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The influence of tetrahydrofuran treatment on hydrogen storage properties of the magnesium

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Abstract The hydriding and dehydriding properties of the tetrahydrofuran (THF) treated magnesium, along with its electronic energy states, crystalline structure and micro morphology have been investigated. The THF treated magnesium absorbs 6.3 wt% hydrogen at 723 K and 3.5 MPa. After hydrogenation, in addition to the expected hydride MgH_2, a new less-stable hydride phase appears at 673 K, but not at a lower temperature. Desorption produces 5.5 wt% hydrogen at 723 K against a back-pressure of 1.3 Pa after 20 cycles of hydriding–dehydriding. The THF treatment improves the kinetics of hydrogen absorption and desorption. The THF treated Mg exhibited reasonable reaction rates with hydrogen at 623 K. XPS (X-ray Photo-electron Spectroscopy) studies show that THF treatment causes the electronic energy state of the magnesium atoms to shift, but the XRD (X-Ray Diffractometer) studies show the crystal structure remains unchanged. It is believed that the chemical state of magnesium surface is activated by THF treatment in favor of hydrogen absorption and desorption. Metallographic observation of the magnesium hydrides reveals some interesting features during hydrogenation.

Introduction

Magnesium has been studied for decades as a hydrogen absorbing material due to its high hydrogen storage capacity (7.6 wt%), light weight and low cost. Unfortunately, pure magnesium absorbs hydrogen only at elevated temperature (>773 K) and under high pressure (>20 MPa) [1, 2]. It is reported that magnesium and magnesium base alloys such as Mg_2Ni and $SmMg_3$ modified by organic compounds absorb hydrogen at lower temperatures and pressures [3–6]. The reported organic modification processes are usually complicated and involves either metal vapor deposition or ball milling with several toxic aromatic compounds [7–9]. The thermodynamic behavior of the organic modified magnesium and alloys such as Pressure–Composition–Temperature isotherms (P–C–T) and hydride formation enthalpy have not been investigated yet. To evaluate the influence of organic compounds on hydrogen storage properties of magnesium and understand the mechanism of the organic compound modification, a single organic agent, tetrahydrofuran (THF), was used to treat magnesium metal. The thermodynamics, hydrogen storage kinetics, crystal structure, electronic energy state and micro-morphology of THF treated magnesium were measured and analyzed by Sieverts volumetric apparatus, XRD (X-ray diffraction), XPS (X-ray photoelectronic spectrum), metallographic microscope in this work.

Experimental details

Sample preparation

One hundred grams of fresh magnesium filings (99.7%, 80–100 mesh) and a polished magnesium strip (15 × 5 × 1 mm) were soaked in THF for 2 weeks. The magnesium filings were filtered from THF solution and

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loaded into a stainless steel reactor of the Sieverts apparatus. The reactor was evacuated at 100 °C by a vacuum pump for 1 h to evaporate the residual THF. Then, the sample was ready for hydrogen absorption. A THF treated Mg strip and a polished untreated strip with same dimension were hydrogenated for 48 h in same reactor at 3.5 MPa and 673 K for metallographic analysis.

Hydrogen storage measurement

A Sieverts apparatus was used to measure the P–C–T (Pressure–Composition–Temperature) isotherms and the hydriding/dehydriding kinetics. Before collecting the data, the THF treated Mg sample was repeatedly charged and discharged with hydrogen at 3.5 MPa and 643 K for ten times to activate the material to its full capacity. The sample was fully charged with hydrogen at 3.5 MPa and 673 K for 4 h before measuring its dehydriding P–C–T isotherms. The hydriding and dehydriding kinetic curves were measured at an initial pressure of 3.5 MPa and at different temperatures.

Instrumental analysis

The changes in magnesium binding energy were measured by a Φ Physical Auger-XPS spectroscopy. The THF treated and untreated magnesium strips were used as the specimens in XPS analysis. Due to identical histories of THF treated magnesium powder and magnesium strip and extreme small diameter of X-ray beam (<5 μm), the XPS information obtained from magnesium strip should be sufficient and objective to represent magnesium powder. The crystal structure was investigated by a Rigaku X-ray diffractometer. The micro-morphologies were observed by a MeF-3 metallurgical microscope.

