure consisting of MgH<sub>2</sub> and fcc-Al phases. The dehydrogenation takes place at relatively high pressure by formation of the Mg<sub>17</sub>Al<sub>12</sub> phase at the MgH<sub>2</sub>/fcc-Al interface. The hydrogen released diffuses through the interconnected fcc-Al/Mg<sub>17</sub>Al<sub>12</sub> network to the surface. In contrast, Mg-4at%Al and pure Mg powders release hydrogen at a low pressure by the nucleation of the hcp-Mg phase on the surface.

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## 1. Introduction

Magnesium hydride is an attractive material for hydrogen storage applications due to its high capacity and availability [1,2]. However, its on-board application in fuel-cell driven vehicles is limited due to its high thermodynamic stability and slow kinetics [3–7]. These shortcomings have been attempted to be surmounted by the addition of alloying elements [8–13]. Recently, the hydrogen storage characteristics of Mg–Al system has been studied extensively [14–21]. One motivation for investigating this system is based on the theoretical calculation that suggests the substitution of 8 mol%Mg with Al in the MgH<sub>2</sub> structure reduces the enthalpy of the magnesium hydride formation from –76 to –28 kJ (molH<sub>2</sub>)<sup>–1</sup> [10]. We have demonstrated that under equilibrium conditions MgH<sub>2</sub> has no solubility for Al and therefore the enthalpy values calculated

from pressure-composition-isotherms are not influenced by the addition of Al [22]. However, hydrogenation of Mg–Al alloys under non-equilibrium conditions may allow the incorporation of Al in the MgH<sub>2</sub> crystal and result in a significant drop in the dehydrogenation temperature [23]. The Mg–Al system offers four stable phases at room temperature: hcp-Mg, γ-Mg<sub>17</sub>Al<sub>12</sub>, β-Al<sub>3</sub>Mg<sub>2</sub> and fcc-Al and an R (epsilon)-phase at high temperature [24]. The pressure-composition-temperature (PCT) studies of the alloy with the Al<sub>3</sub>Mg<sub>2</sub> composition show that this intermetallic hydrogenates in one step resulting in the formation of MgH<sub>2</sub> and fcc-Al [20,21]. The plateau pressure for this intermetallic was found to be much higher than the value for pure Mg. The investigation of a Mg-30at%Al alloy with hcp-Mg and Mg<sub>17</sub>Al<sub>12</sub> microstructure has revealed three distinct reversible transformation steps or plateaus, which have been attributed to the hydrogenation of

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hcp-Mg,  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub> and  $\beta$ -Al<sub>3</sub>Mg<sub>2</sub> phases [20]. The phase transformation step corresponding to the hydrogenation of  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub> phase has been shown to take place at a pressure between the hydrogenation of pure Mg and  $\beta$ -Al<sub>3</sub>Mg<sub>2</sub> [25]. Analysis of the plateau pressures at different temperatures suggests that despite the significant increase in the plateau pressures the enthalpies of hydride formation for the two intermetallic phases were not modified significantly [20,21].

The objective of the present work was to study the evolution of microstructure that accompanies the different phase transformation steps during the PCT experiment in Mg–Al alloys. We selected alloys that at the temperature of investigation (350 °C) consisted of mainly the hcp-Mg phase. Partially hydrogenated and dehydrogenated samples were analyzed using x-ray diffraction (XRD) and scanning electron microscopy (SEM) to identify the phases and their distributions in the microstructure. This paper addresses the role of the microstructure in the development of PCT curves.

## 2. Experimental procedures

Three powders were employed in this study. A pure Mg powder, which was bought from Alfa Aesar (Purity: 99.999%), and two Mg–Al alloy powders with nominal compositions of 10at% and 4at%Al, which were fabricated via the galvanostatic electrodeposition technique, were studied. The details of the electrolyte composition and the electrodeposition procedures for the Mg–Al alloy powders have been reported elsewhere [26,27]. An organometallic based electrolyte was employed to fabricate the Mg–Al alloy powder. A pure graphite rod was used as a cathode and a combination of Mg/Al sheets (depending on the composition of the powder to be synthesized) were used as anodes. A current density of 150 mA/cm<sup>2</sup> at a temperature of 75 °C was applied using a PAR 263 galvanostat/potentiostat and the electrodeposition was carried for a time period of 45 min. In each experiment 5 different cathodes (graphite rods) were employed to synthesize sufficient powder for hydrogenation studies.

