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## Hydrogen Storage Properties of the Tetrahydrofuran Treated Magnesium

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### Abstract:

The electronic structure, crystalline feature and morphology of the tetrahydrofuran (THF) treated magnesium, along with its hydriding and dehydriding properties have been investigated. The THF treated magnesium absorbs 6.3 wt% hydrogen at 723K and 3.5 MPa. After hydrogenation, in addition to the expected MgH<sub>2</sub>, a new less-stable hydride phase appears at 673K, but not at a lower temperature. Desorption produces 5.5 wt% hydrogen at 723K 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 significantly. From 723K to 623K, the THF treated Mg demonstrates acceptable reaction rates. XPS studies show that Tetrahydrofuran treatment causes the electronic energy state of the magnesium surface atoms to change, but the XRD studies show the crystal structure remains unchanged. Metallographic observation of the bulk hydrides of THF treated magnesium reveal they are poly-crystalline with the wide-spreading slip bands and twins within the crystals, indicating the phase transformation upon hydriding causes serious stress and distortion. It appears this microstructural deformation explains the much higher energy requirements (higher pressure and temperature) for magnesium hydrogenation than the simple lattice expansion that accompany hydrogen uptake for LaNi<sub>5</sub> and FeTi.

**Keyword:** Magnesium, Tetrahydrofuran, Hydrogen storage materials, Hydrides

### 1. Introduction

Magnesium, as a hydrogen absorbing material; possesses a series of unique advantages: large 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 known that magnesium modified with organic compounds or alloyed by other transition metals can absorb hydrogen at lower temperatures and pressures [3, 4]. However, the organic modification is usually too complicated and toxic. In this work, a single organic agent, tetrahydrofuran, was used to improve the hydriding-dehydriding properties of magnesium. To understand the mechanism of the organic modification, the crystal structure, electronic energy state, micro-morphology, hydrogen storage kinetics and thermodynamics were investigated by XRD (X-ray diffraction), XPS (X-ray photoelectronic spectrum), optical microscope, and Sieverts volumetric apparatus.

## 2. Experimental details

### Sample preparation

One hundred grams of fresh magnesium filings (99.7%, 80-100 mesh) and a 1mm thick magnesium strip were soaked in tetrahydrofuran (THF) for two weeks. The magnesium filings were filtered from THF solution and loaded into a stainless steel reactor of the Sieverts apparatus. The reactor was evacuated at 100°C by a vacuum pump for one hour to remove the residual THF. Then, the sample was ready for hydrogen absorption. The Mg strip was hydrogenated for 48 hours in a reaction vessel at 3.5 MPa and 673K for metallographic analysis.

### Hydrogen absorption and desorption

A Sieverts apparatus was used to measure the P-C-T (Pressure-Composition-Temperature) isotherms for thermodynamic analysis 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 643K for ten times to activate the material to its full capacity. The sample was fully charged with hydrogen at 3.5 MPa and 673K for four hours before measuring its dehydriding P-C-T isotherms. The hydriding and dehydriding kinetic curves were measured at 3.5 MPa initial pressure and at different temperatures.

### Instrumental analysis

The changes in magnesium binding energy were measured by a  $\Phi$  Physical Auger-XPS spectrum analyzer. The crystal structure was investigated by a Rigaku X-ray diffractometer. The micro-morphologies were observed by a MeF-3 metallurgical microscope.

## 3. Results and discussion

### 3.1 Thermodynamic properties

Fig.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 1.0 MPa respectively at 673K. The higher plateau represents 1.4 wt% storage capacity at 3.0 MPa. The lower one represents 2.6 wt% storage capacity at 1.3MPa. The total hydrogen storage capacity of THF-Mg is 4.0 wt% at 673K. It indicates that two hydrides with different stabilities formed during hydrogenation. The X-ray diffraction spectrum suggests that the main phases in hydrogenated THF-Mg are  $MgH_2$  and the residual Mg. There are some small peaks that are not able to be identified. It may be a kind of the less stable Mg-THF- $H_x$  complex, which could be responsible for the higher plateau. At the lower temperatures, such as 648K and 623K, the P-C-Ts show one plateau only. The hydrogen desorption capacities are 3.5wt% and 2.6wt% respectively. The hydrogenation enthalpy of THF-Mg calculated from its P-C-T diagram using the Vant' Hoff equation is  $\Delta H^0 = -72.4$  kJ/mol  $H_2$ . Comparing this number with the enthalpy of  $MgH_2$  formation  $\Delta H^0 = -74.5$  KJ/mol  $H_2$ ,

