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## Magnesium and titanium: The odd couple

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# Summary

Since their discovery in 1996, switchable mirrors have attracted great interest both for their intriguing physics and for their technological application. A switchable mirror is a thin metallic film, typically deposited on a transparent substrate and therefore mirror-like, which is capable of reversibly changing its optical appearance upon absorption of hydrogen.

The first mirrors were made of rare-earth metals and had a yellowish transparent hydrogenated state. Subsequently Mg-rare-earth and Mg-transition metals mirrors were shown to have improved transparency of the hydrogenated state and much smaller costs. Intriguingly, while loaded with hydrogen some of these mirrors showed a dark, light-absorbing, intermediate state. This “black state” is destroyed upon full hydrogenation and it is due to non-trivial mechanisms of nucleation and growth of the hydride phase.

The possibility to switch a thin film from a light-reflecting to a light-absorbing state, however, suggested their application as smart covers for solar collectors and as highly sensitive optical hydrogen detectors.

At the beginning of the present thesis we therefore searched for suitable materials, that would hopefully show a good optical reflection in the metallic state and a dark appearance in the hydrogenated state. To our great surprise, thin films of co-sputtered Mg and Ti showed the desired characteristics: the black appearance of the hydrogenated state is not destroyed upon full hydrogenation, but it is a final, stable, reversible state of the metal hydride. Furthermore the hydrogen absorption and desorption transitions occur within few seconds, suggesting the application of Mg-Ti alloys as novel hydrogen storage materials.

The physical origin of the optical black state in Mg-Ti thin film alloys is difficult to interpret. In order to understand it we investigated the microstructure of these films, by combining structural, electrical and optical data. Although some hypothesis could already be made, a clear picture was only obtained by probing the local distribution of the Mg and Ti atoms within the alloy’s crystal structure. This was done by combining extended x-ray absorption fine structure (EXAFS) data with a modeling of the absorption isotherms, as measured with Hydrogenography. The results showed that, although the average crystal structure resembles the one expected for a perfectly mixed alloy, magnesium and titanium atoms are distributed with a small degree of chemical short-range order. Such a peculiar microstructure originates from the positive enthalpy of

mixing of magnesium and titanium: during the films deposition Mg and Ti atoms are rapidly cooled on the substrate and, although they would naturally tend to segregate, the rapid quenching freezes the alloy structure into a crystalline “metastable” fine dispersion of Mg-rich and Ti-rich nano-domains.

The technological significance of this discovery can only be understood by considering that, when loaded with hydrogen, most immiscible binary alloys containing magnesium (Mg-V, Mg-Sc, Mg-Y, Mg-La, Mg-Ce, Mg-Gd) undergo a severe segregation into their constituent elements. Mg-Ti alloys, on the other hand, are structurally reversible for several cycles of hydrogen absorption and desorption. We have therefore proven that it is possible to synthesize new lightweight hydrogen absorbing materials, beyond the limits imposed by thermodynamic equilibrium.

The exceptional reversibility observed in Mg-Ti thin film alloys can be understood on the basis of the “spinodal-like” microstructure, composed of Mg-rich and Ti-rich coherently bound domains, together with what could be called *an accident of nature*: upon exposure to increasing hydrogen pressures the Ti-rich domains absorb hydrogen, while Mg-rich parts remain in the metallic phase. This is due to the lower (more negative) enthalpy of hydride formation of  $\text{TiH}_2$  with respect to  $\text{MgH}_2$ . At higher hydrogen pressures also the Mg domains are hydrogenated and the films become black. The *accident* is that the molar volume of Mg and  $\text{TiH}_2$  are almost identical: in the intermediate state, when only Ti-rich areas are loaded with hydrogen, the system is in a structurally stable situation composed of Mg-rich and  $\text{TiH}_2$ -rich domains with (almost) identical volumes, which prevents the segregation observed in other binary Mg-based alloys.

In order to further investigate the role of chemical segregation and structural coherence in Mg-Ti alloys we artificially engineered one dimensional chemical short-range order by depositing Mg/Ti multilayers with various periodicities. Surprisingly, notwithstanding the large lattice mismatch between Mg and Ti, we obtained multilayers with good crystal quality and partially coherent Mg/Ti interfaces. Upon hydrogenation the Ti layers absorb hydrogen before the Mg ones, as expected from a thermodynamic perspective and confirmed with a simple diffusion model. X-ray reflectometry measurements indicate that hydrogen absorption induces a large out-of-plane expansion of both Mg and Ti, well beyond the elastic limits. This has great consequences on the nature of the Mg/Ti interfaces, which must lose their structural integrity and lead to quasi decoupled layers of Mg and Ti.

The effect of “broken” Mg/Ti interfaces is particularly intriguing when looking at the loading isotherms of Mg-based multilayers. What we observed experimentally is that Mg films as thin as 20 nm, when “sandwiched” between Ti layers, exhibit loading pressures similar to the ones expected for bulk magnesium. On the contrary, when sandwiched between elements such as palladium and nickel, magnesium loads at much higher pressures. After studying many

different sample geometries we proposed that a significant increase of hydrogen loading pressure is observed when Mg is adjacent to an element which forms a stable alloy with it (such as Pd and Ni), while immiscible elements (such as Ti, Nb and V) induce a bulk-like quasifree behavior. The Mg-alloy-forming elements have the ability to clamp the Mg layers, inducing elastic stresses during the hydrogen absorption process. By taking into account the long-ranged elastic interaction between two hydrogen atoms dissolved into a metallic lattice, we developed a simple elastic model for the elastic response of a bilayer. The model qualitatively reproduces the variations in hydrogen loading pressures observed experimentally in Pd-capped Mg layers with various thicknesses.

Our observations show that it is possible to *tune* the thermodynamics of hydrogen absorption in Mg thin films by means of elastic clamping. The same model developed for a bilayer predicts an even larger increase of hydrogen equilibrium pressures for 3D magnesium nanoparticles covered with a clamping hard skin. Although Mg has a high gravimetric and volumetric capacity of hydrogen storage at a very low cost, its use as hydrogen storage material is hindered by its poor kinetic and thermodynamic properties. Magnesium hydride is too stable for practical applications, with a hydrogen equilibrium pressure of less than a millibar at room temperature. Increasing the equilibrium pressure of such a material is therefore highly desirable in the perspective of an efficient use of hydrogen as an energy carrier.

Furthermore, the possibility to tune the hydrogen equilibrium pressure of a Mg thin film, combined with the optical changes occurring upon the hydrogenation of magnesium, opens the possibility of using Mg-based multilayers in multistep optical detectors, with good sensitivities in a wide range of hydrogen pressures.