

HYDROGEN STORAGE IN MAGNESIUM BASED ALLOYS

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Introduction

Hydrogen is an appealing energy carrier, in particular for mobile applications such as cars and boats. But, storage remains a critical problem. While high pressure tanks are being used in several prototype cars today, the capacity is small and the volume large and it is likely that safety concerns will also call for alternative solutions. Light metal hydrides are a possible solution to this problem [1]. One example is magnesium hydride, MgH_2 , which contains 7.6% hydrogen by weight. There are two serious problems though: (1) the hydrogen binds so strongly in magnesiumhydride that temperature in excess of 700 K is needed to release the hydrogen, while a release temperature around 400 K would be preferable, and (2) the diffusion of hydrogen through the hydride is so slow that loading and unloading of hydrogen takes very long time [2]. The question is whether the binding energy can be reduced and the rate of diffusion increased by adding other elements to the magnesium while not reducing the mass ratio of hydrogen in the hydride too much. This question is being addressed by computational means.

Theoretical calculations

We have carried out various theoretical calculations based on density functional theory to study how binding energy and diffusivity of hydrogen change in magnesium hydride when other elements are added. The calculations make use of a plane wave basis set, ultrasoft pseudopotentials, the PW91 gradient dependent functional and the VASP code [3,4].

Results

We have carried out various theoretical calculations based on density functional theory to study how binding energy and diffusivity are affected by small addition of other light elements and transition metals to the magnesium. Some examples of results are discussed below.

The addition of aluminum was found to reduce the binding energy of hydrogen in the hydride. With a, Al molefraction of 0.15, the binding energy has been reduced from 0.38 eV to 0.24 eV, corresponding to hydrogen release at 1 bar and 350 K. The calculations were made assuming the rutile structure of the hydride remains stable, but it in fact becomes unstable with respect to phase separation. The calculations, however, illustrate that the addition of a rather small amount of a more electronegative element to the magnesium can significantly reduce the binding energy of the hydrogen in the hydride [5].

Experimental measurements have indicated that the addition of small amount of transition metal, for example titanium, can speed up the unloading of hydrogen from magnesium hydride [6]. A cubic crystal structure with a unit cell of Mg_7TiH_x was found from X-ray crystallography. The compound was synthesized under high pressure. Our calculations have shown that the hydrogen ions sit in tetrahedral holes in the lattice (unlike the rutile structure of pure magnesium hydride) and that $x=16$ [7]. The structure of the hydride is shown in figure 1. A large increase in diffusivity of hydrogen in the magnesium-titanium hydride is predicted from the theoretical calculations as compared with pure magnesium hydride, largely because of greatly reduced formation energy of hydrogen interstitials in the hydride.

Preliminary results on more complex compounds indicate that the lowering of binding energy that can be accomplished by adding a less electronegative element such as aluminum and the acceleration of diffusion that can be accomplished by adding a transition metal do not exclude each other and that a ternary alloy could both have reduced binding energy and fast diffusion. The task remains, however, to find a stable alloy where both the pure metal alloy and the hydride are stable. Theoretical calculations are being carried out to search for such an alloy.

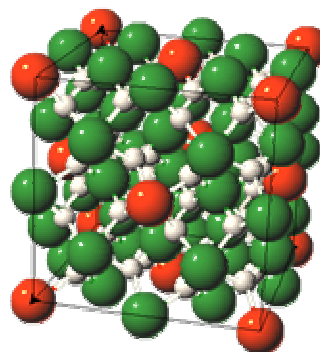


Figure 1. Structure of Mg_7TiH_{16} . The hydrogen ions sit in tetrahedral holes of the cubic Mg-Ti lattice.

References

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