one may notice that THF treatment does little if anything to alter the hydride formation enthalpy. In other words, the organic compound treatment does not noticeably 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 (363K), the decomposition of its hydride occurs only at temperature above 603 K. Although the hydriding temperature of magnesium can be reduced by organic compound modification [4-6], ball milling [7-10] or adding catalysts [11-14], it is clear that the dehydrogenation temperature can not be reduced lower than 573K as long as the final product of the hydrogenation is the  $MgH_2$ .

### 3.2 Hydriding and dehydriding kinetic properties

Fig.2 shows the hydriding and dehydriding kinetic curves of THF-Mg at 643K, 673K and 723K with a backpressure set to 1.3 Pa. The THF-Mg absorbs 6.3wt% and desorbs 5.5wt% hydrogen within two hours at 723K. The shape of hydriding and dehydriding curves show the typical nucleation-growth feature of chemical reactions. Although the dehydriding rates increase with temperature, there is an optimal temperature for fast hydriding rates. For example, THF-Mg has a fast hydriding rate at 673K because of the exothermal nature of hydrogenation reaction. From an application point of view, the hydriding rate (3.4-5.7 wt%/hour) and dehydriding rate (2.8-5.5wt%/hour) at the above three temperatures appear acceptable.

### 3.3 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. Fig.3 shows the XPS spectra of the untreated and THF treated magnesium. By comparison, magnesium 1S, 2P and KL23L23 binding energies shift to the higher direction when treated with THF:  $Mg_{1s}$ ,  $Mg_{2p}$  and  $Mg_{KII}$  increase 0.4, 1.1 and 7.7 eV, respectively. This indicates that during THF contact with magnesium the magnesium valence electrons transfer electron density to the THF molecules. As the binding energy represents the interaction 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 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 [3]. XRD data of THF-Mg and unmodified Mg have identical crystal structures (Fig. 3), but an unknown new phase was found from hydrided THF-Mg (Fig.4). Although most of the THF left the magnesium during evacuation, there still may be some kind of chemical association formed between magnesium atoms and the THF rings that acts as the functional groups providing path with the lower activation energy during hydrogen absorption. The role of hexagonal or pentagon ring structure of graphite

and aromatic organic compounds in improving hydrogen absorption has been reported by other researchers [15-17].

### 3.4 Morphology of Mg hydrides

A 15 mm x 5 mm x 1 mm magnesium strip, soaked in THF for two weeks, was hydrogenated for 48 hours at 3.5 MPa hydrogen pressure and 673K. Fig.5 shows the cross section of the specimen observed under the optical microscope. Some dark brown magnesium hydride granules formed on the both side surface of the strip, and some grew into the inert surface. It appears that the THF treatment 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, see Fig.7-8. The crystalline plain slip bands and the twin grains appear in each hydride particle. The hexagonal lattice of the magnesium has less slippage systems than a cubic lattice such as  $\text{LaNi}_5$ . Unlike the simple lattice expansion in the hydriding of  $\text{LaNi}_5$  or  $\text{FeTi}$ , magnesium hydriding involves lattice transformation, e.g. crystal lattice reconstruction. Because of inadequate slippage systems in magnesium, many twin grains in addition to slippage bands form in the crystal reconstruction process. This process requires more energy to overcome the high internal stress and severe deformation. This may explain the higher temperature and pressure requirements for magnesium hydrogen absorption than  $\text{LaNi}_5$  and  $\text{FeTi}$ .

