

CHANGES OF HYDROGEN STORAGE PROPERTIES OF MgH₂ INDUCED BY BORON ION IRRADIATION

Kumric S.^{*}, Matovic Lj., Novakovic N., Siljegovic M., Jovanovic Z., Kacarevic-Popovic Z., Grbovic Novakovic J.

Vinča Institute of Nuclear Sciences, P.O.Box 522, 11000 Belgrade, Serbia

^{*}Fax +381 11 2439 454

E-mail: skumric@vinca.rs

Introduction

In order to improve MgH₂ storage properties i.e. to decrease the desorption temperature and improve desorption kinetics many efforts have been made [1]. The concept of metal hydride destabilization (including MgH₂) relies on the capability to identify compounds or elements that can lead to a reduction of the reaction enthalpy. This concept is very general and therefore a large number of potential destabilization methods exist such as: addition of impurities and/or catalysts [2], stress and strain introduction by ball milling or ion bombardment [3]. In order to reveal the most important factors governing the sorption properties of MgH₂, it is crucial to obtain a better understanding of the changes induced by the destabilization processes. All these methods brought out some improvements in kinetics and desorption temperature, but without decidedly explication of reaction mechanism. For instance, ball milling cause mechanical deformation, surface modification and metastable phase formation, which generally promote the solid-gas reaction. It also introduces defect zones which may accelerate the diffusion of hydrogen and defect clusters which may lower its barrier for nucleation. It was also confirmed [3] that near-surface area of MgH₂ plays the crucial role in hydrogen desorption kinetics. Recently it was reported that complex hydride Mg[BH₄]₂ desorbs hydrogen at 500 K in the step that depends on covalent boron-hydrogen interaction [4], so the alternative way of decreasing MgH₂ stability could be by replacing the strong Mg-H ionic bond with weaker B-H covalent one.

In attempt to comprehend and improve desorption behavior of MgH₂ we have investigated the influence of structural changes introduced by the B³⁺ ions irradiation within surface layer of MgH₂ relating the concentration and type of produced defects to MgH₂ sorption properties. Understanding these relations may help to overcome some of the material miss-drawings and provide a possibility to investigate stability of particular light ions induced material modifications during hydrogen cycling.

Results and the discussion

The commercial (Alfa Aeser) MgH₂ powder was pressed on the Al foil to obtain thin layer and homogeneously irradiated using ¹¹B ions (charge state +3, energy 45 keV with ion fluences ranging from 10¹² to 10¹⁶ ions/cm²) at the ion source of TESLA Accelerator Installation at Vinca Institute of Nuclear Sciences, Belgrade. To obtain a better insight in the performed interaction, Monte Carlo numerical simulations using SRIM software package full cascade calculations, were carried out. It was established that the electronic (ionisation) effects are dominant for ¹¹B stopping mechanism. The maximum of penetration depth distribution was for ¹¹B is 216 nm while the production of vacancies by incident beam is negligible. All produced vacancies are from Mg and H recoils.

X ray analysis was used to identify the crystalline phases and lattice parameters as well as the crystalline size and strain of irradiated samples by means of Siemens KRISTALOFLEKX D-500 device, with Cu-K α Ni filtrated radiation ($\lambda=1.5406$ Å). Lattice parameters were refined from the fitted data using the least square procedure. Standard deviation obtained was 1%. Williamson-Hall plots were used to separate the effect of the size and strain in the nanocrystals.

Two features from Table 1 are visible: a sharp decrease in microstrain, particle size and crystallite size in the sample B12 induced by ionization effects and their pronounced relaxation in the samples B15 and B16 which could be a consequence of an ordering of interacting defects when their concentration exceeds a critical value.

All samples exhibit the broadening of typical β -MgH₂ peaks indicating a decrease of crystallite size (XRD diffractograms not shown). The amorphization is more pronounced in samples irradiated at lower fluencies (samples B12). There are no peaks corresponding to γ -MgH₂ phase.

The thermal behavior of the samples was studied by TPD measurements at a constant heating rate of 5 K/min, from room temperature to 973 K, under starting vacuum of 3 \times 10⁻⁶ mbar, utilizing home made equipment, with a quadruple mass spectrometer EXTORR XT300 and by DSC analysis using 151R Setaram Instruments at a

constant heating rate of 15 K/min under argon atmosphere.

