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IN-SITU NEUTRON POWDER DIFFRACTION ON TiF_3-CATALYZED MAGNESIUM FOR HYDROGEN STORAGE APPLICATIONS

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Introduction

Magnesium-hydrogen system has been extensively studied for potential applications in solid-state hydrogen storage. Since magnesium hydride is a quite stable hydride phase (with the heat of formation of -74.5 kJ/mole [1]) it operates at temperatures which are too high for many hydrogen storage applications. Another major obstacle in the commercialization of Mg-based hydrogen storage systems is the sluggish kinetics of hydrogenation and dehydrogenation of this system in its pure state. This has led the focus of the research towards finding an optimum catalyst to facilitate H_2 dissociation and recombination on the surface [2].

One of the additives that have been shown to significantly enhance the hydrogen sorption kinetics is titanium fluoride (TiF_3) [3, 4, 5]. In these cited studies, the authors demonstrate that TiF_3 milled with MgH_2 powder has superior catalytic properties compared to other titanium halides, most notably $TiCl_3$. Based on X-ray photoelectron spectroscopy (XPS) observations, the authors in Ref. 4 correlate this major enhancement with the formation of Ti-F-Mg type of bonds. X-ray diffraction (XRD) [4] and neutron powder diffraction (NPD) [5] measurements propose this reaction to occur upon cycling:

$$\mathrm{MgH2 + 2/3TiF3 \rightarrow 2/3TiH2 + MgF2 + 1/3H2}, \quad \Delta G = -197\ \mathrm{kJ/mol}$$

We performed in-situ neutron powder diffraction in conjunction with pressure-composition-temperature measurements to verify the proposed sorption route and systematically study the structural characteristics of Mg powder catalyzed by 15wt% TiF_3 during the hydrogen/deuterium absorption/desorption process.

Experimental Details

NPD experiments were carried out on the C2 high-resolution neutron powder diffractometer at the NRU reactor at the Chalk River Laboratories. The instrument is equipped with a 800-wire position-sensitive detector covering a range of 80 degrees. Data were collected in the angular range from 5 to 117^0 using a Si (5 3 1) monochromator at a wavelength of 1.3287 Å. The sample was synthesized by ball-milling MgH_2 and 15wt.% TiF_3 for an hour under inert Ar atmosphere. The sample was the loaded in a steel sample holder for neutron diffraction/PcT (pressure-composition-temperature) measurements under helium atmosphere using a glove box. The sample was heated to 300 ^{0}C and kept under dynamic vacuum for 12 hours to insure complete hydrogen desorption.

The diffraction measurements were performed during various stages of Mg to MgD_2 phase transformation and vice versa. Using a custom design Sievert-type apparatus for *in-situ* neutron powder diffraction [6], the deuterium loading and unloading were performed at a temperature that was regulated to be 300 °C. For neutron diffraction, deuterium is the preferred isotope because of its larger coherent scattering length and smaller incoherent scattering length as compare with hydrogen.

Results

In-situ neutron diffraction was used to study the hydrogen/deuterium sorption behavior and microstructure of Mg powders catalyzed by 15 wt.% TiF_3. From the calibrated volume and the measured pressure drop/increase in it, the amount of deuterium absorbed or desorbed in the sample was determined. In addition, since minimum wait time of 30 minutes was allowed between each incremental sorption step, pressure-composite isotherms that are quite close to the equilibrium were established. The isotherms are shown in Figure 1.

