2000

Amorphous and nanocrystalline hydrogen storage alloy materials for nickel-metal hydride batteries

Sun Li

University of Wollongong

Recommended Citation
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.
AMORPHOUS AND NANOCRYSTALLINE HYDROGEN STORAGE ALLOY MATERIALS FOR NICKEL-METAL HYDRIDE BATTERIES

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

DOCTOR OF PHILOSOPHY

from

UNIVERSITY OF WOLLONGONG

by

LI SUN, B. E.

Department of Materials Engineering

August 2000
DECLARATION

I hereby declare that the work presented in this thesis is original and was carried out by the candidate at the Department of Materials Engineering, the University of Wollongong, New South Wales, Australia; and has not been submitted for a degree to any other university or institution.

Li Sun
Rechargeable nickel-metal hydride (Ni-MH) batteries employing hydrogen storage alloys as their negative electrode materials have been some of the most promising power sources for many important applications. For most commercial Ni-MH batteries, their negative electrodes are of rare-earth system alloys, which have low theoretical discharge capacities (e.g., LaNi5 alloy has a theoretical discharge capacity of only about 370 mAh/g). The capacities of the negative alloy electrodes restrict the further improvement of the capacities of nickel-metal hydride batteries.

Magnesium-based hydrogen storage alloys are promising energy conversion and storage materials because they possess very high theoretical hydrogen storage capacity, e.g., the theoretical discharge capacity of Mg2Ni alloy is approximately 1000 mAh/g. Also magnesium is abundant in nature, light in weight and relatively low in cost. FeTi-type hydrogen storage alloys are also prime candidates for hydrogen storage systems and have high theoretical discharge capacities of about 500 mAh/g. FeTi-type alloys are also the cheapest of the promising hydrogen conversion and storage alloys. However, for a long period, it has been thought that Mg-based and FeTi type hydrogen storage alloys were unsuitable for Ni-MH negative electrodes.
Abstract

because of their slow hydriding/dehydriding kinetics at ambient temperature and their susceptibility to corrosion in alkaline solution.

Amorphous and nanocrystalline metals and alloys have the features of new alloy compositions and new atomic configurations, which are different from those of crystalline alloys. These features enable various kinds of characteristics to be achieved such as excellent mechanical properties, useful physical properties and unique chemical properties, which have not been obtained for conventional crystalline alloys. Thus, there appear to be some possibilities to achieve high discharge capacities for amorphous and nanocrystalline Mg-based and FeTi-type alloys.

The purposes of this study are to exploit the electrode properties of novel amorphous and nanocrystalline Mg-based and FeTi-type hydrogen storage alloys as high performance and low cost negative materials for the Ni-MH batteries. For these purposes, amorphous and nanocrystalline Mg-based and FeTi-type hydrogen storage alloys were prepared by mechanical alloying and milling methods using a planetary ball mill. Their structures were determined by X-ray diffraction, differential thermal analysis and transmission electron microscopy. Their electrode behaviour was investigated in a 6 M KOH solution at room temperature.
A nanocrystalline FeTi alloy with an average grain size of about 8 nm can be obtained by mechanically milling a crystalline FeTi alloy for 40 hours. Alternatively, an amorphous FeTi alloy can be obtained by mechanically alloying mixtures of Fe and Ti powders for 40 hours. Crystalline FeTi alloy has an extremely low discharge capacity of only 3 mAh/g at a discharge current density of 50 mA/g, which is negligibly small compared with its theoretical discharge capacity. Therefore, crystalline FeTi alloy is not suitable for use as a rechargeable anode material in an alkaline solution at room temperature. The nanocrystalline FeTi alloy has an improved discharge capacity of 54 mAh/g at the first discharge, which is much higher than that of crystalline FeTi alloy, but is only around 10% of the calculated theoretical electrochemical capacity of FeTi alloy. Due to its good discharge capacity during the first twenty cycles, it may be possible to improve the electrochemical discharge capacity of FeTi-type alloy with good cycle life by achieving a nanocrystalline structure. The amorphous FeTi alloy achieves its highest discharge capacity of 220 mAh/g at the first charge-discharge cycle at a discharge current density of 50 mA/g. This discharge capacity is almost comparable with the capacities of commercial alloys used in Ni-MH batteries. Although the discharge capacity of the amorphous FeTi alloy decreases rapidly with prolonged charge-discharge cycles, it still has a discharge capacity of 78 mAh/g at the twentieth cycle. Thus, it is an effective method in achieving high discharge capacity for the FeTi-type alloy to form an amorphous or nanocrystalline structure.

Department of Materials Engineering, University of Wollongong, NSW 2522, Australia
In order to determine the effect of the preparation method for Mg-based alloys on their discharge capacity, the crystalline Mg-based alloys used were obtained in two ways: sintering elemental powders and induction melting. At a discharge current density of 50 mA/g, crystalline Mg$_2$Ni alloys prepared by sintering Mg and Ni powders have extremely low discharge capacities of only 15 or 18 mAh/g. Induction melted crystalline Mg$_2$Ni alloy also has an extremely low discharge capacity of 18 mAh/g. The discharge capacity of sintered crystalline Mg$_2$Ni$_{0.6}$Co$_{0.4}$ alloy is still very poor (about 20 mAh/g), demonstrating that cobalt addition does not alter the discharge capacity of crystalline Mg-Ni alloys. All the discharge capacities are negligibly small in comparison with their theoretical discharge capacity. Thus, the crystalline Mg$_2$Ni-type alloy is not suitable for use as a rechargeable anode material in an alkaline solution at room temperature.

A nanocrystalline Mg$_2$Ni alloy with an average grain size of about 13 nm can be fabricated by mechanical milling induction melted (IM) crystalline Mg$_2$Ni alloy. The initial discharge capacity of the nanocrystalline Mg$_2$Ni alloy is about 111 mAh/g, which is much higher than that of the IM crystalline Mg$_2$Ni alloy (only 18 mAh/g). Like the nanocrystalline FeTi alloy, the discharge capacity of nanocrystalline Mg$_2$Ni alloy is only 10 % of the calculated theoretical electrochemical capacity of Mg$_2$Ni alloy.
All the mechanically alloyed sintered Mg-Ni and Mg-Ni-Co alloy electrodes studied have completely or mainly amorphous structures, showing very high initial discharge capacities (around 300 mAh/g) compared with their crystalline counterparts. The addition of a small amount of Co to amorphous Mg-Ni alloy can increase its initial discharge capacity and cycle life. Increasing the Co addition in the amorphous Mg-Ni alloy results in a lower initial discharge capacity but a slightly better cycle life. All the results indicate that the amorphous structure is a key factor in order to obtain high initial discharge capacities for Mg-based alloy electrodes. In the mechanical alloying process, the ball milling parameters have significant effects on the discharge capacities of the Mg-based alloy electrodes. Increasing the ball milling time and the ratio of ball to sample weight are effective methods to further improve the discharge capacity for Mg-based alloy electrodes.

Assuming that the composition of amorphous alloys can be obtained in a certain range, non-stoichiometric uniform amorphous MgNi$_x$V$_y$ alloys ($x = 1, 1.28; y = 0, 0.1, 0.2, 0.4$) have been firstly synthesised by mechanically alloying induction melting Mg$_2$Ni alloy, Ni and V powders based on a stoichiometric amorphous MgNi alloy component. The results indicate that non-stoichiometric amorphous Mg-based alloys can be obtained by either increasing the Ni content or adding a range of vanadium or both, through the mechanical alloying method. The non-stoichiometric Mg-based alloy electrodes studied have shown improved initial discharge capacities (more than 400 mAh/g) compared with the stoichiometric amorphous MgNi alloy.
Abstract

(about 330 mAh/g). These results describe a novel method of achieving better Mg-based alloy electrodes with high discharge capacities. The method enables a larger composition range to be achieved with a range of different elemental additions.