The electrodeposited Mg–Al and pure Mg powders were coated with Ni using an organometallic Ni compound [28]. Ni was added as a catalyst to enhance the dissociation of the hydrogen gas. During the Ni coating process, which takes approximately 6 h, the powders were exposed to 110 °C. All processes, including the electrodeposition, were carried out in a glove box to avoid the contamination of powders by oxygen and moisture.

Pressure-composition-isotherms were developed for both pure Mg and Mg–Al powders at 350 °C. A Hiden-Isochema HTP1-S-Analyzer, which works on the principle of volumetric analysis (Sievert's type), was used to establish the isotherms. The sample was loaded into the specimen chamber and sealed inside a glove box. Then the chamber was transferred to a small glove box attached to the hydrogenation system. After loading the specimen chamber, the sample was heated to the temperature of the experiment before pressurizing the specimen chamber. The sample chamber was pressurized in steps. After each instantaneous increase in pressure, sufficient time was given such that no detectable change in pressure was observed before applying the next pressure

increment. This time was decided by the software based on the system capability for detecting changes in pressure. The hydrogen pressure in the chamber during the PCT experiments was initially increased by 0.025 MPa at each step. As the pressure was raised to higher levels, the pressure step size was also increased to 0.05, 0.1 and 0.25 MPa, respectively. The total absorption/desorption time for the pure Mg and the Mg-10at%Al powders were 44 h and 86 h, respectively. The volume of the hydrogenation chamber with the loaded sample holder was measured using helium. The absorption of hydrogen as a function of pressure was calculated from the pressure change at each step.

The XRD technique was applied to identify phases using the Philips APD 3720 system. Tungsten was added to the powders as an internal standard for the instrumental error correction. A JEOL 6400 SEM was employed for morphological and microstructural characterization. The powders were embedded in an epoxy and then metallographically polished to reveal the cross-section of the powders. Diamond paste along with lapping oil was used to avoid any contamination and oxidation. The difference in the average atomic numbers of different phases was exploited in backscattered mode to identify their distribution. The composition of the powders as well as individual phases was analyzed using a JEOL Superprobe 733 electron probe microanalyzer (EPMA). Point scans were made on many particles and at sufficient number of places to obtain reasonable statistics.

The Mg-10at%Al alloy powder was tested to identify the phase evolution during the development of PCT curve at 350 °C. This goal was achieved by partially hydrogenating or dehydrogenating samples along the path of the PCT curve. The sample from each experiment was evaluated for phases, and their distribution in the microstructure. It should be noted that the cooling of samples to room temperature was conducted at the hydrogen pressure where the test was stopped. During cooling period a small amount of hydrogen may be absorbed by the sample, but this re-hydrogenation is expected to be insignificant.

## 3. Results

### 3.1. Phase and compositional evaluations of initial powders

The XRD profiles of the pure Mg, Mg-4at%Al and Mg-10at%Al powders are shown in Fig. 1. The primary phase present in these powders is hcp-Mg while Mg<sub>17</sub>Al<sub>12</sub> and fcc-Al phases are also observed in the Mg–Al powders. On the basis of Mg–Al phase diagram, the fcc-Al phase is not expected to form. However, we have demonstrated that the nucleation of the hcp-Mg phase on the graphite substrate used in this study is energetically not favorable and dendrites formed upon electrodeposition always exhibit a small amount of the fcc-Al phase at their root [29,30].

A comparison of the peak intensity ratios showed that the total amount of Mg<sub>17</sub>Al<sub>12</sub> and fcc-Al phases in the powders increases with increasing the Al content. While the electrodeposition of the Mg–Al alloys takes place in the form of supersaturated fcc-Al or hcp-Mg [30], the precipitation of the

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