

University of Wollongong - Research Online

Thesis Collection

Title: Effect of catalysts on hydrogen storage properties of MgH₂

Author: Abbas Ranjbar

Year: 2010

Repository DOI:

Copyright Warning

You may print or download ONE copy of this document for the purpose of your own research or study. The University does not authorise you to copy, communicate or otherwise make available electronically to any other person any copyright material contained on this site.

You are reminded of the following: This work is copyright. Apart from any use permitted under the Copyright Act 1968, no part of this work may be reproduced by any process, nor may any other exclusive right be exercised, without the permission of the author. Copyright owners are entitled to take legal action against persons who infringe their copyright. A reproduction of material that is protected by copyright may be a copyright infringement. A court may impose penalties and award damages in relation to offences and infringements relating to copyright material.

Higher penalties may apply, and higher damages may be awarded, for offences and infringements involving the conversion of material into digital or electronic form.

Unless otherwise indicated, the views expressed in this thesis are those of the author and do not necessarily represent the views of the University of Wollongong.

Research Online is the open access repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

2010

Effect of catalysts on hydrogen storage properties of MgH₂

Abbas Ranjbar

University of Wollongong, abbasr@uow.edu.au

Follow this and additional works at: <https://ro.uow.edu.au/theses>

University of Wollongong

Copyright Warning

You may print or download ONE copy of this document for the purpose of your own research or study. The University does not authorise you to copy, communicate or otherwise make available electronically to any other person any copyright material contained on this site.

You are reminded of the following: This work is copyright. Apart from any use permitted under the Copyright Act 1968, no part of this work may be reproduced by any process, nor may any other exclusive right be exercised, without the permission of the author. Copyright owners are entitled to take legal action against persons who infringe their copyright. A reproduction of material that is protected by copyright may be a copyright infringement. A court may impose penalties and award damages in relation to offences and infringements relating to copyright material.

Higher penalties may apply, and higher damages may be awarded, for offences and infringements involving the conversion of material into digital or electronic form.

Unless otherwise indicated, the views expressed in this thesis are those of the author and do not necessarily represent the views of the University of Wollongong.

Recommended Citation

Ranjbar, Abbas, Effect of catalysts on hydrogen storage properties of MgH₂, Doctor of Philosophy thesis, Institute for Superconducting and Electronic Materials - Faculty of Engineering, University of Wollongong, 2010. <https://ro.uow.edu.au/theses/3152>

NOTE

This online version of the thesis may have different page formatting and pagination from the paper copy held in the University of Wollongong Library.

UNIVERSITY OF WOLLONGONG

COPYRIGHT WARNING

You may print or download ONE copy of this document for the purpose of your own research or study. The University does not authorise you to copy, communicate or otherwise make available electronically to any other person any copyright material contained on this site. You are reminded of the following:

Copyright owners are entitled to take legal action against persons who infringe their copyright. A reproduction of material that is protected by copyright may be a copyright infringement. A court may impose penalties and award damages in relation to offences and infringements relating to copyright material. Higher penalties may apply, and higher damages may be awarded, for offences and infringements involving the conversion of material into digital or electronic form.

Effect of catalysts on hydrogen storage properties of MgH_2

A thesis submitted in fulfilment of the requirements for
the award of the degree

Doctor of Philosophy

from

University of Wollongong

by

Abbas Ranjbar

(B.S. Physics, M.S. Physics)

Institute for Superconducting and Electronic Materials

February 2010

Dedicated to

My love

Masi

تقديم به همسر و همسفر عزيزم

CERTIFICATION

I, Abbas Ranjbar, declare that this thesis, submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy, in the Institute for Superconducting and Electronic Materials, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications at any other academic institution.