Finally, it is demonstrated that the initial discharge capacity of amorphous Mg-based alloy electrodes is higher than that of rare-earth system and zirconium-based Laves phase alloys in commercial batteries. Thus, Mg-based hydrogen storage alloys are very promising negative materials for the Ni-MH battery. Also the results have shown that FeTi-type alloys having improved discharge capacity and good cycle life can be obtained by achieving an amorphous or nanocrystalline structure.
I would like to express my deep appreciation and gratitude to my supervisors, Professor H.K. Liu, Professor S.X. Dou, and Professor D.H. Bradhurst, for their academic guidance, constant encouragement and support throughout the course of this thesis work.

Sincerely thank the Head of the Department of Materials Engineering, Professor D. Dunne, for his kind permission to use the facilities. Special thanks are made to Mr. G. Li and Mrs. B. Allen for their great help.

Many thanks go to Mr. G.X. Wang, Dr. S. Zhong, Dr. M. Ionescu, Mr. N. Mackie, Dr. J. Chen, Dr. X.L. Wang, Dr. Y. Pei, Mr. D. Milliken, Dr. D. Wexler, Dr. Y.C. Guo, Dr. H.J. Li, Mr. C. Rossi, Mr. K. Uprety, Mr. X.K. Fu and all the members at the Institute for Superconducting and Electronic Materials, and to all the technicians at the Department of Materials Engineering. Thanks are also due to Mrs. R. Cambareri, and Mrs. J. De Mestre for their help in official matters.

I wish to thank Mr. A. Kaneko in Santoku Metal Industry Co., Japan for the preparation of the Mg$_2$Ni alloy by induction melting.
Acknowledgements

Thanks also go to the Australian DETYA for providing the author the OPRS scholarship, and to the University of Wollongong for providing the UPA scholarship.

Finally, I would like specially to express my deep gratitude to my wife, Z.H. Lin, and my daughter, J.Y. Sun, for their love, understanding, patience and constant support during these years, especially to my wife who sacrificed much and encouraged me greatly throughout my studies. My grateful acknowledgement is also made to my parents, brothers, parents-in-law, sisters-in-law, for their encouragement and support.
LIST OF SYMBOLS AND ABBREVIATIONS

\(a\) activity

\(d\) average grain size (diameter)

\(\gamma\) fugacity coefficient

\(B\) average grain boundary thickness

\(C_{th}\) theoretical electrochemical discharge capacity

\(E^{o}\) standard potential

\(F\) Faraday constant

\(F_r\) volume fraction of nanocrystalline materials

\(G\) Gibbs free energy

\(G_a\) Gibbs free energy of amorphous phase

\(G_c\) Gibbs free energy of metal mixture

\(G_i\) Gibbs free energy of intermetallic compound

\(M\) molarity

\(or\) metal

\(R\) gas constant

\(or\) resistance

\(T\) absolute temperature

\(W\) Warburg impedance
### List of Symbols and Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM</td>
<td>ball milling</td>
</tr>
<tr>
<td>DTA</td>
<td>differential thermal analysis</td>
</tr>
<tr>
<td>EDS</td>
<td>energy dispersive spectroscopy</td>
</tr>
<tr>
<td>EIS</td>
<td>electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>EXAFS</td>
<td>extended X-ray absorption fine structure</td>
</tr>
<tr>
<td>GFA</td>
<td>glass-forming ability</td>
</tr>
<tr>
<td>GFR</td>
<td>glass-forming composition range</td>
</tr>
<tr>
<td>HREM</td>
<td>high resolution electron microscopy</td>
</tr>
<tr>
<td>IM</td>
<td>induction melting</td>
</tr>
<tr>
<td>MA</td>
<td>mechanical alloying</td>
</tr>
<tr>
<td>MM</td>
<td>mechanical milling</td>
</tr>
<tr>
<td>MH</td>
<td>metal hydride</td>
</tr>
<tr>
<td>Mm</td>
<td>Misch metal</td>
</tr>
<tr>
<td>RDF</td>
<td>radial distribution function</td>
</tr>
<tr>
<td>RE</td>
<td>rare earth metal</td>
</tr>
<tr>
<td>RQ</td>
<td>rapid quenching</td>
</tr>
<tr>
<td>RSP</td>
<td>rapid solidification processing</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SSA</td>
<td>solid state amorphisation</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TG</td>
<td>thermogravimetric analysis</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
CONTENTS

DECLARATION........................................................................................................i

ABSTRACT...........................................................................................................ii

ACKNOWLEDGEMENTS......................................................................................viii

LIST OF SYMBOLS AND ABBREVIATIONS.......................................................x

CONTENTS .........................................................................................................xii

CHAPTER 1  INTRODUCTION..............................................................................1

CHAPTER 2  LITERATURE REVIEW.................................................................7

2.1 Amorphous metals and alloys.................................................................7

2.1.1 Introduction..............................................................................................7

2.1.2 Methods for achieving amorphous alloys..........................................8

2.1.2.1 Rapid quenching (RQ) from melt.......................................................8

2.1.2.2 Mechanical alloying (MA) and mechanical milling (MM)........10

2.1.2.3 Other methods..................................................................................10

2.1.3 Formation of amorphous alloys..........................................................10

2.1.3.1 Criteria for formation of amorphous phase prepared by RQ....10

2.1.3.2 Composition of amorphous phase prepared by RQ.................11
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1.4</td>
<td>Structure characteristics of amorphous alloys</td>
<td>13</td>
</tr>
<tr>
<td>2.1.4.1</td>
<td>Structure</td>
<td>13</td>
</tr>
<tr>
<td>2.1.4.2</td>
<td>Crystallisation</td>
<td>13</td>
</tr>
<tr>
<td>2.2</td>
<td>Amorphous alloys prepared by mechanical alloying/mechanical milling</td>
<td>14</td>
</tr>
<tr>
<td>2.2.1</td>
<td>Introduction</td>
<td>14</td>
</tr>
<tr>
<td>2.2.2</td>
<td>High energy ball mills and milling parameters</td>
<td>15</td>
</tr>
<tr>
<td>2.2.3</td>
<td>Formation of amorphous alloys by MA/MM</td>
<td>16</td>
</tr>
<tr>
<td>2.2.3.1</td>
<td>Thermodynamics and kinetics</td>
<td>16</td>
</tr>
<tr>
<td>2.2.3.2</td>
<td>Glass forming ranges of amorphous alloys by MA/MM</td>
<td>19</td>
</tr>
<tr>
<td>2.2.4</td>
<td>Structure of amorphous alloys prepared by MA/MM</td>
<td>23</td>
</tr>
<tr>
<td>2.3</td>
<td>Nanocrystalline materials</td>
<td>25</td>
</tr>
<tr>
<td>2.3.1</td>
<td>Introduction</td>
<td>25</td>
</tr>
<tr>
<td>2.3.2</td>
<td>Structure of nanocrystalline materials</td>
<td>26</td>
</tr>
<tr>
<td>2.3.3</td>
<td>Synthesis and processing of nanocrystalline materials</td>
<td>29</td>
</tr>
<tr>
<td>2.3.3.1</td>
<td>Gas condensation technique</td>
<td>31</td>
</tr>
<tr>
<td>2.3.3.2</td>
<td>Mechanical milling/alloying</td>
<td>33</td>
</tr>
<tr>
<td>2.4</td>
<td>Hydrogen storage alloys</td>
<td>34</td>
</tr>
<tr>
<td>2.4.1</td>
<td>Introduction</td>
<td>34</td>
</tr>
<tr>
<td>2.4.2</td>
<td>Types of hydrogen storage alloys</td>
<td>35</td>
</tr>
<tr>
<td>2.4.3</td>
<td>Thermodynamics</td>
<td>38</td>
</tr>
<tr>
<td>2.4.4</td>
<td>FeTi-type hydrogen storage alloys</td>
<td>41</td>
</tr>
<tr>
<td>2.4.4.1</td>
<td>Formation of FeTi hydrides</td>
<td>41</td>
</tr>
<tr>
<td>Section</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>2.4.4.2 Activation of FeTi alloy</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>2.4.4.3 Amorphous and nanocrystalline FeTi alloys</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>2.4.5 Magnesium-based hydrogen storage alloys</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>2.4.5.1 Introduction</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>2.4.5.2 Mg-Ni hydrogen storage alloys</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>2.4.5.3 Substitution of Mg$_2$Ni alloys</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>2.4.5.4 Amorphous and nanocrystalline Mg-Ni alloys</td>
<td>57</td>
<td></td>
</tr>
<tr>
<td>2.5 Metal-hydride electrodes for Ni-MH batteries</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>2.5.1 Introduction</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>2.5.2 Principles of Ni-MH batteries</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td>2.5.2.1 Charge-discharge mechanism</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>2.5.2.2 Overcharge and overdischarge reactions</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>2.5.3 Equilibrium potential of metal hydride electrodes (Electrochemical P-C isotherms)</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>2.5.4 Kinetic properties of metal hydride electrodes</td>
<td>69</td>
<td></td>
</tr>
<tr>
<td>2.5.5 Electrochemical impedance analysis of metal hydride electrodes</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td>2.6 Summary</td>
<td>73</td>
<td></td>
</tr>
<tr>
<td>CHAPTER 3 EXPERIMENTAL DETAILS</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>3.1 Metals and chemicals</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>3.2 Preparation of alloys</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>3.2.1 Fe-Ti Alloys</td>
<td>75</td>
<td></td>
</tr>
</tbody>
</table>
3.2.2 Magnesium-based alloys.................................................................77
  3.2.2.1 Sintered Mg-based alloys.........................................................77
  3.2.2.2 Induction melted Mg$_2$Ni alloy................................................77