### Conclusion

It was found that THF-Mg absorbs 6.3 wt% hydrogen at 723K and 3.6 wt% hydrogen at 643K, at an overpressure of 3.5 MPa. The hydride desorbs 5.5 wt% hydrogen at 723K and 3.3 wt% hydrogen at 643K, at a backpressure of 1.3 Pa. The hydriding and dehydriding kinetics of THF- Mg with respect to untreated magnesium was found to be to 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 which the untreated magnesium can not store any hydrogen under these conditions. A less stable hydride phase with an unidentified structure was discovered along with the expected  $\text{MgH}_2$  phase at 673K, 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 THF-Mg hydrides indicating that the hydriding and dehydriding of magnesium involves microstructure reconstruction. This may be one of the reasons why higher energy conditions are required for magnesium hydrogen storage than for  $\text{LaNi}_5$  or  $\text{FeTi}$ .

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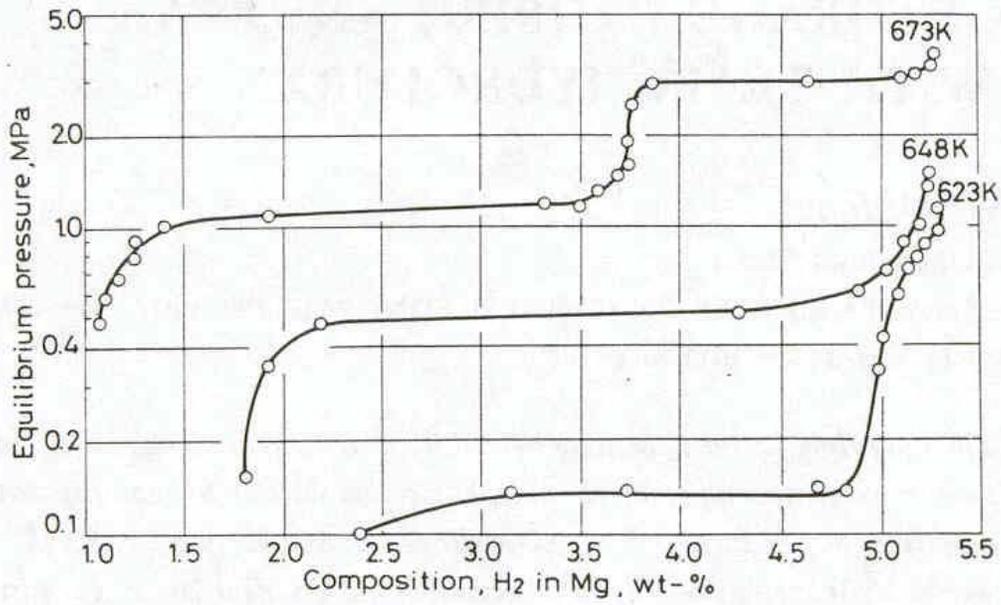


Fig.1 Hydrogen desorption Pressure-Composition-Temperature isotherms of THF treated magnesium

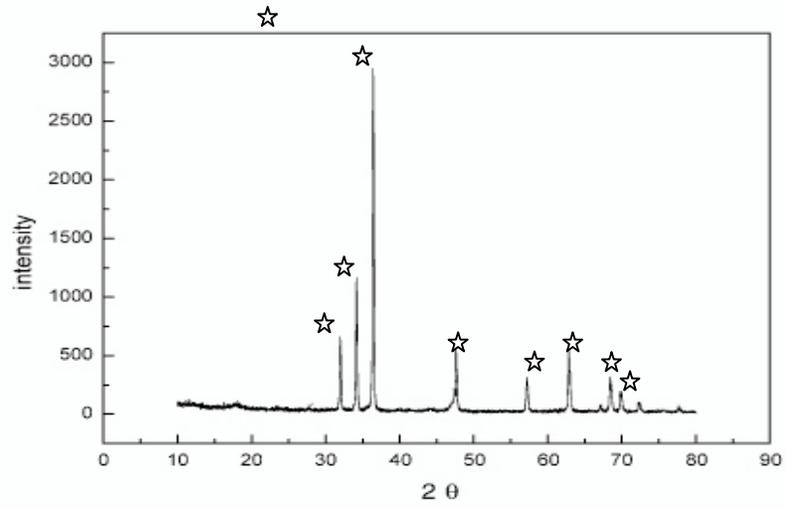


Fig. 2 XRD of THF treated magnesium  
( Mg)

