University of Wollongong

Research Online

University of Wollongong Thesis Collection 1954-2016

University of Wollongong Thesis Collections

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

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

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 MgH₂

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 MgH₂ 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 MgH₂. 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 MgH₂-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 MgH₂-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, $Ti_{0.4}Mn_{0.22}Cr_{0.1}V_{0.28}$, was ball milled with MgH₂ 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 $Ti_{0.4}Mn_{0.22}Cr_{0.1}V_{0.28}$ and multi-walled carbon nanotubes with MgH₂ was investigated. $Ti_{0.4}Mn_{0.22}Cr_{0.1}V_{0.28}$ improved two steps of hydrogen absorption: dissociation of hydrogen molecules and transformation of hydrogen atoms into the Mg/BCC interface to form MgH₂ 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 MgH ₂ –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 MgH ₂	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 MgH ₂	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 $MgH_2 + 20$ 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	
$MgH_2 + 20$ 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	
$MgH_2 + x$ 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 MgH ₂ + x 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	
MgH ₂ + x wt% SiC ($x = 5, 10, 20$ wt%), at $T = 350$ °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
Fig. 5.3. X-ray diffraction patterns of the MgH ₂ +5wt% SiC+10wt% Ni sample after
dehydrogenation
Fig. 5.4. SEM images for the samples: (a1) pure MgH ₂ , (a2) MgH ₂ –SiC 5wt%,
(a3) MgH ₂ –SiC 5wt%–Ni 10wt%. The scale bar for all of the samples is 1083
Fig. 5.5. Mapping of the MgH ₂ –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
Fig. 5.6. DSC curves for all samples
Fig. 5.7. Hydrogen absorption for all samples at 300 °C and 30 atm
Fig. 5.8. Hydrogen desorption for the samples at 300 °C and 0.1 atm pressure
Fig. 5.9. Comparison of PCI absorption/desorption curves of the MgH ₂ +5wt% SiC
and MgH ₂ +5wt% SiC+10wt% Ni samples
Fig. 5.10. The resulting curves of different kinetic equations applied to absorption
data of (a) un-doped MgH ₂ , and (b) MgH ₂ –SiC–Ni90
Fig. 5.11. The resulting curves of different kinetic equations applied to desorption
data of (a) undoped MgH ₂ , and (b) MgH ₂ –SiC–Ni91
Fig. 6.1. Change of hydrogen pressure as a function of ball milling time96
Fig. 6.2. XRD patterns of as-prepared samples
Fig. 6.3. Mapping of the MgH ₂ -10wt% 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) V98
Fig. 6.4. SEM images for the as-prepared samples: (a) pure MgH_{2} , (b) BPWR 100,
(c) BPWR 200
Fig. 6.5. DSC traces for as-prepared samples

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	
Fig. 8.7. XRD patterns of all samples after hydrogenation	125
Fig 8.8. DSC traces for all samples after hydrogenation	127