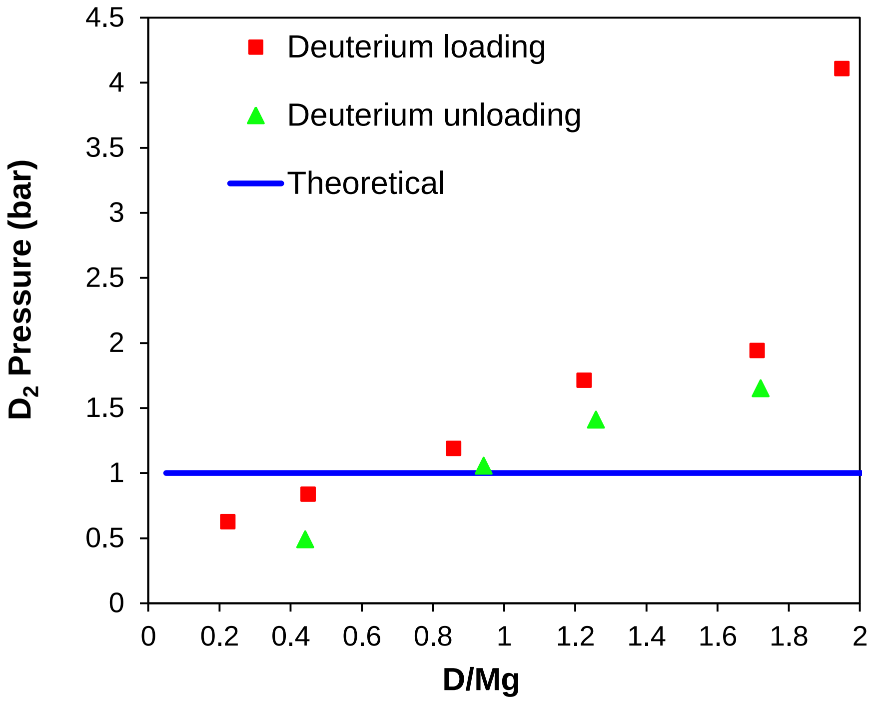

Figure 1. D_2 absorption and desorption pressure-composite isotherms at 300 °C for TiF_3-catalyzed Mg. The theoretical equilibrium pressure for bulk MgD_2 is superimposed as blue line.

Figure 2 shows the *in-situ* neutron diffraction patterns obtained at various stages of D_2 loading/unloading. No apparent reflections of β-MgD_2 can be observed up to D/Mg ~0.22 (as determined from the PcT measurements). One possible interpretation could be that the newly formed MgD_2 is nanocrystalline, hence broad, low intensity Bragg reflections would get buried in the background. However no significant changes can be observed in the peak intensity of the α-Mg phase, suggesting no Mg is converting into MgD_2. The most plausible explanation is that α-Mg takes up large amounts of deuterium before it converts to the rutile β-MgD_2. This is remarkable because it has been theoretically proved and experimentally observed that bulk Mg could only dissolve negligible amounts of D_2 in its lattice before forming the β phase. The presence of Ti fluoride catalyst appears to modify the thermodynamics of Mg-D in a way that the uptake of deuterium in α-Mg has become energetically more favorable and the β-MgD_2 has become energetically less favorable. This thermodynamic modification may result in the extended deuterium solubility limit for TiF_3-catalyzed Mg.

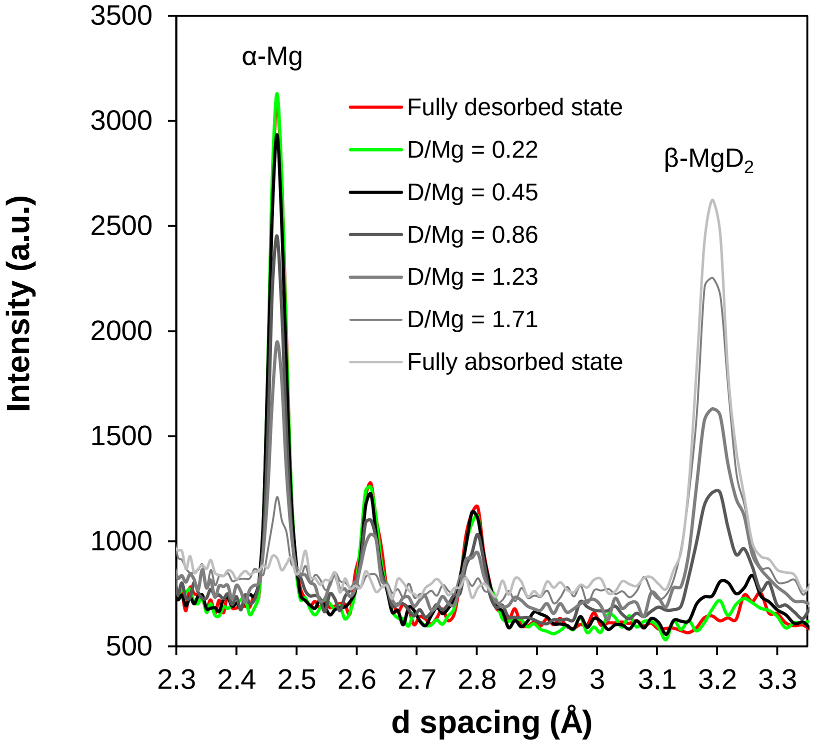

Figure 2. *In-situ* measured neutron diffraction patterns during various stages of Mg to MgD_2 phase transformation and vice versa.