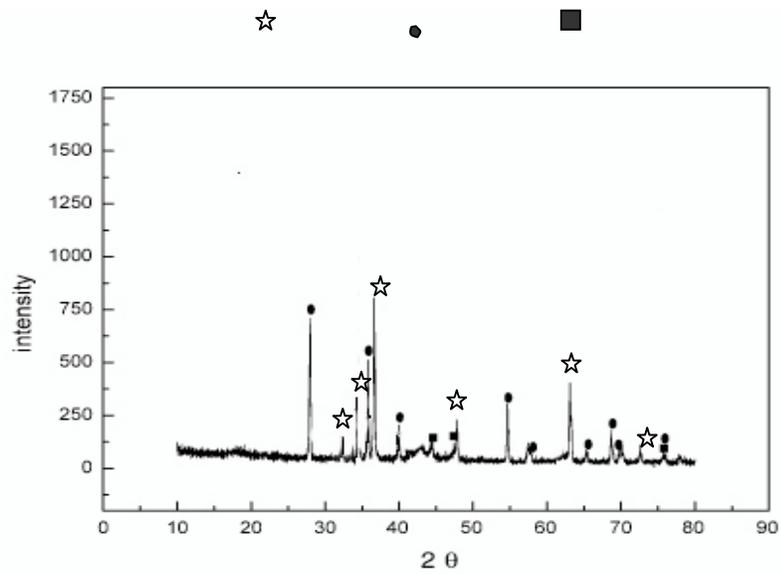


Fig 3. XRD of THF treated magnesium after hydrogenation  
( Mg, MgH<sub>2</sub>, unknown)

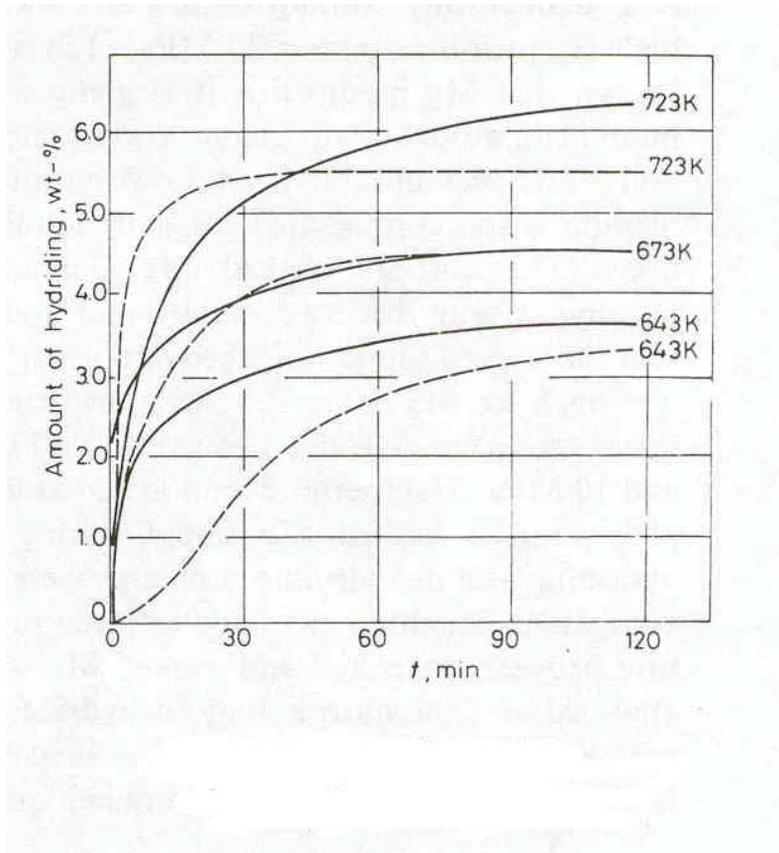


Fig.4 Hydrogen absorption and desorption kinetics of THF treated magnesium  
 ( — absorption, ----- desorption )