Abbas Ranjbar

28 Feb. 2010

Acknowledgements

It is my great pleasure to express my gratitude to my supervisors, Professor Huakun Liu and Dr. Zaiping Guo, for their inspiration, guidance, encouragement, and financial and spiritual support. I feel fortunate to have been associated with them, and I believe that I still can learn much from them. I wish to express my special thanks to Professor Shixue Dou for being a model of dignity and remarkable managerial skill. I owe my deep gratitude to Professor X. B. Yu, Dr. A. Calka, and Dr. D Wexler for their invaluable assistance and suggestions.

I would like to express my gratitude to my colleagues Dr. G. Peleckis, Dr. S. Aminorroaya, Dr. Z. G. Huang, J. Mao, C. K. Poh, and M. Ismail for all their support and encouragements.

I also would like to thank all non-teaching staff members, particularly Darren Attard, Joanne George, Ron Kinnel, and Virginie Schmelitschek for their invaluable assistance in many regards. Special thanks go to Dr. Tania Silver for her critical help thorough error checking of my papers and this thesis.

I wish to express my heartfelt thanks to my lovely mother, brother, and sisters for their care, spiritual support, and fondness towards me.

Finally, and the most importantly, I am indebted to my wife, Masi, who cheered me up whenever I needed it. This thesis would not have been possible without her trustworthy love, patience, and encouragement. I owe her my deepest appreciation.

Abstract

Hydrogen is the best energy carrier for all kinds of environmentally friendly energy sources such as wind and solar energy. Among the various types of material for hydrogen storage, magnesium is one of the most promising candidates. The objective of this thesis is enhancement of the hydrogen storage properties of MgH_2 using different kinds of catalysts and ball-milling methods.

To increase defects and decrease both grain size and agglomeration, and therefore hydrogen diffusion paths, a hard nanopowder, SiC, was added to MgH_2 . Less than 10wt% of SiC improved the sorption kinetics, while more than 10wt% SiC blocked Mg particles and had negative effects.

In addition to increasing defects and extra improvement of the surface area, the effects of doping Ni into the MgH_2 -SiC system were investigated. Additional improvement in sorption kinetics and hydrogen capacity was achieved by this combination. The rate-limiting step changed from “surface controlled” for the pure sample to “nucleation and three-dimensional growth of the existing nuclei” for the MgH_2 -SiC-Ni sample.

As Ti-based body-centred cubic (BCC) alloys have shown superior catalytic effects on the hydrogen storage properties of magnesium, a new type of BCC, $\text{Ti}_{0.4}\text{Mn}_{0.22}\text{Cr}_{0.1}\text{V}_{0.28}$, was ball milled with MgH_2 with different ball-to-powder weight (BPWR) ratios. The conversion of magnesium to magnesium hydride was much faster in presence of this

catalyst. Both desorption temperature and hydrogen absorption/desorption kinetics were improved by adding the catalyst and increasing the BPWR.

With the aim of improving the different steps of hydrogen sorption in Mg, a combination of ball milling $\text{Ti}_{0.4}\text{Mn}_{0.22}\text{Cr}_{0.1}\text{V}_{0.28}$ and multi-walled carbon nanotubes with MgH_2 was investigated. $\text{Ti}_{0.4}\text{Mn}_{0.22}\text{Cr}_{0.1}\text{V}_{0.28}$ improved two steps of hydrogen absorption: dissociation of hydrogen molecules and transformation of hydrogen atoms into the Mg/BCC interface to form MgH_2 particles. The effects of CNTs could include promotion of Mg aggregation along the grain boundaries and facilitated penetration of hydrogen atoms into interior layers of Mg grains. These effects were in reverse order during hydrogen desorption.

With the aim of finding optimised fabrication conditions for the Mg-Ni system, various fabrication methods such as casting, ball-milling, and the combination of casting and ball milling, and their influence on the hydrogen sorption properties of Mg-6 wt% Ni alloys were studied. Preparation of *Mg + Ni* by ball milling led to remarkable hydrogen sorption properties in comparison with casting as a consequence of introducing defects and active sites during the ball milling.

