

In situ Neutron Diffraction on TiF₃-catalyzed Mg: Observation of Extended Deuterium Solubility Limit in α -Mg

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In situ neutron diffraction was used to study the hydrogen/deuterium sorption behavior and microstructure of Mg powders catalyzed by 15 wt.% TiF₃. Comparing to hydrogen, the use of deuterium significantly reduces the incoherent scattering background. The diffraction measurements were performed during various stages of Mg to MgD₂ phase transformation and vice versa. Using a custom design Sievert-type apparatus, the deuterium loading and unloading were performed at a temperature that was regulated to be 300 °C. 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 2 shows the in-situ neutron diffraction patterns obtained at various stages of D₂ loading/unloading. No apparent reflections of β -MgD₂ can be observed up to D/Mg \sim 0.22. One may argue that this is due to the very nanocrystalline MgD₂ nuclei that have very limited correlation length. This is however hardly true, because there are trivial changes in the peak intensity of the α -Mg as well as the intensity level of the scattering background. Another plausible explanation is that: The α -Mg takes up large amounts of D before it converts to the rutile MgD₂. This is remarkable, because it has been theoretically proved [1] and experimentally observed [2] that bulk Mg could only dissolve negligible amount of D in its lattice before forming the β -phase.

Finally, comparing the measured equilibrium pressure with the theoretical one at 300 °C (superimposed in Figure 1), 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 -MgD₂ has become energetically less favorable. This thermodynamic

modification may result in the extended deuterium solubility limit for TiF₃-catalyzed Mg.

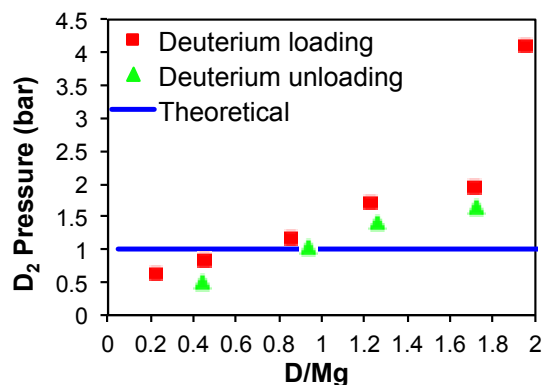


Fig. 1 D₂ absorption and desorption pressure-composite isotherms at 300 °C for TiF₃-catalyzed Mg. The theoretical equilibrium pressure for bulk MgD₂ is superimposed as blue line.

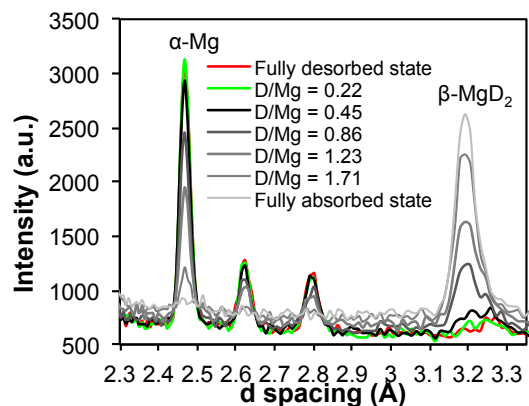


Fig. 2 In-situ measured neutron diffraction patterns during various stages of Mg to MgD₂ phase transformation and vice versa.

References

- [1] H.G. Schimmel et al., *J Alloys Compd.*, 2005, **404–406**, 235–237.
- [2] H.G. Schimmel et al., *J. Am. Chem. Soc.* 2005, **127**, 14348–14354.