Results and discussion

Thermodynamic analysis

Figure 1 shows the dehydriding pressure–composition isotherms (P–C–T diagram) of THF treated magnesium (for simplicity written as THF–Mg later). Two plateaus with different widths were observed at 3.0 and 1.2 MPa, respectively, at 673 K. The higher plateau represents 1.5 wt% storage capacity at 3.0 MPa. The lower one represents 2.5 wt% storage capacity at 1.3 MPa. The total hydrogen storage capacity of THF–Mg is 4.0 wt% at 673 K. The two plateaus imply that there are two hydrides with different thermodynamic stabilities formed during hydrogenation. XRD results are given in Figs. 2 and 3. The X-ray diffraction spectrum suggests that the main phases in hydrogenated THF–Mg are MgH_2 and the residual Mg. But, there are some small peaks still remaining unidentified. It is possible that these small peaks correspond to a less stable Mg–THF–H_x complex, which could be responsible for the higher plateau. At the lower temperatures,

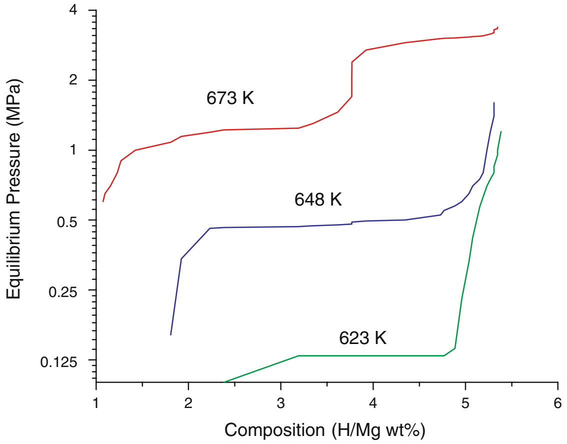

Fig. 1 Hydrogen desorption Pressure–Composition–Temperature isotherms of THF treated magnesium

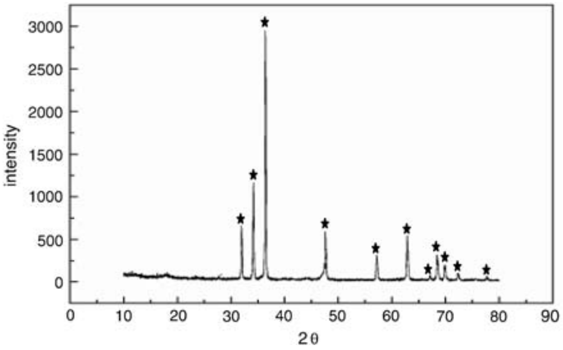

Fig. 2 XRD of THF treated magnesium (* – Mg)

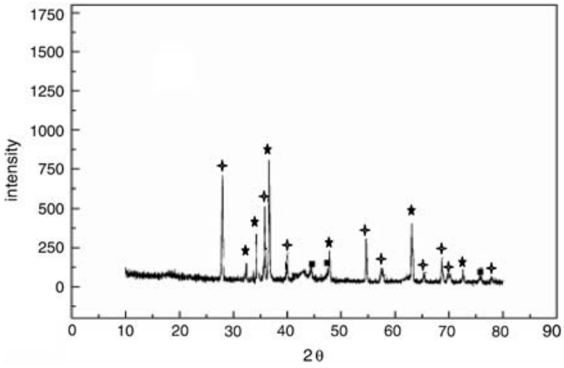

Fig. 3 XRD of THF treated magnesium after hydrogenation (* – Mg, + – Mg H_2,· – Unknown phase)

such as 648 and 623 K, the P–C–Ts show one plateau only. The hydrogen desorption capacities are 3.5 and 2.6 wt%, respectively. The hydrogenation enthalpy of THF–Mg calculated from its P–C–T diagram using the Vant' Hoff equation is $\Delta H°= -72.4$ kJ/mol H_2. Comparing this number with the enthalpy of MgH_2 formation $\Delta H°= -74.5$ KJ/mol H_2, one may notice that THF treatment slightly reduces the hydride formation enthalpy, but not significantly. In other words, the organic compound treatment does not remarkably change the thermodynamic stability of hydride. Although it has been reported [4, 5] that the organic complex modified magnesium can absorb hydrogen even at low temperature (363 K), the decomposition of its hydride occurs only at temperature above 603 K. Although the hydriding temperature of magnesium and magnesium base alloys can be reduced noticeably by organic compound modification [4–8], ball milling [10–13] or adding catalysts [14–17], it is not feasible to lower dehydrogenation temperature below 573 K as long as the final product of the hydrogenation is the MgH_2. However, there may be an opportunity that certain less stable organo-Mg–H complex offers low decomposition temperature. More systematic study is needed.