3.3 Mechanical milling and alloying....................................................78
  3.3.1 Ball milled Fe-Ti alloys............................................................79
  3.3.2 Ball milled sintered Mg-based alloys.........................................79
  3.3.3 Ball milling of induction melted Mg-based alloys.............................80

3.4 Electrode fabrication......................................................................81

3.5 Charge/discharge properties..........................................................82

3.6 Physical analyses.............................................................................83
  3.6.1 X-ray diffraction and thermal analysis measurements..................83
  3.6.2 Particle size, morphology and microstructural examination.........84

CHAPTER 4 FORMATION AND ELECTRODE PROPERTIES OF
AMORPHOUS AND NANOCRYSTALLINE FeTi ALLOYS.........................85

4.1 Introduction.....................................................................................85

4.2 Formation of nanocrystalline and amorphous FeTi alloys................87
  4.2.1 FeTi alloy by mechanical milling.............................................87
  4.2.2 FeTi alloy by mechanical alloying...........................................92

4.3 Particle distribution and morphologies of FeTi alloys....................94

4.4 Effect of small amounts of oxygen on the mechanical alloying........98
CHAPTER 5  Mg-Ni ALLOY ELECTRODES PREPARED BY SINTERING AND SUBSEQUENT BALL MILLING WITH NICKEL POWDERS...114

5.1 Introduction...114

5.2 Effect of sintering process on properties of Mg2Ni alloy electrodes...116
   5.2.1 Structures of sintered Mg2Ni alloys before and after ball milling...116
   5.2.2 Discharge capacities of ball milled sintering Mg-Ni alloy electrodes...121

5.3 Effects of ball milling time on discharge capacity...122

5.4 Effects of ratio of ball to sample weight during ball milling...123

5.5 Discharge performance of ball milled Mg-Ni alloys...128

5.6 Conclusions...132

CHAPTER 6 EFFECT OF Co ADDITION ON Mg-Ni ALLOY ELECTRODES PREPARED BY SINTERING FOLLOWED BY BALL MILLING...134

6.1 Introduction...134

6.2 Preparation and structure of the alloys...136
Contents

6.3 Differential thermal analysis ......................................................... 137
6.4 SEM morphologies and X-ray mapping analysis ................................ 139
6.5 Electrochemical discharge ability of the alloys .................................. 144
6.6 Conclusions .............................................................................. 149

CHAPTER 7 SYNTHESIS AND ELECTRODE PROPERTIES OF NON-
STOICHIOMETRIC AMORPHOUS Mg-BASED ALLOYS MADE BY BALL
MILLING ....................................................................................... 151

7.1 Introduction ............................................................................ 151
7.2 Nanocrystalline Mg$_2$Ni alloy .................................................... 153
7.3 Amorphous and non-stoichiometric amorphous Mg-Ni alloys .......... 159
7.4 Non-stoichiometric amorphous Mg-Ni-V alloys .............................. 163
    7.4.1 Structure and stability .......................................................... 163
    7.4.2 SEM morphologies and X-ray mapping analysis .................... 165
    7.4.3 Discharge capacities of non-stoichiometric Mg-Ni-V alloys ...... 170
7.5 Conclusions ............................................................................ 175

CHAPTER 8 SUMMARY .................................................................... 177

REFERENCES .................................................................................. 183

PUBLICATIONS ............................................................................ 205
CHAPTER 1 INTRODUCTION

Since the 1980s, the rechargeable nickel-metal hydride (Ni-MH) battery employing a hydrogen storage alloy as its negative electrode material has been one of the most promising power sources for many important applications such as mobile phones, lap-top computers and electric vehicles. This is because the nickel-metal hydride battery has the following attractive features: (1) stores hydrogen in the solid hydride phase; (2) high energy density; (3) high power; (4) long life; (5) tolerance to overcharge and overdischarge; (6) quick charge-discharge capability; (7) no memory effect; and (8) environmentally friendly properties [1,2].

As the anode material in a Ni-MH battery, the properties of the hydrogen storage alloy play a key role in the performance of the battery. Of all the hydrogen storage alloys widely studied previously, the rare-earth system alloys (AB5-type) and zirconium-based Laves phase alloys (AB2-type) have been used for the commercial production of Ni-MH batteries [1,2].

For most commercial Ni-MH batteries, their negative electrodes are of Mm-based alloys (Mm: misch metal) which have low theoretical discharge capacities (e.g.,
LaNi$_5$ alloy has a theoretical discharge capacity of only about 370 mAh/g). The capacities of the negative alloy electrodes restrict further improvement of the capacities of Ni-MH batteries.

On the other hand, the costs of rare earth, zirconium, vanadium, titanium and the other main elements in rare earth system alloys (AB$_5$-type) and zirconium-based Laves phase alloys (AB$_2$-type) are so high that the large-scale application of the Ni-MH battery is limited. Thus, the search for high discharge capacity, light weight and economical anode materials for the Ni-MH battery becomes the most important step for the large-scale application of this battery.

Mg-based hydrogen storage alloys [3,4] are promising energy conversion and storage materials because they possess very high theoretical hydrogen storage capacity, e.g., the theoretical discharge capacity of Mg$_2$Ni alloy is approximately 1000 mAh/g. Also magnesium is abundant in nature, light in weight and relatively low in cost. FeTi-type hydrogen storage alloys are also prime candidates for hydrogen storage systems [5,6] and have high theoretical discharge capacities of about 500 mAh/g. FeTi-type alloys are also the cheapest of the promising hydrogen conversion and storage alloys. However, crystalline Mg-based hydrogen storage alloys have very poor discharge capacities as Ni-MH electrodes [7,8] because of their slow hydriding/dehydriding kinetics at ambient temperature.
It is well known that amorphous and nanocrystalline metals and alloys are often novel materials which attract the attention of materials scientists because of their excellent properties compared with their crystalline counterparts [9-13]. Thus, there appear to be some possibilities to achieve high discharge capacities for amorphous and nanocrystalline Mg-based and FeTi-type alloys. These are the reasons for this study, which is motivated by the need to explore the electrode properties of novel amorphous and nanocrystalline Mg-based and FeTi-type hydrogen storage alloys prepared by mechanical milling (MM) and mechanical alloying (MA) using a high energy ball milling method.

The preparation methods, formation principles, structure, and unique properties of amorphous and nanocrystalline metals and alloys are reviewed in Chapter 2, in particular the methods of mechanical milling and mechanical alloying. The formation, characterisation, and applications of hydrogen storage alloys are also summarised in Chapter 2. Finally, the basic principles and electrochemical reaction of metal-hydride electrodes and Ni-MH batteries are also reviewed.