Key words: hydrogen storage, magnesium hydride, ball milling, catalyst, silicon carbide, nickel, Ti-based body centred cubic, carbon nanotube

Table of Contents

Acknowledgement.....	i
Abstract.....	ii
Table of Contents.....	iv
List of Tables.....	x
List of Figures.....	xi
Chapter 1: Introduction.....	1
Chapter 2: Literature review.....	5
2.1 Background.....	5
2.1.1 Transportation.....	8
2.2 Energy sources and carriers.....	9
2.3 Hydrogen: the best candidate.....	10
2.4 Hydrogen storage.....	14
2.4.1 High pressure gas storage.....	17
2.4.2 Liquid hydrogen.....	18
2.4.3 Solid state hydrogen storage.....	19
2.5 Hydrogen storage by physisorption.....	19
2.5.1 Carbon nanotubes.....	20
2.5.2 Zeolites.....	23
2.5.3 Metal Organic Frameworks (MOFs).....	24
2.5.4 Graphite Nanofibers (GNFs).....	25
2.6. Hydrogen storage by chemisorption.....	26
2.6.1 Complex hydrides.....	27
2.6.1.1 Sodium Aluminium Hydride.....	28

2.6.1.2 Lithium Aluminium Hydride.....	29
2.6.1.3 Magnesium Aluminium Hydride.....	30
2.6.1.4 Calcium Aluminium Hydride.....	31
2.6.1.5 Sodium Borohydride.....	31
2.6.1.6 Lithium Borohydride.....	32
2.6.1.7 Magnesium Borohydride.....	33
2.6.1.8 Calcium Borohydride.....	34
2.6.1.9 Lithium imide and lithium amide.....	35
2.6.2 Metal hydrides.....	37
2.7 Magnesium Hydride.....	41
2.7.1 Introduction.....	41
2.7.2 History.....	41
2.7.3 Structure and Properties.....	42
2.7.4 Thermodynamics.....	44
2.7.5 Ball milling.....	45
2.7.6 Additives.....	46
2.7.6.1 Transition Metals.....	46
2.7.6.2 Metal oxides.....	48
2.7.6.3 Intermetallics.....	49
2.7.6.4 Graphite and Carbon Nanotubes.....	50
Chapter 3: Experimental methods and materials.....	52
3.1 Materials.....	52
3.2 Materials synthesis.....	53
3.2.1 Uni-Ball-Mill 5.....	53
3.2.2 QM-3SP2.....	54

3.3 Physical analysis.....	56
3.3.1 X-Ray diffraction.....	56
3.3.2 Transmission Electron Microscopy.....	57
3.3.3 Scanning Electron Microscopy.....	58
3.3.4 BET.....	59
3.4 Hydrogen sorption properties.....	59
3.4.1 Differential Scanning Calorimeter.....	59
3.4.1.1 DSC Q100.....	59
3.4.1.2 Mettler Toledo DSC1.....	60
3.4.2 Hydrogen Content.....	61
Chapter 4: Hydrogen storage properties of MgH₂-SiC composites	64
4.1 Introduction.....	64
4.2 Sample Preparation.....	65
4.3 Structure.....	66
4.3.1 X-ray diffraction.....	66
4.3.2 TEM analysis.....	68
4.4 Morphology.....	69
4.5 Thermal analysis.....	71
4.6 Hydrogenation and desorption.....	72
4.6.1 Hydrogen Absorption.....	73
4.6.2 Hydrogen Desorption.....	74
4.6.3 PCI.....	75
4.8 Conclusion.....	77
Chapter 5: Effects of SiC nanoparticles with and without Ni on the hydrogen storage properties of MgH₂	79