Hydriding and dehydriding kinetic properties

Figure 4 shows the hydriding and dehydriding kinetic curves of THF–Mg at 643, 673 and 723 K with a back pressure set to 1.3 Pa. The THF–Mg absorbs 6.3 wt% and desorbs 5.5 wt% hydrogen within 2 h at 723 K. The shape of hydriding and dehydriding curves shows the typical nucleation-growth feature of chemical reactions. The dehydriding rates increase with temperature. For example, THF–Mg has a fast hydriding rate at 673 K because of the exothermal nature of hydrogenation reaction. From an application point of view (discharging 90% stored hydrogen within 30 min), the dehydriding rate at the above three temperatures appear acceptable, but the hydriding rate needs to be improved (charging 90% hydrogen within 10 min).

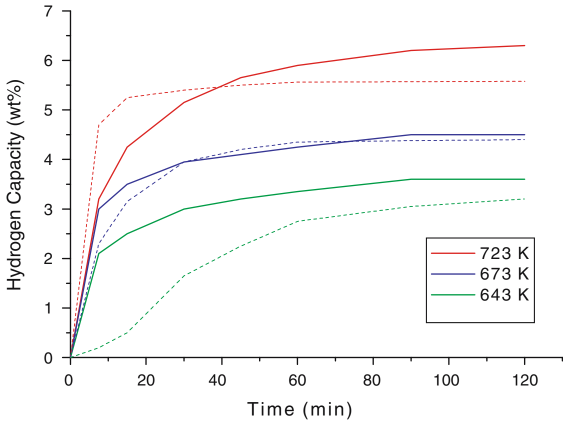

Fig. 4 Hydrogen absorption and desorption kinetics of THF treated magnesium (—) (solid line) absorption, - - - - - - (dot line) desorption

The change of the electronic binding energy of the THF treated magnesium

It is significant to understand why magnesium can absorb a reasonable amount of hydrogen after it is treated with THF while the untreated pure magnesium is not able to absorb the hydrogen at same temperature and pressure. Figure 5 shows the XPS spectra of the untreated and THF treated magnesium strip. By comparison, magnesium 1S, 2P and KL23L23 binding energies shift to the higher value when treated with THF: Mg_{1s}, Mg_{2p} and Mg_{KII} increase 0.4, 1.1 and 7.7 eV, respectively. This indicates that the magnesium valence electrons transfer electron density to the THF molecules due to THF interaction with magnesium. As the binding energy represents the association between the nucleus and the surrounding electrons, an increase of the binding energy means a higher chemical affinity. THF treated magnesium atoms at the surface are therefore chemically activated and can therefore react with hydrogen more easily at the moderate condition. Imamura et al. [3] investigated electron transfer using Electron Spin Resonance. They believe that the electron transfer between the aromatic material and magnesium forms an EDA (Electron donor–acceptor) species. Our results appear supporting his conclusion. XRD data of THF–Mg and unmodified Mg have identical crystal structures (Fig. 2), but an unknown new phase was found from hydrided THF–Mg (Fig. 3). Although most of the THF left the magnesium during evacuation, there is still certain chemical association or

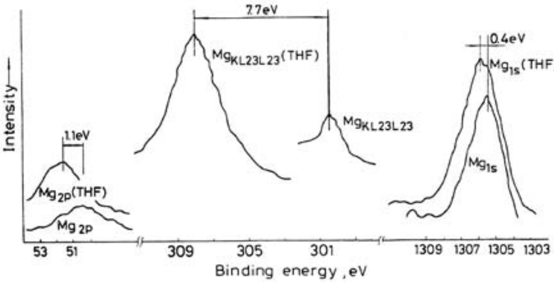

Fig. 5 XPS spectrograms of THF treated magnesium and untreated magnesium

Mg–THF organo-metal complex remained between magnesium atoms and the THF rings, which acts as the functional groups absorb hydrogen with the lower activation energy and form less stable Mg–THF–H complex. The role of hexagonal or pentagonal ring structure of graphite and aromatic organic compounds in improving hydrogen absorption has been reported by other researchers [18–19].