Chapter 3 records the materials including the metals and chemicals, which were used in this study, and describes the experimental methods and the procedure used to obtain the research results.
The investigations of the formation and electrode properties of amorphous and nanocrystalline FeTi alloys are described in Chapter 4. A nanocrystalline FeTi alloy with average grain size of about 8 nm was produced by mechanically milling the vacuum arc melted FeTi alloy. An amorphous FeTi alloy with particle size about 10 μm and specific surface area 2.49 m²g⁻¹ was mechanically alloyed by milling Fe and Ti powders using a planetary ball mill. Both amorphous and nanocrystalline FeTi alloys exhibited higher discharge capacities as metal hydride electrodes in comparison with crystalline FeTi alloy.

Although conventional metallurgical techniques can be used to manufacture Mg-Ni alloy electrodes, MM and MA methods improve the discharge capacities of the electrodes significantly [14-17]. Chapter 5 describes an investigation of the effects of the preparation parameters of the MM and MA methods on the discharge capacities and cycle lives of Mg-Ni alloys. Mg-Ni alloy electrodes were manufactured by a powder metallurgical technique (PMT) followed by ball milling (BM) with Ni powders. The discharge capacities of the electrodes were significantly improved by ball milling. An amorphous structure is a key factor in order to achieve high discharge capacities. Increasing the ball milling time and the ratio of ball to sample weight are also effective methods to further improve the discharge capacity for Mg-Ni alloys.
Cobalt is a very important element in AB$_5$-type hydride electrodes. It can greatly improve the cycle life of AB$_5$-type hydride electrodes [18-21], especially commercialised AB$_5$-type electrodes. In Chapter 6, an investigation is described of the effect of Co addition on Mg-Ni alloy hydride electrodes prepared in two different ways: 1) by ball milling the Mg$_2$Ni alloy prepared by sintering a mixture of Mg and Ni powders with Co powders; and 2) by ball milling Mg$_2$Ni$_{0.6}$Co$_{0.4}$ alloy prepared by sintering a mixture of Mg, Ni and Co powders with Ni powder. As a negative electrode, a Mg$_2$Ni$_{0.6}$Co$_{0.4}$ alloy ball-milled with Ni powder for 60 hours possesses the highest discharge capacity. The Mg$_2$Ni alloy ball-milled with Ni powder has a relatively low initial discharge capacity. However, both of these initial discharge capacities are much higher than that of the Mg$_2$Ni alloy ball-milled with Co powder.

In Chapter 7, the preparation and properties of non-stoichiometric amorphous alloys are described. Non-stoichiometric amorphous Mg-Ni and Mg-Ni-V alloys were synthesised by ball milling induction melted (IM) crystalline Mg$_2$Ni alloy with Ni and/or V powders. All the non-stoichiometric amorphous Mg-based alloys result in Mg-based alloy electrodes with very high discharge capacities by comparison with crystalline Mg$_2$Ni alloys. The results indicate that non-stoichiometric amorphous Mg-based alloys can be obtained either by increasing the Ni content, adding a range of other elements or both, using a ball milling method. The non-stoichiometric Mg-based alloy electrodes studied have shown improved initial discharge capacities compared with the stoichiometric amorphous MgNi alloy. These results describe a
novel method of achieving better Mg-based alloy electrodes with high discharge capacities and improved cycle life. The method enables a larger composition range to be achieved with a range of different elemental additions.

The main research results of the present study are summarised in Chapter 8, followed by the list of references. Finally, a list is included of the author's publications completed during the course of this Ph.D. research.
2.1 Amorphous metals and alloys

2.1.1 Introduction

It has been well known since the 1960s that amorphous alloys can be made by rapid quenching (RQ) from the liquid and the vapour phase [22-30]. A large number of investigations have shown that amorphous metals and alloys prepared by rapid solidification processing (RSP) have the features of new alloy compositions and new atomic configurations which are totally different from those of crystalline alloys. These features enable various kinds of characteristics to be achieved such as excellent mechanical properties, useful physical properties and unique chemical properties [10,11,31-34], which have not been obtained for conventional crystalline alloys. Recently, solid state amorphisation (SSA) by mechanical alloying (MA) and mechanical milling (MM) has become the most effective method to obtain amorphous alloys [35-46]. In this section (2.1), the preparation methods, formation and structure of amorphous metals and alloys are briefly reviewed. In section 2.2, solid state amorphisation by MM/MA, which was used for the preparation of amorphous hydrogen storage alloys in this study, is discussed in detail.
2.1.2 Methods for achieving amorphous alloys

2.1.2.1 Rapid quenching (RQ) from melt

This is one of the most commonly used methods in preparing amorphous alloys. Amorphous alloys formed by RQ are also named metallic glasses because they are formed when liquids are cooled but fail to crystallise and instead continuously and uniformly congeal into solids. The basic principle of obtaining amorphous alloys by RQ from the melt is that the liquid must be converted very rapidly from a droplet or jet into a thin layer or wire in contact with a highly thermally conductive metal to produce thin splats, ribbons or wires. The cooling rates achieved by some rapid quenching devices are about $10^6 \, ^\circ\text{C}/s$.

In 1960, Duwez and his collaborators were successful in making a continuous metastable series of Cu-Ag alloys without any two-phase region. In the same year they also discovered the first amorphous alloys made by rapid quenching [22,23]. Later on, the methods of making continuous rapidly quenched ribbons were invented: single-roller melt-spinning [47], twin-roller melt-spinning [48,49], melt-extraction [50], and the drop-smasher [51,52]. Figure 2.1 shows the principles of these four methods. Furthermore, a number of different methods have been used for the production of RQ wires, such as, in-rotating-water splat-processing [54,55], which is
a variant of melt-spinning: the alloy jet impinges on the inner surface of a rotating vessel containing water held in an annular shape by a centrifugal force.

Figure 2.1  Principal methods of rapid quenching from the melt: (a) drop-smasher; (b) melt-spinning; (c) pendant-drop melt-extraction; (d) twin-roller quenching device [53].
2.1.2.2 *Mechanical alloying (MA) and mechanical milling (MM)*

This is another commonly used method in preparing amorphous alloys, which is promising for the production of amorphous alloys on a large scale. (see section 2.2 for details).

2.1.2.3 *Other methods*

Evaporation deposition [56] and sputtering deposition [57] were used to make various amorphous alloys with more alloy compositions and wider composition ranges than liquid-quenching. Amorphisation by irradiation, such as ion-implantation [58,59], has also been achieved. Moreover, a laser treatment method has been employed to make a layered amorphous alloy [60]. Also, amorphous chromium can be electrodeposited from chromic acid solution with additives [61,62].

2.1.3 *Formation of amorphous alloys by RQ*

2.1.3.1 *Criteria for formation of amorphous phase prepared by RQ*

In the formation of amorphous alloys prepared by the RQ, the glass-forming ability (GFA) is measured by the critical cooling rate, which is necessary to turn a melt into a glass, avoiding crystallisation. For rapid solidification processes, such as melt-spinning, the critical cooling rate should be approximately up to $10^7 \text{C/s}$. Then the alloy can be vitrified by such a process [36].
2.1.3.2 Composition of amorphous phase prepared by RQ

Amorphous alloys can be achieved in certain ranges of compositions in many alloy systems. Within a given alloy system, the glass-forming composition range (GFR) for an alloy system depends on the production method and conditions. Table 2.1 lists some examples of compositions which can be made amorphous by standard techniques such as melt-spinning.