5.1 Introduction.....	79
5.2 Samples' Preparation.....	80
5.3 X-ray diffraction.....	81
5.4 Morphology.....	83
5.5 Thermal analysis.....	85
5.6 Hydrogenation and desorption.....	86
5.6.1 Hydrogen Absorption.....	86
5.6.2 Hydrogen desorption.....	87
5.6.3 PCI.....	88
5.7 Hydriding/dehydriding kinetic investigation.....	89
5.8 Conclusion.....	92
Chapter 6: Hydrogen storage properties of Mg-BCC composite.....	94
6.1 Introduction.....	94
6.2 Sample Preparation.....	94
6.3 X-ray diffraction.....	96
6.4 Morphology.....	97
6.5 Thermal analysis.....	100
6.6 Hydrogenation and desorption.....	101
6.6.1 Hydrogen Absorption.....	101
6.6.2 Hydrogen desorption.....	102
6.6.3 PCI.....	103
6.8 Conclusion.....	104
Chapter 7: Effects of BCC alloy with and without CNT on the hydrogen storage properties of MgH₂.....	105
7.1 Introduction.....	105

7.2 Samples' preparation.....	105
7.3 X-ray diffraction of as-prepared samples.....	106
7.4 Morphology.....	107
7.5 Desorption Temperature.....	109
7.6 Hydriding and dehydriding.....	110
7.6.1 Hydrogen absorption and desorption at 300 °C.....	110
7.6.2 Hydrogen absorption and desorption at 250 °C.....	111
7.7 XRD after dehydrogenation.....	112
7.8 Discussion.....	113
7.9 Conclusion.....	115
Chapter 8: A multi-scale production approach for Mg hydrogen storage	
alloys.....	117
8.1 Introduction.....	117
8.2 Sample preparation.....	118
8.3 X-ray patterns.....	119
8.4 Morphology.....	120
8.5 Hydrogen absorption and desorption.....	122
8.5.1 Hydrogen absorption.....	122
8.5.2 Hydrogen desorption at 250 °C.....	124
8.6 XRD patterns of hydrogenated samples.....	125
8.7 Desorption Temperature.....	126
8.8 Conclusion.....	127
Chapter 9: Summary and Conclusion.....	129
10.1 MgH ₂ -SiC composites.....	129
10.2 Mg-SiC-Ni nanocomposites.....	130

10.3 MgH ₂ -BCC composites.....	131
10.4 MgH ₂ -BCC-CNT composition.....	132
10.5 Mg-Ni as-cast, ball-milled and ball-milled-cast samples.....	133
References	135
Acronyms	154
Publications	155

List of Tables

Table 2.1 Fossil fuel reserves.....	2
Table 2.2 Motivity factors for different fuels.....	7
Table 2.3 Comparison between Φ_{us} of fossil fuels and hydrogen.....	8
Table 2.4 US DOE hydrogen storage targets for mobile application.	11
Table 2.5 Comparison of main characteristics of various hydrogen storage methods.....	12
Table 2.6 Hydrogen storage capacity of some complex hydrides.....	13
Table 2.7 Kinetic equations related to different rate-limiting steps. f = reacted fraction, t = time, k = reaction rate constant, CV = contracting volume model and JMA = Johnson-Mehl- Avrami model.	35
Table 3.1 Description of used materials.	52
Table 4.1 Absorption rates, capacity, and hysteresis factor for MgH_2 and $MgH_2 + x$ wt% SiC ($x = 5\%$, 10% , or 20%) samples.	74
Table 8.1 A brief information about the fabricated samples with used code.	119

