Activation mechanism in the hydrogen storage material MgH₂

Hydrogen, produced by electrolysis of water, has huge potential as a sustainable energy carrier for storage of the “green” electricity produced by renewable sources. It can be used in fuel cells or even burnt directly in internal combustion engines. But a major obstacle to the expansion of hydrogen-based technology is the lack of compact and safe storage systems. For this purpose, metal hydrides, MHₓ, are being intensively studied. They allow reversible loading and release of hydrogen according to the reaction: M + xH → MHₓ. The hydrogen atoms are densely and securely packed in the metal lattice by chemical bonding.

Among the materials considered for hydrogen storage, magnesium hydride MgH₂ has great advantages. It can store 7.6 weight % hydrogen, and magnesium itself is abundant and non-toxic. Hydrogen is readily incorporated in magnesium powders under moderate gas pressure and released by lowering the pressure, dependent on temperature [desorption is endothermic so any accidental release of hydrogen is self-interrupting]. The feasibility of MgH₂ has already been demonstrated for application at the industrial scale by the French company McPhy Energy, created in 2008, which exploits techniques based on Néel Institute research.

The kinetics of hydrogen sorption in pure Mg is relatively slow but transition metal “additives”, which are secondary phases intimately mixed into the hydrogen storage medium by ball milling (fr: broyage), have been found to be very efficient reaction accelerators. The additive’s exact role is still unclear. The ball-milling process itself has beneficial effects: it produces dispersed, nanosized particles resulting in reduced hydrogen diffusion path lengths and increased coverage of the MgH₂ grains. In addition, two other explanations have been proposed: (1) a positive effect of microstrains induced by the mismatch of the thermo-mechanical properties, and (2) a “gateway” role of the transition elements where the oxygen-free Mg/transition metal interfaces, formed during ball-milling, are more permeable to hydrogen than oxidized surfaces, and therefore facilitate its sorption.

We have used X-Ray diffraction to understand the role of a transition metal alloy [titanium vanadium chromium TiVCr] in the sorption of hydrogen by magnesium. Our samples were composites consisting of an intimate mixture obtained by ball-milling MgH₂ and TiVCr alloy together. To measure the evolution of the crystal phases present during hydrogen absorption and desorption, apparatus was developed specially for an in-situ study on X-Ray beam line ID15 at the European Synchrotron Radiation Facility, Grenoble (T. Andrieux et al., J. Appl. Crystallogr. 2014). This apparatus can collect diffraction patterns at a high repetition rate: one pattern every 40 sec. The samples were contained in a sapphire capillary connected to a high-temperature, high pressure, gas loading system. The structural properties of the materials were investigated continuously while they underwent reaction under controlled temperature and hydrogen pressure (Fig. 1).

Analysis of the data provided identification and quantification of the different chemical phases present during hydrogen absorption and desorption reactions at temperatures 100-500 C. Lattice parameter values reflect volume changes resulting from hydrogen sorption. In particular, variations of the transition metal alloy’s lattice parameters (adjusted for thermal expansion) showed that hydrogen was being inserted in the metal lattice of the additive to form a solid solution TiVCrHₓ. While TiVCrHₓ shows a monotonic, progressive decrease in its volume as a function of dehydrogenation when studied as a pure material, it undergoes a sudden, anomalous volume change around 350 C in the composite mixture, coincident with the rapid decomposition of the MgH₂ fraction. Conversely, a similar behavior was observed upon hydrogenation of the composite.

These results provide clear evidence for a cooperative effect between the additive and the primary hydrogen storage medium MgH₂. We can assign the volume changes of the TiVCrHₓ phase to be directly related to hydrogen exchange between the additive and Mg or MgH₂ at the scale of the grains in the composite. These significant volume changes are obviously playing a role in modifying the mechanical strains at the Mg/additive interface within the composite.

In conclusion, the results elucidate the interaction between the additive and MgH₂ during reversible hydrogen loading and release. The present methods which were dedicated to MgH₂ composites could be used for the investigation and design of other efficient hydrogen storage systems, or more widely, to other applications in which composite materials are involved in solid-gas reactions. Our results could not have been obtained without performing the in-situ experiments at an intense synchrotron X-Ray source.