The glass-forming alloys may be classified as: late transition metal-metalloids, early transition metal-metalloid, early transition metal-late transition metal, aluminium-based, lanthanide-based, alkaline-earth and actinide-based alloys and so on.
Table 2.1  Examples of composition ranges of glass-forming alloys [36,63,64]

<table>
<thead>
<tr>
<th>Type</th>
<th>Alloy</th>
<th>Glass-forming range (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Late transition metal-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>metalloid</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe\textsubscript{100-x}B\textsubscript{x}</td>
<td>(x=12-25)</td>
</tr>
<tr>
<td></td>
<td>Ni\textsubscript{100-x}B\textsubscript{x}</td>
<td>(x=17-18.5, 31-41)</td>
</tr>
<tr>
<td></td>
<td>Pd\textsubscript{100-x}Si\textsubscript{x}</td>
<td>(x=14-22)</td>
</tr>
<tr>
<td></td>
<td>Pt\textsubscript{100-x}Sb\textsubscript{x}</td>
<td>(x=34-36.5)</td>
</tr>
<tr>
<td></td>
<td>Co\textsubscript{70.5}Fe\textsubscript{4.5}Si\textsubscript{13}B\textsubscript{10}, Fe\textsubscript{80}P\textsubscript{13}C\textsubscript{7}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe\textsubscript{40}Ni\textsubscript{40}B\textsubscript{20}, Pd\textsubscript{40}Ni\textsubscript{40}P\textsubscript{20}</td>
<td></td>
</tr>
<tr>
<td>Early transition metal-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>metalloid</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ti\textsubscript{100-x}Si\textsubscript{x}</td>
<td>(x=15-20)</td>
</tr>
<tr>
<td></td>
<td>Re\textsubscript{65}Si\textsubscript{35}, W\textsubscript{80}Ni\textsubscript{20}, W\textsubscript{60}Ir\textsubscript{20}B\textsubscript{20}</td>
<td></td>
</tr>
<tr>
<td>Early transition metal-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Late transition metal</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cu\textsubscript{100-x}Zr\textsubscript{x}</td>
<td>(x=25-60)</td>
</tr>
<tr>
<td></td>
<td>Fe\textsubscript{100-x}Zr\textsubscript{x}</td>
<td>(x=9, 72, 76)</td>
</tr>
<tr>
<td></td>
<td>Nb\textsubscript{100-x}Ni\textsubscript{x}</td>
<td>(x=40-70)</td>
</tr>
<tr>
<td></td>
<td>Ni\textsubscript{100-x}Zr\textsubscript{x}</td>
<td>(x=10-20, 33-80)</td>
</tr>
<tr>
<td></td>
<td>Ta\textsubscript{100-x}Ni\textsubscript{x}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ta\textsubscript{55}Rh\textsubscript{45}, Zr\textsubscript{60}Ni\textsubscript{25}Al\textsubscript{15}</td>
<td></td>
</tr>
<tr>
<td>Aluminium-based</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Al\textsubscript{100-x}La\textsubscript{x}</td>
<td>(x=10, 50-80)</td>
</tr>
<tr>
<td></td>
<td>Al\textsubscript{75}Cu\textsubscript{15}V\textsubscript{10}, Al\textsubscript{70}Ni\textsubscript{15}Si\textsubscript{15}, Al\textsubscript{80}Ni\textsubscript{10}Y\textsubscript{10}, Al\textsubscript{85}Ni\textsubscript{5}Y\textsubscript{5}Co\textsubscript{2}</td>
<td></td>
</tr>
<tr>
<td>Lanthanide-based</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>La\textsubscript{100-x}Al\textsubscript{x}</td>
<td>(x=18-34)</td>
</tr>
<tr>
<td></td>
<td>La\textsubscript{100-x}Au\textsubscript{x}</td>
<td>(x=18-26)</td>
</tr>
<tr>
<td></td>
<td>La\textsubscript{100-x}Ge\textsubscript{x}</td>
<td>(x=17-22)</td>
</tr>
<tr>
<td></td>
<td>La\textsubscript{55}Al\textsubscript{25}Ni\textsubscript{20}</td>
<td></td>
</tr>
<tr>
<td>Alkaline-earth</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mg\textsubscript{100-x}Zn\textsubscript{x}</td>
<td>(x=25-32)</td>
</tr>
<tr>
<td></td>
<td>Ca\textsubscript{100-x}Al\textsubscript{x}</td>
<td>(x=12.5-47.5)</td>
</tr>
<tr>
<td></td>
<td>Mg\textsubscript{65}Cu\textsubscript{25}Y\textsubscript{10}, Be\textsubscript{40}Zr\textsubscript{10}Ti\textsubscript{50}</td>
<td></td>
</tr>
<tr>
<td>Actinide-based</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>U\textsubscript{100-x}Co\textsubscript{x}</td>
<td>(x=24-40)</td>
</tr>
</tbody>
</table>
2.1.4 Structure characteristics of amorphous alloys

2.1.4.1 Structure

In a single-phase solid alloy the distinctive feature of the amorphous state is that it has no microstructure. There is no crystal lattice in which to have defects such as grain boundaries and dislocations. But it has a structure in the way its atoms are arranged, and this structure is important in determining its properties. Some metallic glass structural models have been established, such as the dense random-packed hard sphere model [65], local-coordination model [66,67] and so on.

For a metallic glass, however, the structure can be described only on a statistical basis because there are no unit cells. Almost all the analysis of metallic glass structure has been based on a radial distribution function (RDF) which is obtained by neutron and X-ray scattering experiments [68]. The research results indicate the structure of metallic glasses is similar to the topological and chemical composition short-range order [68, 69].

2.1.4.2 Crystallisation

Since the amorphous state is essentially a metastable one, it inherently possesses the possibility of transforming into a more stable crystalline state. However, the most promising properties of metallic glasses, e.g., the excellent magnetic behaviour or the
high hardness and strength combined with ductility and high corrosion resistance, have been found to deteriorate drastically during crystallisation. Understanding the micro-mechanisms of crystallisation to impede or control crystallisation is therefore a prerequisite for most applications, as the stability against crystallisation determines their effective work limits. Any of the property changes of amorphous alloys may be used to monitor their crystallisation, but thermal analyses are the most commonly used methods in determining the crystallisation temperatures of amorphous alloys [70, 71].

2.2 Amorphous alloys prepared by MA/MM

2.2.1 Introduction

Mechanical alloying (MA) is a high energy ball milling technique, in which elemental blends are milled to achieve alloying at the atomic level. In addition to elemental blends, pre-alloyed powders and ceramics, such as oxides, nitrides, etc., can also be used to produce alloys and composites by this technique. In 1970, Benjamin [72] and his group developed this technique at the Inco Paul D. Merica Research Laboratory as a part of the programme to produce oxide dispersion strengthened Ni-base superalloys for gas turbine applications. In 1983, Koch et al. [35] from Oak Ridge National Laboratory had done such a breakthrough work that MA has become a field of research all over the world in many laboratories. In this seminal work, Koch et al. reported the formation of Ni₆₀Nb₄₀ amorphous phase by
MA, starting with elemental Ni and Nb powders, using a Spex 8000 shaker mill. Two years before this report, Yermakov and his group demonstrated the amorphisation of several Y-Co [73] intermetallic compounds (i.e. YCo$_3$, Y$_2$Co$_5$ and Y$_2$Co$_{17}$) and Gd-Co intermetallic compounds [74] by milling in a planetary mill. This also opened up a new area which is now commonly referred to as amorphisation by "mechanical milling" (MM) as opposed to amorphisation of dissimilar powders, MA, which involves material transfer. The most widely studied solid state amorphisation technique is mechanical alloying.

Even though Benjimin developed the MA technique, almost all the stable and metastable structures produced by rapid solidification processing (RSP) have been realised by MA. In addition, extended solid solution and amorphous phase formation in the case of liquid immiscible systems [75,76] have been observed by MA which are difficult to obtain by RSP, making the MA process superior in many respects.

### 2.2.2 High energy ball mills and milling parameters

Mechanical alloying/milling is usually carried out in high energy mills such as vibratory mills [35] (Spex 8000 mixer/mill), planetary mills [9,73,74] (Fritsch and Retsch mills), and attritor mills [78] (Szegvari attritor). The energy transfer to the powder particles in these mills takes place by a shearing action or impact of the high velocity balls with the powder. In addition to the above mills, several other mills such as the Anutech uniball mill [79,80], rod mill [81], modified rod mill [82] and
other specially designed mills [83] have been used for mechanical alloying/milling. Among the laboratory mills, the Spex 8000 shaker mill and Fritsch Pulverisette are the mostly widely used.