Morphology of Mg hydrides

A THF treated and untreated magnesium strips were hydrogenated for 48 h at 3.5 MPa hydrogen pressure and 673 K. Both strips were cut, polished and etched along the cross section. Under microscope with 50 magnifications, it is just a shiny and smooth surface in untreated strip. However, some dark magnesium hydride granules are formed on the both side surface of the THF-treated strip, and some grew into the inert surface (Fig. 6). It appears that the THF treatment clears the surface and creates chemically active sites with favorable energy condition for magnesium hydride to nucleate and grow from the surface toward the interior area. The magnesium hydride granules are polycrystalline with different orientations (Fig. 7, 8). The crystalline plain slip bands and the twin grains formed during Mg → MgH_2 transformation appear in each hydride particle.

Conclusion

It was found that THF treated magnesium (THF–Mg) absorbs 6.3 wt% hydrogen at 723 K and 3.6 wt% hydrogen at 643 K, at a pressure of 3.5 MPa. The hydride desorbs 5.5 wt% hydrogen at 723 K and 3.3 wt% hydrogen at 643 K, at a back pressure of 1.3 Pa. The hydriding and dehydriding kinetics of THF–Mg was found to be acceptable for hydrogen storage applications. Although the THF treatment does not change the thermodynamic stability of the magnesium hydride significantly, it does increase the electron energy of the magnesium atoms at the surface and creates chemically active sites. This makes THF–Mg capable of storing a considerable amount of hydrogen at moderate conditions under which the untreated magnesium cannot store any hydrogen. A less stable hydride phase with an unidentified structure was founded along with the expected MgH_2 phase in THF–Mg at 3.0 MPa hydrogen pressure and 673 K, but not at lower temperatures. Metallographic observations showed that each individual Mg hydride granule consisted of several crystals with different orientation. A great deal of the slip bands and twin grains exist in

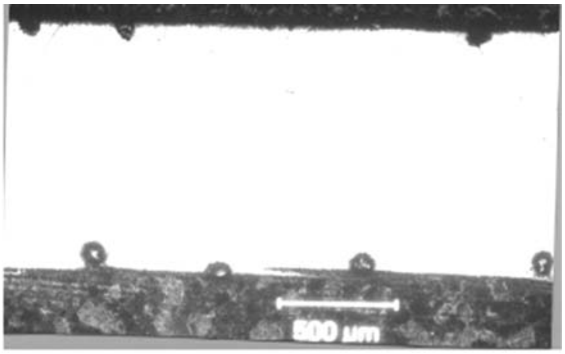

Fig. 6 Magnesium hydride granules formed on the surface of the magnesium specimen after 48 h hydriding at 673 K and 3.5 MPa

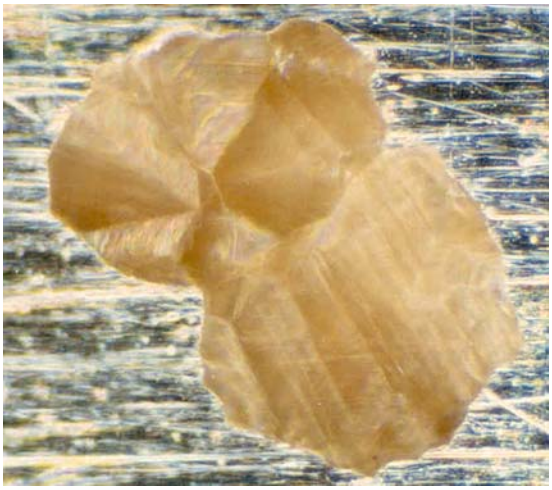

Fig. 7 The granule of the MgH_2 consists of several crystals with different orientation

Fig. 8 The great deal of slippage and twins form during Mg → MgH_2 phase transformation

THF–Mg hydrides indicating that the hydriding and dehydriding of magnesium involves microstructure reconstruction.

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