List of Figures

Figure 2.1. Evolution of Annual Crude Oil Production.	5
Figure 2.2. 1973 and 2007 regional shares of CO ₂ emissions per capita.	7
Fig. 2.3. Transport percentage shares of CO ₂ emissions in 2005.	8
Fig 2.4. Schematic diagram of a PEM fuel cell.	14
Fig 2.5. Typical compressed hydrogen storage tank.	17
Fig. 2.6. A 120 liter liquid hydrogen tank (left) and its schematic structure (right).	18
Fig. 2.7. Schematic physisorption on surface.	20
Fig 2.8. (a) Piece of a graphene sheet, (b) and (c) models of a carbon nanotube.....	21
Fig 2.9. Adsorption sites in bundles of single wall nanotubes.	21
Fig. 2.10. Framework structures of zeolites: (a) zeolite A, (b) zeolites X and Y, and (c) zeolite Rho.	23
Fig. 2.11. Crystal structure of metal organic frameworks: (a) MOF-5; (b) HKUST-1 (cavities, yellow and blue balls); (c) MIL-101, and (d) MOF-74 or CPO-27-Co(Ni) (metals, cyan; oxygen, red; carbon, grey).	25
Fig. 2.12. Schematic diagram of a catalytically grown carbon nanofiber.	26
Fig 2.13. Hydrogen absorption process in metals.	27
Fig 2.14. Crystal structure of Mg(AlH ₄) ₂ along the <i>a</i> -axis (a) and the <i>c</i> -axis (b).	30
Fig. 2.15. Ideal PCI curve (left-hand side) and the corresponding Van't Hoff plot (right-hand side) for a metal hydride.	37
Fig. 2.16. Crystal structure of β-MgH ₂	43
Fig 3.1. Milling vial and magnet mounted in Uni-Bball-Mill for the mechanical strong impact mode.....	53

Fig. 3.2. Motion of balls in the magnetic ball mill.	54
Fig 3.3. a) QM-3SP2 planetary ball mill. b) A schematic diagram of the planetary ball mill.....	55
Fig 3.4. DSC Q100.....	58
Fig 3.5. Mettler Toledo DSC1 apparatus.....	59
Fig. 3.6. (a) AMC Gas Reaction Controller. (b) A schematic of the chambers in the GRC unit.....	61
Fig. 4.1. Change of hydrogen pressure inside the ball-milling vial as a function of the ball-milling time.....	66
Fig. 4.2. X-ray diffraction patterns of the as-milled samples.....	67
Fig. 4.3. TEM images of the as-prepared $\text{MgH}_2 + 20 \text{ wt\% SiC}$ sample: (a) bright-field and (b) dark-field images at low magnifications; (c) dark-field image at higher magnification. Inset in (c) is the SAED pattern of the as-prepared $\text{MgH}_2 + 20 \text{ wt\% SiC}$ sample.....	69
Fig. 4.4. SEM images of the as-milled samples after 24 h ball milling: (a) un-doped; (b) 5 wt% SiC; (c) 10 wt% SiC; and (d) 20 wt% SiC doped MgH_2 samples.....	70
Fig. 4.5. DSC curves of as-milled samples after 24 h ball milling.....	72
Fig. 4.6. Comparison of hydrogen absorption kinetics of the MgH_2 and the $\text{MgH}_2 + x \text{ wt\% SiC}$ ($x = 2, 5, 10, 20$), at 350°C under 30 bar hydrogen.....	73
Fig. 4.7. Hydrogen desorption of the MgH_2 and the $\text{MgH}_2 + x \text{ wt\% SiC}$ ($x = 2, 5, 10, 20$) under an initial hydrogen pressure of ~ 0.1 bar at 350°C	75
Fig. 4.8. Comparison of PCI absorption and desorption curves of the MgH_2 and the $\text{MgH}_2 + x \text{ wt\% SiC}$ ($x = 5, 10, 20 \text{ wt\%}$), at $T = 350^\circ\text{C}$	76
Fig 5.1. Change of hydrogen pressure inside the ball milling vial as a function of the ball-milling time.....	81