During MA/MM processes, the kinetics of alloying and other phase transformations depend on the energy transferred to the powder from the balls. The energy transfer is governed by many parameters such as the type of mill, milling speed, type and size of the balls, ball/powder weight ratio, dry or wet milling, atmosphere in the mill and the duration of milling.

2.2.3 Formation of amorphous alloys by MA/MM

2.2.3.1 Thermodynamics and kinetics

The ball milling sequence consists primarily of collision, shearing, wearing and cold-welding. The mechanical alloying process is characterised by repeated cold-welding and fracturing of the powder particles trapped between the colliding balls during milling. The mechanical milling process is mainly repeated fracture due to impact stress and shear stress during milling.
Figure 2.2  Schematic free energy changes for MA and MM [84].

The MA process synthesises amorphous alloy powders by reacting elemental crystalline powders through solid state chemical diffusion, being often accompanied by the negative heat of formation. In the MM process, however, crystalline alloy or compound powders are transformed into amorphous solid powders by destroying the periodic long-range order of atomic arrangement without any changes of chemical composition due to long distance solid-state diffusion. It is usually accompanied by a positive heat of formation. As shown in Figure 2.2, MA is a chemical reaction of \( mA \) (crystal) + \( nB \) (crystal) \( \rightarrow A_mB_n \) (amorphous) proceeding from a higher free
energy state to a lower one, providing the continuous evolution in the local chemical composition through long-range solid state chemical diffusion. In MM, a phase transformation of $A_mB_n$ (crystal) $\rightarrow$ $A_mB_n$ (amorphous) going from the ground state to an excited state is caused by destroying the long-range order of atomic arrangement, without any changes of chemical composition due to long distance solid-state diffusion [84].

For any transformation, a driving force is required. The solid state amorphous transformation can be considered as an intermediate stage of transformation of a metastable crystalline state to an equilibrium crystalline state as shown in Figure 2.3 [37]. The thermodynamic condition for SSA by MA is that the free energy of the amorphous phase must be lower than that of the initial metal mixture and the terminal intermetallic compound in that system ($G_a < G_c$). For the amorphous phase to form in preference to the more stable intermetallic compounds ($G_i < G_a$), the time scale for the formation of the former, $\tau_{c-a}$, should be much shorter when compared to that of the latter, $\tau_{c-i}$. Moreover, as the amorphous phase is metastable, the time scale $\tau_{a-i}$ should be much longer than $\tau_{c-a}$ so that the amorphous phase formation can be observed. Thus, the kinetic conditions for SSA are that $\tau_{c-a} \ll \tau_{c-i}$ and $\tau_{c-a} \ll \tau_{a-i}$.
2.2.3.2 Glass forming ranges of amorphous alloys by MA/MM

Amorphous phase formation has been most widely investigated by MA [41]. During MA, the XRD peaks of the pure metals normally become gradually broader and less intense; finally, the composite becomes amorphous. Eckert et al. [84] have reported...
different glass forming composition ranges (GFRs) at different milling intensities in a planetary mill in the Ni-Zr system. In the Ni-Zr system, however, Weeber et al. [85,86] found a new type amorphisation reaction in which crystalline intermetallic compounds form as intermediate products when a planetary mill is used for MA. Mechanical alloying in a vibratory mill results in direct formation of an amorphous phase without any intermediate stage. Oleszak et al. [87] reported that prolonged milling times could result in the crystallisation of the amorphous phase formed by MA at shorter milling times. Recently, in MA of Co-Ti alloys, it has been observed a cyclic amorphous ↔ crystalline transformation on continuous milling for the Co_{50}Ti_{50} composition [88]. Thus, the formation of amorphous phase by MA/MM is a very complicated process which not only depends on the alloy system, but is also affected by many ball milling parameters.

Amorphous phase formation by MA has been observed in a large number of binary and ternary alloy systems over wide composition ranges. Table 2.2 lists some examples of amorphous phase formed by mechanical alloying pure metal mixtures.
Table 2.2  Some examples of amorphous phase formed by mechanical alloying pure metal mixtures

<table>
<thead>
<tr>
<th>System</th>
<th>Glass forming composition range (at.%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hf-Cu</td>
<td>30-70</td>
<td>89</td>
</tr>
<tr>
<td>Nb-Ge</td>
<td>25-27</td>
<td>90</td>
</tr>
<tr>
<td>Nb-Ni</td>
<td>20-80</td>
<td>91,92</td>
</tr>
<tr>
<td>Ti-Cu</td>
<td>10-87</td>
<td>93</td>
</tr>
<tr>
<td>Ti-Ni</td>
<td>10-70</td>
<td>94</td>
</tr>
<tr>
<td>Ti-Si</td>
<td>20-60</td>
<td>95</td>
</tr>
<tr>
<td>Zr-Co</td>
<td>27-92</td>
<td>96,97</td>
</tr>
<tr>
<td>Zr-Cu</td>
<td>40-60</td>
<td>97,98</td>
</tr>
<tr>
<td>Zr-Fe</td>
<td>30-78</td>
<td>96,97,99</td>
</tr>
<tr>
<td>Zr-Ni</td>
<td>27-85</td>
<td>96,97,100,101</td>
</tr>
<tr>
<td>Cu-Nb-M</td>
<td>Cu_{44}Nb_{42}M_{14} (M= Ge, Si, Sn)</td>
<td>102</td>
</tr>
<tr>
<td>Fe-Zr-B</td>
<td>(Fe_{75}Zr_{25})<em>{100-x}B</em>{x} (x=0-15)</td>
<td>103</td>
</tr>
<tr>
<td>Ti-Ni-Al</td>
<td>Ti_{50}Ni_{2}Al_{50-x} (x=10, 25)</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td>Ti_{60}Ni_{x}Al_{40-x} (x=15, 20)</td>
<td>104</td>
</tr>
<tr>
<td>Ti-Ni-Cu</td>
<td>Ti_{40}Ni_{60-x}Cu_{x} (x=0-40)</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>Ti_{50}Ni_{50-x}Cu_{x} (x=0-30, 50)</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>Ti_{60}Ni_{40-x}Cu_{x} (x=0-20, 40)</td>
<td>94</td>
</tr>
</tbody>
</table>
Figure 2.4  Glass forming composition ranges achieved by different methods in the Ni-Nb system [92].
The mechanical alloying (MA) technique has many advantages over the rapid solidification processing (RSP) technique. One of them is that the glass forming range of alloys prepared by MA is much wider than that for alloys prepared by RSP. The glass forming range of alloys prepared by RSP is in general restricted to the deep eutectics because of kinetic constraints. For alloys prepared by MA, the glass forming range is centred at the equiatomic composition. Figure 2.4 shows the glass forming range for alloys prepared by MA in the Ni-Nb system compared with other techniques. The figure clearly shows that the glass forming range obtained by MA is much wider in comparison with melt quenching. This gives us many opportunities to manufacture amorphous alloys over a large composition range by MA in which the amorphous alloys cannot be fabricated by RSP.

