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THE STUDY OF NANODISPERSED COMPOSITE MgH_2-Ti: EXPERIMENT AND THEORY

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Abstract

In order to obtain faster hydrogen sorption kinetics, MgH_2-Ti nanocomposites were prepared by high-energy ball milling, under Ar using 10:1 ball to powder ratio and 10% of catalyst. Microstructural and morphological characterization, performed by XRD and optical microscopy analysis, show a correlation with thermal stability and hydrogen desorption properties investigated by DTA. In order to obtain deeper insight into bonding mechanisms of Ti in MgH_2 fully relaxed structure, we have performed ab initio electronic structure calculations of MgH_2 + Ti system, using Full Potential Linearized Augmented Plane Wave method, as implemented in WIEN2K code.

Introduction

Among the metal hydrides, MgH_2 is considered as potential hydrogen storage material for vehicular application because of its high capacity and low cost. However, the slow reaction kinetics of the Mg–H system at low temperatures limits the practical application of MgH_2. Experiments show, however, that hydrogen binds too strongly in the Mg, having a binding energy of 0.39 eV/atom, and the hydride must therefore be heated to more than 247°C to release the hydrogen [1]. The dissociation of hydrogen molecules at the surface of Mg and the diffusion of hydrogen through the hydride are also so slow that loading and unloading of hydrogen takes excessively long time. Alloying or mixing magnesium with catalytic transition elements (TM), such as Ni, Co, Fe, and with intermetallic compounds [2,3] could significantly improve the hydriding and dehydriding kinetics of MgH_2. The task remains, however, to find Mg-TM alloy that remains stable during hydrogenation and dehydrogenation.

In the present work we have study the influence of 3d-transitional metal Ti on hydrogen desorption in the Mg–H system both from theoretical and experimental point of view.

Experimental Part

Magnesium hydride and Ti powders were used as starting material. Ball milling was performed in a Turbula Type T2C Mixer 20 hour under Ar atmosphere.

The microstructure of the powders was characterized by X-ray diffraction (XRD) with a Siemens KRISTALOFLEKX D-500, equipped with Cu-Kα Ni filtrated radiation. Hydrogen desorption was investigated by DTA using a SDT 2090 (TA Instruments) under 99.999% pure Ar flow. Heating runs at a fixed heating rate of 15 K/min were carried out.

Preliminary MgH_2 electronic structure calculation was performed using XRD refined cell parameters. For MgH_2-Ti compound atomic positions relaxation was performed without cell parameters optimization. The reason for that is the specific choice of supercell, without significant Ti states overlapping. Therefore, the reasonable assumption was that structure relaxation due to imposing of Ti atoms in the structure has negligible effect on overall cell size and c/a ratio.

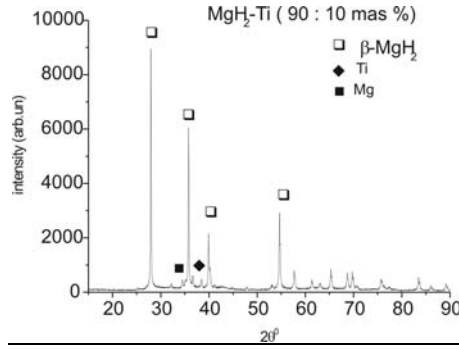

Fig.1. XRD spectra for MgH_2-Ti composites

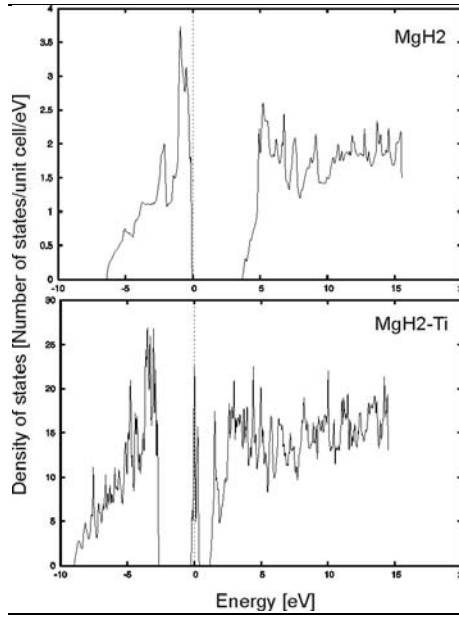

Fig. 2. a) Densities of states (DOS) of MgH_2 and b) MgH_2-Ti compound

Results

In the Fig.1 XRD spectra for MgH_2-Ti composites are presented. The main effect is the diffraction peak broadening, related to the microstructural refinement imparted by ball milling. One can also see that in these experimental conditions there is no formation of binary alloys or intermetallic compounds between Mg and Ti. It is worth to notice that diffraction patterns of MgO are usually present after milling, which is not the case for this sample. The density of states (DOS) and the charge distribution were performed to address the intrinsic mechanism of the effect of titanium on the dehydriding properties of magnesium hydride. The total DOS-es of MgH_2 and MgH_2–Ti systems were plotted in Fig. 2.

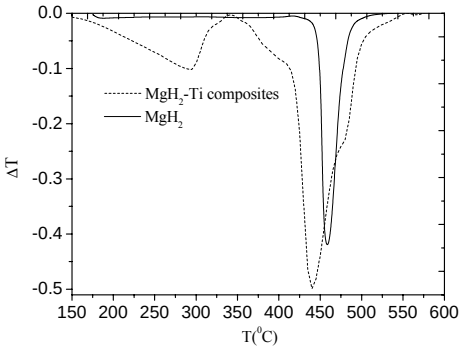

Fig.3 DTA traces of MgH_2-Ti composite and pure MgH_2

Density of states obtained by FPLAPW method given in Fig. 2 show that the addition of the titanium to the MgH_2 result in appearance of narrow Ti d states in the gap and at low energy side of conduction zone. Another consequence is Fermi energy shift toward higher energies. The Fermi level is positioned at first Ti d states peak. Structure relaxation results in shifting of nearest neighbor H atoms closer to Ti and stronger bonding, leading to Mg-H bond strength weakening. The both finding goes in favor of overall reduction of structure stability compared to that of pure MgH_2. That is confirmed by low temperature DTA peak at 290^0C. in Fig. 3.

Conclusion

The influence of Ti on the stability of MgH_2 was investigated by means of the electronic structure and the total energy calculation by using the FLAPW method and DTA analysis. DOS analysis has shown that the bonding between magnesium and hydrogen was weakened, although the interaction between titanium and hydrogen is stronger which is confirmed by preliminary DTA analysis

Acknowledgment

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