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HYDROGEN DESORPTION FROM VACANT MgH₂

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ABSTRACT

The hydrogen desorption properties of vacant MgH₂ structure were investigated both experimentally and theoretically. Ion irradiation by Ar⁸⁺ and Xe⁸⁺ ions were used to induce structural changes in MgH₂. Hydrogen desorption properties were investigated by temperature programmed desorption (TPD). To obtain deeper insight in structural changes during desorption theoretical calculations were performed using DFT approach within Abinit code. Results showed that there are several mechanisms involved in desorption process, which depend on defect concentration, their position and their interaction and ordering. It has been demonstrated that the changes in near-surface area play the crucial role in desorption kinetics.

INTRODUCTION

Magnesium and magnesium based alloys have a great potential as rechargeable hydrogen storage materials since its high hydrogen storage capacity (7.6 wt %) and reversible, relatively simple, endothermic hydrogen desorption reaction. However, slow kinetics and relatively high dehydrogenation temperature still limit its practical application [1]. Severe attempts have been made to overcome these drawbacks. The most used method is nanostructuring of material by mechanical milling with different types of dopants like transition metals, intermetallics, oxides, carbides [2-5], etc. Metal oxides such as VO₂ and CeO₂ that have vacant structure were proved as very effective catalysts [4, 5].

The other way to destabilize the MgH₂ structure and improve its hydrogen desorption kinetics is ion irradiation. By inert, heavy ion irradiation it is possible to create a considerable amount of defects, particularly vacancies and to control their quantity and depth distribution through sample [6]. It is especially important for the surface layer modification which condition is crucial for the hydrogen desorption properties of material. On the other hand, DFT calculations can give an insight in the stability of the system and consequently, the possible mechanism of desorption process. From these calculations one can also

determine the influence of vacancy position and concentration on the hydrogen desorption energy [7].

In this paper, mechanism of hydrogen desorption from MgH₂ irradiated with Ar⁸⁺ and Xe⁸⁺ ions is investigated and correlated with DFT calculation findings.

EXPERIMENTAL

Commercial (Alfa Aesar, (AA), of purity 98%, with initial mean particle diameter of 38 μm) MgH₂ powder was prepared as explained in our previous work and homogeneously irradiated using 120 keV and Ar⁸⁺ (sample A16) and Xe⁸⁺ (sample S16) ions with fluence of 10¹⁶ ions/cm² [6]. Interaction of incident ions with material was calculated using Monte Carlo method as implemented in SRIM package. X-ray analysis was by Siemens KRISTALLOFLEX D-500 device, with Cu-Kα Ni filtrated radiation (λ=1.5406 Å). Malvern 2000SM Mastersizer laser scattering particle size analysis system was used to obtain the quantitative MgH₂ particle size distributions. Homemade apparatus with a quadruple mass spectrometer EXTORR XT300 were used for TPD measurements. The kinetic parameters were deduced using non-isothermal approach.

For DFT calculations Abinit code and Troulliere Martins pseudopotentials were used. (110) plane was exposed and the supercell consists of 12 parallel atomic planes with total of 96 atoms, with H two-fold bonded surface atoms. The surface of the supercell was separated from its periodic image by 1,5 nm of vacuum.

RESULTS AND DISCUSSION

In the table 1 are given number of produced vacancies per incident ion and range of maximum ions in the sample. It can be seen that the Xe⁸⁺ ions produce about 50 % more vacancies than Ar⁸⁺ which are deposited nearer to

Table 1. SRIM, XRD, laser scattering and kinetic data for commercial (AA) and samples irradiated with Xe⁸⁺ (S16) and Ar⁸⁺ (A16) ions with fluence of 10¹⁶ ions/cm²

Sample	Produced vacancies per ion	Range maximum position (nm)	Crystallite size (nm)	Mean particle size (μm)	Avrami-parameter	E _a ^{des} (kJ/mol)
AA	-	-	83	38	3	372
S16	1818	85	45	21.7	4	97
A16	1244	175	76	22.6	2	215

the surface. XRD data showed small decrease in crystallite size for irradiated samples and shift of peaks towards higher angles as a consequence of material disordering. Besides, there are visible peaks of $\text{Mg}(\text{OH})_2$ and MgO phases in samples S16 and A16 as a consequence of high reactivity of MgH_2 towards oxygen and moisture from air. Mean particle size of irradiated samples is also reduced, but with no significant difference between samples A16 and S16. Hydrogen desorption temperatures are 720, 643 and 665 K for samples AA, S16 and A16 consequently. The best fitting of thermal data was achieved by using Avrami-Erofeev nucleation models and results given in table 1 show significant decrease in apparent activation energy for hydrogen desorption for both irradiated samples, but more pronounced for the sample S16. There can also be seen change in the dimensionality of nucleus growth from 3D in sample AA to 2D for A16 and random in S16. It can be assumed that the reduction of temperature and activation energies are caused

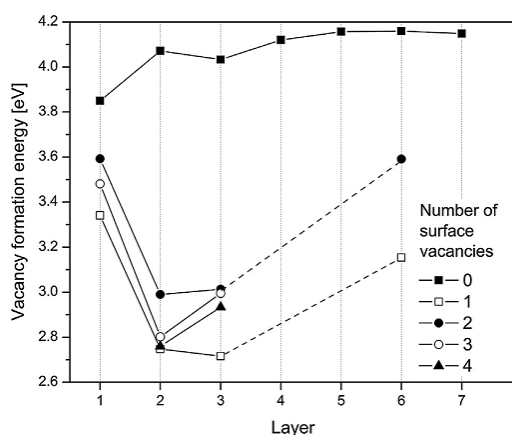


Figure 1. The H-vacancy formation energies in the (110) MgH_2 sub-surface layers as a function of surface coverage with H atoms. Configurations with 1 and 3H vacancies in 3rd and 6th layer are connected with dashed line.

by the increase of diffusion coefficient of hydrogen in subsurface layers of destabilized MgH_2 and increase in the number of active sites for hydrogen molecule recombination, both results of the vacant surface structure. This explanation is supported by Park et al. on type and behavior of defects in the magnesium hydride in conditions of extremely poor hydrogen, existing during dehydrogenation process [8]. These effects are dominant for the sample S16 that has more

vacancies closer to the sample surface. So, the concentration of defects has effect on desorption temperature and activation energy, while their position influences the reaction mechanism.

Results of DFT calculation (Fig. 1) showed that H-desorption energy strongly depends on number of surface H atoms and their configuration. Surface vacancies considerably lower the H-vacancy formation energies as well in the sub-surface layers. These results suggest that the role of surface

hydrogen concentration and distribution is decisive for the H-desorption kinetics, not only because of lowering the potential barrier for further H-desorption, but an increased number of surface hydrogen vacancies supports creation of the sub-surface vacancies network and make diffusion of bulk hydrogen atoms toward the surface easier.

CONCLUSION

The influence of structural changes induced by heavy ion irradiation using Ar and Xe ions on desorption properties of MgH₂. To obtain deeper insight in structural changes DFT calculations using Abinit code has been performed. It has been shown that the large concentration of the surface and near-surface vacancies promotes diffusion of H atoms toward the surfaces of grains, which lowers temperature and activation energy of H₂ desorption. Not only that concentration, but also the depth distribution of vacancies have strong influence on the desorption process.

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