2.2.4 Structure of amorphous alloys prepared by MA/MM

X-ray diffraction and calorimetry data [35,99,105], and hydrogen-storage characteristics [106] suggest that amorphous powders prepared by MA and amorphous alloys prepared by RSP are structurally quite similar. As shown in Figure 2.5, the total reduced atomic pair radial distribution ($G$), as a function of the interatomic distance ($r$), for amorphous Ni$_{40}$Ti$_{60}$ alloys prepared by MA and by RSP is almost identical, in spite of the large difference between the preparation methods.
Figure 2.5  Total reduced atomic pair radial distribution of amorphous Ni$_{40}$Ti$_{60}$ alloys prepared by MA (solid line) [105] and by RSP (dashed line) [107].
2.3 Nanocrystalline materials

2.3.1 Introduction

Materials scientists have been conducting research investigations for many years to develop materials which are stronger, stiffer and lighter than the existing materials. The high technology industries in the developed countries have encouraged these efforts. As discussed in section 2.1 several novel and non-equilibrium processing methods have been developed during the past few decades to improve the performance of the existing materials: these include rapid solidification from the liquid state, mechanical alloying and milling, plasma processing, and vapour deposition. A central theme in all these methods is to prepare the materials in a highly nonequilibrium (metastable) state through melting, evaporation, irradiation, storing of mechanical energy, application of pressure, etc.[56] The material is then brought to another lower energy metastable state by quenching or related processes when it can exist as a supersaturated solid solution, metastable crystalline or quasicrystalline phase, or even in an amorphous state, avoiding the formation of the crystalline structure.

A novel way of transforming a material to a metastable state is to reduce its grain size to very small values of a few nanometers where the proportion of grain boundaries is equivalent to, or higher than, that of the grains. Materials with such small grain sizes
are referred to as nanocrystalline materials. Nanocrystalline materials are defined as single or multi-phase polycrystals, with a crystal size typically within the range 1-100 nanometers. Because of their ultrafine grain sizes, nanocrystalline materials exhibit a variety of properties that are different and often considerably better than those of conventional coarse-grained polycrystalline materials [9,12]. These include higher catalytic activity [110], more uniform corrosion [111] and superior localised corrosion resistance [112], improved strength/hardness [113-123], enhanced diffusivity [124-127], higher electrical resistivity [128], increased specific heat [129,130], higher thermal expansion coefficient [131,132] and better magnetic properties [133-135] compared with conventional coarse grained materials.

2.3.2 Structure of nanocrystalline materials

The structures of nanocrystalline materials are dominated by their ultrafine grain sizes and their large number of grain boundaries. Much work has been done to study the structure of nanocrystalline materials. Most of the results have been interpreted according to a two component microstructure: perfect long range ordered atomic arrangement within the grains and a random interfacial atomic arrangement [9,131,136,137]. Figure 2.6 is a schematic representation of a hard sphere model of an equiaxed nanocrystalline metal. Two types of atoms can be distinguished: crystal grain atoms with nearest neighbour configuration corresponding to lattice atoms and boundary atoms with a variety of interatomic spacings, differing from boundary to boundary.
Figure 2.6 Schematic representation of equiaxed nanocrystalline metal. Solid circle: individual grain atoms; open circle: grain boundary atoms [9].

A typical high resolution image of a nanocrystalline palladium sample is shown in Figure 2.7, which indicate that the grains in nanocrystalline palladium are rather equiaxed, similar to the atom clusters from which they were formed.
Figure 2.7  High resolution transmission electron micrograph of a typical area in nanocrystalline palladium [138].

Because of their ultrafine grain size, nanocrystalline materials have a significant fraction of their atoms in grain boundary environments, where they occupy positions relaxed from their normal lattice sites. For conventional high-angle grain boundaries, these relaxations extend over about two atom planes on either side of the boundary, with the greatest relaxation existing in the first plane [139,140]. Figure 2.8 shows the percentage of atoms in grain boundaries (including grain boundary junctions) of a nanocrystalline material as a function of grain diameter, assuming that the average
grain boundary thickness ranges from 0.5-1.0 nm, about 2 to 4 atomic planes. Assuming that grains have the shape of spheres, the volume fraction of nanocrystalline materials associated with the boundaries can be calculated as \[ Fr = \frac{3B}{d} \] (2.1)

where \( Fr \) is the volume fraction of nanocrystalline materials associated with the boundaries, \( B \) is the average grain boundary thickness and \( d \) is average grain diameter. Therefore, the volume fraction of nanocrystalline materials will be 3 % for 100 nm grains, increase to about 30 % for 10 nm grains, and 50 % for 5 nm grains.

2.3.3 Synthesis and processing of nanocrystalline materials

In principle, any method capable of producing very fine grain size polycrystalline materials can be used to produce nanocrystalline materials. If a phase transformation is involved, e.g. liquid to solid or vapour to solid, then steps have to be taken to increase the nucleation rate and decrease the growth rate during formation of the product phase. The methods include inert gas condensation [143], mechanical milling [144], chemical vapour deposition [145], sputtering [146], spray conversion processing [147], electrodeposition [148], sol-gel processing [149], spark erosion [150], plasma processing [151], quenching a melt under high pressure [152]. Among these, gas condensation and mechanical milling methods are the most commonly used to produce 3 dimensionally equiaxed nanocrystalline materials.
Figure 2.8  Percentage of atoms in grain boundaries (including grain boundary junctions) of a nanocrystalline material as a function of grain diameter [141].
2.3.3.1 **Gas condensation technique**

A typical apparatus [9,153] for the gas condensation method which is widely used for synthesis of nanocrystalline materials by the in situ consolidation of gas-condensed clusters is shown schematically in Figure 2.9. In this method, a metal or a mixture of metals is evaporated inside an ultrahigh vacuum (UHV) chamber filled with helium gas. As a result of interatomic collisions with the helium atoms in the chamber, the evaporated metal atoms lose their kinetic energy and condense in the form of small crystals of loose powder which accumulate, because of convective flow, on a vertical liquid nitrogen filled cold finger. The powder is stripped off the cold finger by moving an annular Teflon ring down the length of the tube into a compaction device. The scraping and compaction processes also are carried out under UHV conditions to maintain cleanness of the particle surfaces (and subsequent interfaces) and also to minimise the amount of any trapped gases.
Figure 2.9  Schematic drawing of a gas-condensation chamber for the synthesis of nanocrystalline materials [153].
2.3.3.2 **Mechanical milling/alloying**

Unlike gas-condensation methods, mechanical milling produces its nanostructures not by cluster assembly but by the structural decomposition of coarser-grained structures as the result of severe plastic deformation. This has become a popular method to make nanocrystalline materials because of its simplicity, the relatively inexpensive equipment needed, and the applicability to essentially all classes of materials. The major advantage often quoted is the possibility for easily scaling up to tonnage quantities of material for various applications [154].

This process consists of repeated welding, fracturing, and re-welding of powder particles in a dry high energy ball mill. In this process, a metal, an alloy, or mixtures of elemental or pre-alloyed powder are subjected to grinding under a protective atmosphere in equipment capable of high energy compressive impact forces such as attrition mills, vibrating ball mills, and shaker mills (see section 2.2.2). A majority of the work on nanocrystalline materials has been carried out in highly energetic small shaker mills. It has been shown that nanometre sized grains can be obtained in almost any material after sufficient milling time. The grain sizes were found to decrease with milling time down to a minimum value, which appeared to scale inversely with the melting temperature. Further, mechanical alloying of immiscible metals can be achieved in very large metastable solid solubilities, presumably related to solute segregation at the nanocrystalline grain boundaries [144,155-157].

Department of Materials Engineering, University of Wollongong, NSW 2522, Australia
2.4 Hydrogen storage alloys

2.4.1 Introduction

Historically the first interest in metal hydride technology was initiated after the second world war for nuclear reactor applications. The interest in metal-hydrides and the development of their applications started in the early 1970s with the discovery of hydrogen absorption by LaNi$_5$ [158] at Philips Research Laboratories in Holland, and by FeTi [5] at the Brookhaven National Laboratory in the USA. Since then, the research and application development of various hydrogen storage alloys have advanced rapidly. It has been observed that many metals, intermetallics and alloys react reversibly with hydrogen to form hydrides. In the 1970s and 1980s, the practical applications for these new materials included hydrogen storage for a multitude of purposes, hydrogen compression and purification, heat pumps, refrigeration, and thermal storage [159]. In the later 1980s, utilising hydrogen storage alloys instead of cadmium as an anode material in alkaline rechargeable batteries had brought about a revolution in power sources. By 1990, the first Ni-MH batteries reached the marketing stage [160]. In late 1997, a hybrid electric vehicle power-assisted by high power Ni-MH battery was commercialised in Japan by Toyota [1]. The Ni-MH battery is the third practical secondary battery and now a key component not only for advanced information and telecommunication systems, but
also for next generation vehicles in which energy could be used efficiently with low emissions to the environment. The key materials for this high-tech battery would be the hydrogen storage alloys. Thus, more recently attention has been given to the investigation and development of various hydrogen storage alloys with high hydrogen absorption capacities and low costs.