Table 1. Crystallite size, microstrain and average particle size of samples.

Name	Crystallite size [nm]	Micro-strain [%]	Average particle size (μm)
MgH ₂ as received	83	$1.4 \cdot 10^{-3}$	38
B12	54	$4.9 \cdot 10^{-4}$	14
B15	76	$1.3 \cdot 10^{-3}$	22
B16	76	$1.3 \cdot 10^{-3}$	21

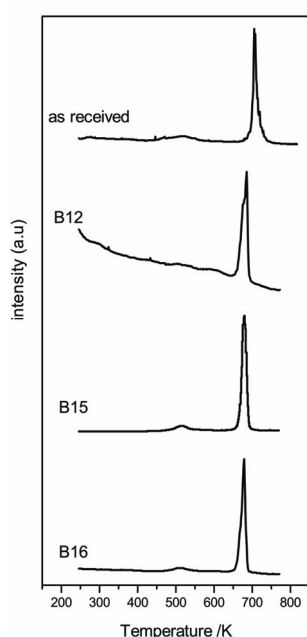


Fig.1. Results of TPD measurements, for a commercial MgH₂ (as received) and samples irradiated at different 45 keV B³⁺ ion fluences: 10¹² (B12), 10¹⁵ (B15), and 10¹⁶ ion/cm² (B16).

It can be seen from Fig.1 that the commercial MgH₂ sample completely release hydrogen in a single process around 706 K. In samples irradiated with higher fluences (10¹⁵ and 10¹⁶) two desorption peaks are visible, suggesting the existence of at least two different mechanisms of hydrogen release, or/and two different kinds of hydrogen atoms existing in the samples [3]. Sample irradiated with 10¹² shows noticeable onset at lower temperature. It should be noted here that the chemical state of B in dehydrogenated products, which can bond with metal or be in elemental or amorphous B–H_x states, will

affect greatly the thermodynamic parameters of dehydrogenation. It was found that the low temperature peak originates from several competing processes: [BH₄] decomposition, desorption from OH⁻ ions and water molecules. DSC measurements confirmed the obtained results by TPD.

Conclusions

In this paper we have presented the results of modifications of MgH₂ induced by 45 keV B³⁺ ion irradiation with different fluences, ranging from 10¹² to 10¹⁶ ions/cm². The effects of ion irradiation are estimated by numerical calculations using SRIM package. The induced material modifications and their consequences on hydrogen dynamics in the system are investigated by several experimental techniques: XRD, TPD and DSC analyses. The results confirmed that the near-surface area of MgH₂ plays the crucial role in hydrogen kinetics and that various concentrations of induced defects substantially influence H diffusion and desorption kinetics in MgH₂.

Acknowledgments

This work is financially supported by Serbian Ministry of Science and Technology under grants 141009, 142016 and 142027.

References

- Schlapbach L, Zuttel A. Hydrogen-storage materials for mobile applications. *Nature* 2001;414:353-358.
- Oelerich W, Klassen T, Bormann R. Metal oxides as catalysts for improved hydrogen sorption in nanocrystalline Mg-based materials. *J Alloys Comp* 2001;315:237–242.
- Grbović Novaković J, Matović Lj, Milovanović S, Drvendžija M, Novaković N, Rajnović D, Šiljegović M, Kačarević Popović Z, Ivanović N. Changes of hydrogen storage properties of MgH₂ induced by heavy ion irradiation. *Int J Hydrogen Energ* 2008;33:1876-1879.
- Li HW, Kikuchi K, Nakamori Y, Ohba N, Miwa K, Towata S, Orimo S. Dehydrogenating and rehydrogenating processes of well-crystallized Mg(BH₄)₂ accompanying with formation of intermediate compounds. *Acta Materialia* 2008;56:1342–1347.
- Bassetti A, Bonetti E, Pasquini L, Montone A, Grbovic J, Vittori Antisari M. Hydrogen desorption from ball milled MgH₂ catalyzed with Fe. *Eur Phys J B* 2005;43:19–27.