Another interesting and intriguing observation was the variation of the powder diffraction pattern's background level during cycling. Figure 3 shows the evolution of the background value measured in a flat region, away from any Bragg peaks during the first two cycles of absorption/desorption at 300 ^{0}C. It is fully expected that the background increases with D_2 absorption and decreases during desorption. What is unexpected, especially in the case of a *in-situ* experiment, is the significant difference in the background of the patterns corresponding to the fully desorbed (and fully absorbed) states of the first and second cycles. One possible explanation may be in the evolution of microstructure upon cycling, the fact that the main grain growth occurs during the first sorption cycles; some amorphous components would lead to an increase of the background level. Perhaps a more reasonable explanation lays in the previous observations that TiH_2 is a by-product of the ball-milling during sample preparation [3, 4] and the fact that hydrogen has a much higher incoherent scattering length than deuterium. Due to higher stability of titanium hydride as compared with magnesium hydride, the hydrogen initially trapped as TiH_2 cannot be fully desorbed during the initial hydrogen desorption, significantly contributing to the background of that was considered the initial fully desorbed state. During cycling, this hydrogen will be gradually desorbed and substitute out by F, hence the background level decreases.

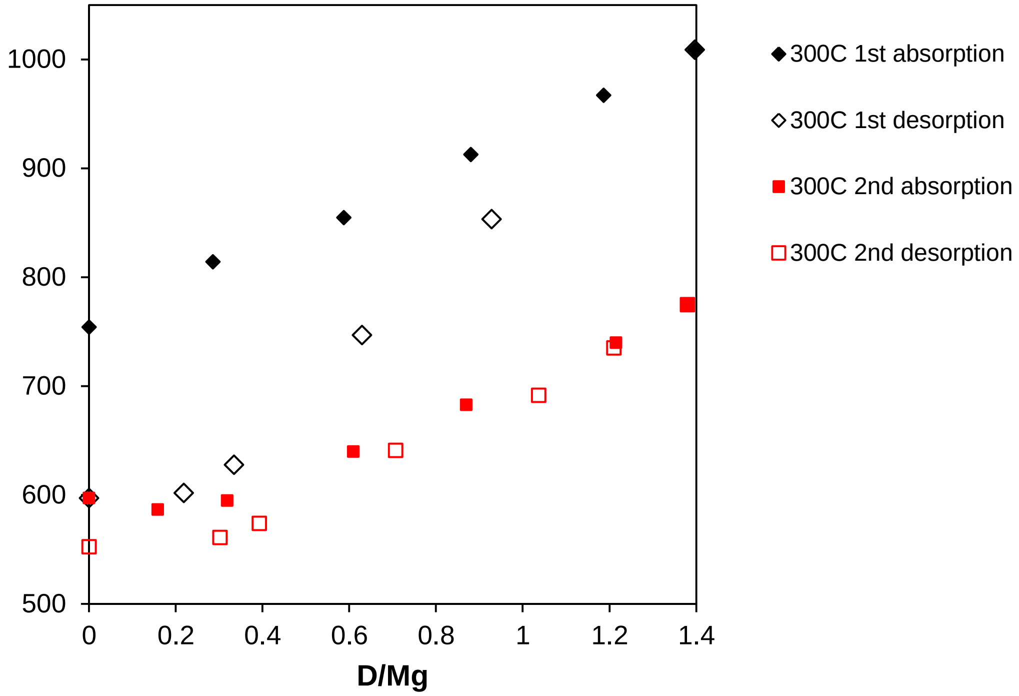

Figure 3. Background levels of powder diffraction patterns collected at different stages of deuterium absorption/desorption during the first and second cycles.

Conclusions

In-situ neutron powder diffraction measurements where performed in conjunction with PcT measurements to study the dynamical and structural characteristics of deuterium absorption/desorption in magnesium powder catalyzed by 15 wt.% titanium fluorite. At 300 ^{0}C the sample was found to absorb up to about 2 D/Mg. The most rapid part of deuterium uptake happens during the stage when Mg stays in the α phase and deuterium is in solid solution. It was found that the solubility limit of D in Mg is significantly increase by the presence of the catalyst as compare with pure Mg powder. The next stage of absorption involves the formation of β – MgD_2 phase and the absorption continues to be fast.

References

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