Fig. 5.2. XRD patterns for as-prepared samples.....	82
Fig. 5.3. X-ray diffraction patterns of the $\text{MgH}_2+5\text{wt}\% \text{ SiC}+10\text{wt}\% \text{ Ni}$ sample after dehydrogenation.....	83
Fig. 5.4. SEM images for the samples: (a1) pure MgH_2 , (a2) $\text{MgH}_2\text{--SiC } 5\text{wt}\%$, (a3) $\text{MgH}_2\text{--SiC } 5\text{wt}\%\text{--Ni } 10\text{wt}\%$. The scale bar for all of the samples is 10	83
Fig. 5.5. Mapping of the $\text{MgH}_2\text{--SiC--Ni}$ sample: (b1) shows a micrograph of the overall area of the sample to be mapped. (b2), (b3) and (b4) show the elemental mapping of Mg, Ni and Si, respectively.....	84
Fig. 5.6. DSC curves for all samples.....	85
Fig. 5.7. Hydrogen absorption for all samples at 300 °C and 30 atm.....	86
Fig. 5.8. Hydrogen desorption for the samples at 300 °C and 0.1 atm pressure.....	87
Fig. 5.9. Comparison of PCI absorption/desorption curves of the $\text{MgH}_2+5\text{wt}\% \text{ SiC}$ and $\text{MgH}_2+5\text{wt}\% \text{ SiC}+10\text{wt}\% \text{ Ni}$ samples.....	88
Fig. 5.10. The resulting curves of different kinetic equations applied to absorption data of (a) un-doped MgH_2 , and (b) $\text{MgH}_2\text{--SiC--Ni}$	90
Fig. 5.11. The resulting curves of different kinetic equations applied to desorption data of (a) undoped MgH_2 , and (b) $\text{MgH}_2\text{--SiC--Ni}$	91
Fig. 6.1. Change of hydrogen pressure as a function of ball milling time.....	96
Fig. 6.2. XRD patterns of as-prepared samples.....	97
Fig. 6.3. Mapping of the $\text{MgH}_2\text{--}10\text{wt}\% \text{ BCC}$ with BPWR 200: (a) shows a micrograph of the overall area of the sample to be mapped, (b) elemental mapping of Ti, (c) Mn, (d) Cr, and (e) V.....	98
Fig. 6.4. SEM images for the as-prepared samples: (a) pure MgH_2 , (b) BPWR 100, (c) BPWR 200.....	99
Fig. 6.5. DSC traces for as-prepared samples.....	100

Fig. 6.6. Hydrogen absorption curves for the samples at 350°C and under 30 atm hydrogen pressure.....	101
Fig. 6.7. Hydrogen desorption curves for the samples at 350 °C and under 0.1 atm hydrogen pressure.....	102
Fig. 6.8. PCI curves of pure MgH ₂ and BPWR 200 samples at 350 °C.....	103
Fig. 7.1. XRD patterns for as-milled samples.....	107
Fig. 7.2. SEM images of all samples: a) pure MgH ₂ , b) Mg-BCC, c) Mg-BCC-CNT.....	108
Fig. 7.3. Backscattered electron composition (BEC) image of the Mg-BCC sample (left and its EDS element analysis (right)).....	108
Fig. 7.4. Initial hydrogen release of all as-prepared samples in profile release mode.....	110
Fig. 7.5. Hydrogen absorption of the samples at 300 °C and 30 atm.....	111
Fig. 7.6. Hydrogen desorption at 300 °C and 0.1 atm for all samples.....	111
Fig. 7.7 Hydrogen absorption at 250 °C and 30 atm.....	112
Fig. 7.8. Hydrogen desorption at 250 °C and 0.1 atm for all samples.....	112
Fig. 7.9. XRD patterns for the samples after dehydrogenation. The enlarged area in the inset shows the shift of the peak with highest intensity.....	113
Fig. 8.1. XRD patterns of as-prepared samples.....	120
Fig. 8.2. SEM images of all samples: a) the cast, b) uniBM-cast, c) BM- powder and d) BM-cast.....	121
Fig. 8.3. Backscattered electron composition BEC image of the BM-cast sample; Bright particles are Mg ₂ Ni.....	121
Fig. 8.4. Hydrogen absorption at 250 °C and 20 atm.....	122
Fig. 8.5. Hydrogen absorption at 200 °C and 20 atm.....	123

Fig. 8.6. Hydrogen desorption at 250 °C and 0.1 atm.....	124
Fig. 8.7. XRD patterns of all samples after hydrogenation.....	125
Fig 8.8. DSC traces for all samples after hydrogenation.....	127