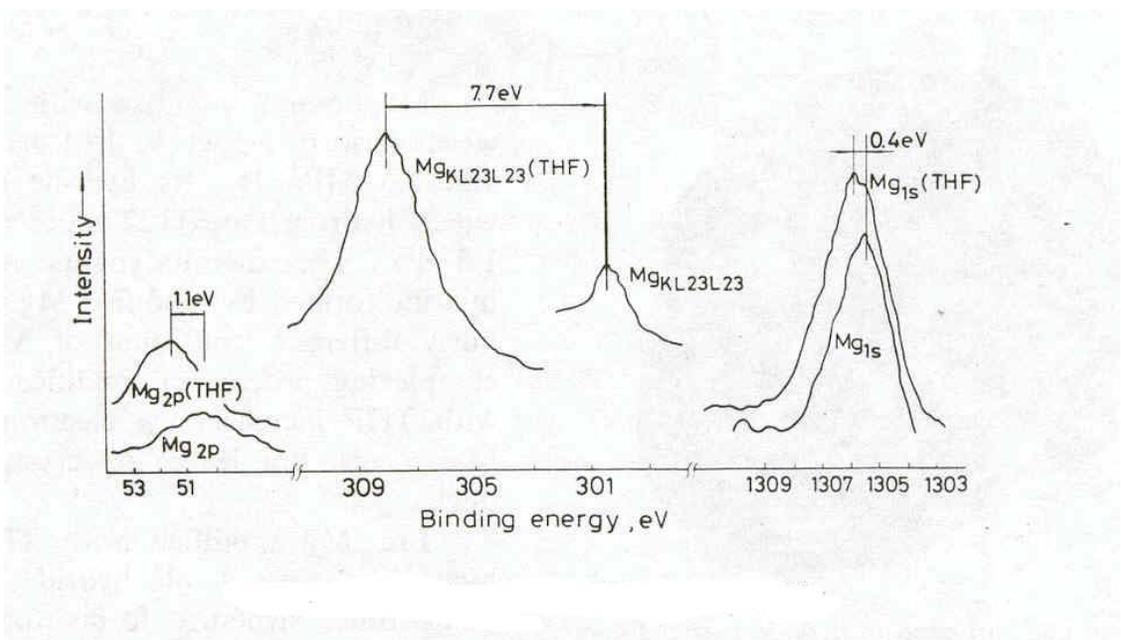


Fig. 5 XPS spectrograms of magnesium and THF treated magnesium

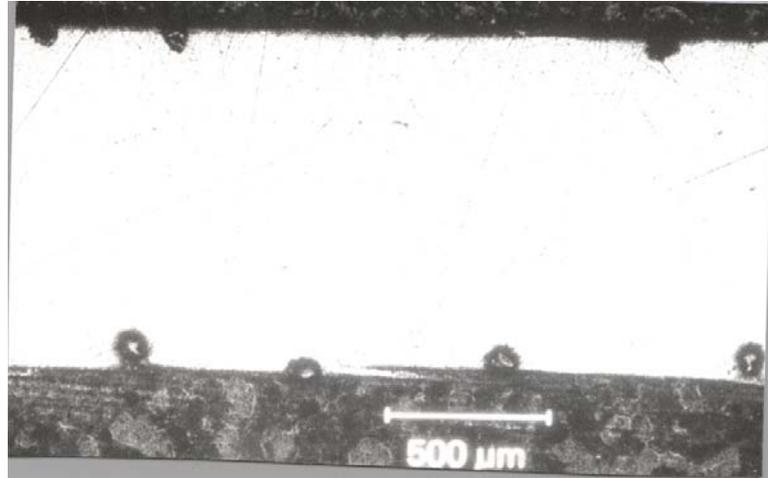


Fig.6 Magnesium hydride granules formed on the surface of the magnesium specimen after 48 hour holding at 673K and 3.5 MPa. (X 50)



Fig.7 The granule of the MgH<sub>2</sub> consists of several crystals with different orientation (x500)



Fig.8 The great deal of slippage and twins form during Mg->MgH<sub>2</sub> phase transformation (x500)