2.4.2 Types of hydrogen storage alloys

Hydrogen is a highly reactive element and has been shown to form hydrides and solid solutions with thousands of metals and alloys. A hydride “family tree” of the elements, alloys and complexes is shown in Figure 2.10. The research work in this thesis focuses mainly on metastable hydrogen storage alloys.

The hydrogen storage alloys in common use are classified in terms of their stoichiometric composition into four categories including AB\textsubscript{5}-type, AB\textsubscript{2}-type (Laves-phase type), AB-type and A\textsubscript{2}B-type [161,162]. In these alloys, the A component is the one which forms the stable hydride. The B component performs several functions [163]: (i) it can play a catalytic role in enhancing the hydriding/dehydriding characteristics; (ii) it can alter the equilibrium pressures for the hydrogen absorption/desorption and raise it or lower it to a desired level, and (iii) it could also add to the stability of the alloys because some of the A component could be readily oxidized. The hydriding/dehydriding characteristics of these alloys could
be altered by a partial substitution or a small addition of other elements. Anani and his coworkers [163] summarised the roles of these substitutes or additives as follows:

(i) to increase or decrease the crystal lattice constants thereby changing the equilibrium pressure for hydrogen absorption/desorption; (ii) to decrease the hysteresis during hydrogen absorption/desorption; (iii) to catalyse hydriding/dehydriding reactions and (iv) to improve the stability of these alloys thus preventing oxide formation on one or more of the components. Table 2.3 lists some examples of typical hydrogen storage alloys.

**Figure 2.10**  Family tree of hydriding alloys and complexes [161]. TM=transition metal.
### Table 2.3 Some examples of typical hydrogen storage alloys

<table>
<thead>
<tr>
<th>Type</th>
<th>Hydrogen storage alloys</th>
</tr>
</thead>
</table>
| AB<sub>5</sub> | LaNi<sub>5</sub>, LaNi<sub>4</sub>Cu, LaNi<sub>2.5</sub>Co<sub>2.5</sub>, LaNi<sub>5-x</sub>Al<sub>x</sub> (x=3.5-4.8)  
CaNi<sub>5</sub>, LaNi<sub>5-x</sub>Sn<sub>x</sub> (x=0-5), LaNi<sub>5-x</sub>Ge<sub>x</sub> (x=0-5)  
La<sub>0.9</sub>Zr<sub>0.1</sub>Ni<sub>4.5</sub>Al<sub>0.5</sub>, LaNi<sub>3.5</sub>Co<sub>0.8</sub>Mn<sub>0.4</sub>Al<sub>0.3</sub>  
MmNi<sub>5</sub> (Mm = misch metal),  
MmNi<sub>4.5</sub>Al<sub>0.5</sub>, MmNi<sub>4.5</sub>Mn<sub>0.5</sub>,  
MmNi<sub>3</sub>Co<sub>1.5</sub>Al<sub>0.5</sub>, MmNi<sub>3.5</sub>Co<sub>0.8</sub>Mn<sub>0.4</sub>Al<sub>0.3</sub>. |
| AB<sub>2</sub> | TiCr<sub>2</sub>, TiMn<sub>2</sub>, ZrMn<sub>2</sub>, ZrV<sub>2</sub>, ZrV<sub>0.4</sub>Ni<sub>1.6</sub>,  
Ti<sub>0.5</sub>Zr<sub>0.5</sub>V<sub>0.75</sub>Ni<sub>1.5</sub>, Zr<sub>0.8</sub>Ti<sub>0.2</sub>V<sub>0.6</sub>Mn<sub>0.3</sub>Pd<sub>0.1</sub>Ni<sub>0.8</sub>Fe<sub>0.2</sub>. |
| AB | FeTi, TiNi, TiFe<sub>1-x</sub>Mn<sub>x</sub> (x=0.1-0.3), TiFe<sub>0.8</sub>Ni<sub>0.15</sub>V<sub>0.05</sub>.  
TiFe<sub>0.8</sub>Ni<sub>0.15</sub>Nb<sub>0.05</sub>. |
| A<sub>2</sub>B | Mg<sub>2</sub>Ni, Mg<sub>2</sub>Cu, Ti<sub>2</sub>Ni, Mg<sub>2</sub>Ni<sub>0.5</sub>Cu<sub>0.5</sub>, Mg<sub>2</sub>Ni<sub>0.75</sub>V<sub>0.25</sub>,  
Mg<sub>2</sub>Ni<sub>0.75</sub>Fe<sub>0.25</sub>, Mg<sub>1.92</sub>Al<sub>0.08</sub>Ni, Mg<sub>1.9</sub>Al<sub>0.1</sub>Ni<sub>0.8</sub>Mn<sub>0.2</sub>,  
Mg<sub>1.9</sub>Ca<sub>0.1</sub>Ni<sub>0.8</sub>Cu<sub>0.2</sub>. |
2.4.3 Thermodynamics

The typical behaviour of a metal-hydride system is illustrated by a pressure-composition-temperature relationship (P-C-T curve) or P-C isotherm. For hydrogen storage alloys, the most important properties are related to the presence of a 'plateau pressure' in the P-C-T curve which represent the coexistence of two condensed phases when hydrogen is loaded over the solubility limit. Typical pressure-composition-temperature isotherms (P-C-T curves) of gas-solid reactions are schematically plotted in Figure 2.11a. Initially, a small amount of hydrogen dissolves in the alloy as a solid solution (α-phase). The hydrogen occupies interstitial sites in the lattice and its concentration depends strongly on the hydrogen pressure. After the solid solution is saturated, a hydride phase (β-phase) nucleates and grows. During the α-β phase transition at a constant temperature, the equilibrium pressure ideally remains constant because the number of degrees of freedom is one, according to the Gibbs phase rule. For the two coexisting solid phases the hydride grows according to the chemical reaction:

\[
2(y-x)^{-1} MH_x + H_2 \rightarrow 2(y-x)^{-1} MH_x
\]  

(2.2)

where \(x, y\) correspond to the hydrogen contents of the phase boundaries expressed as \(H/M\), M: hydride. The hydrogen plateau pressure \(P_{H_2}\) increases with increasing temperature according to the van't Hoff relation:
\[ \ln P_{H_2} = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \]  \hspace{1cm} (2.3)

where \( R \) is the gas constant, \( T \) is the absolute temperature. \( \Delta H \) and \( \Delta S \) are the enthalpy and entropy changes per mole \( H_2 \), respectively. In an equilibrium state, these thermodynamic data can be calculated from van't Hoff plots in Figure 2.11b.

![Diagram showing pressure-composition-temperature curves and van't Hoff plots](image)

**Figure 2.11** (a) Pressure-composition-temperature (P-C-T) curves of the hydrogen storage alloys H system, and (b) van’t Hoff plots [164].

The enthalpy of formation of hydride can be calculated from the slope of the straight line obtained by plotting \( \ln P_{H_2} \) versus \( 1/T \). The entropy change of hydride can be calculated from the intercept of the straight line (\( 1/T=0 \)). The bigger the \( |\Delta H| \) is, the
smaller the $P_{H_2}$ is and the more stable the hydride is. Figure 2.12 gives the van't Hoff plots for various hydrides.

![Van't Hoff plots for various hydrides from desorption data (where M is misch metal) [165].](image)

**Figure 2.12** Van't Hoff plots for various hydrides from desorption data (where M is misch metal) [165].
2.4.4 FeTi-type hydrogen storage alloys

2.4.4.1 Formation of FeTi hydrides

Figure 2.13 shows the Fe-Ti binary alloy phase diagram, which indicates that iron and titanium form two stable intermetallic compounds, FeTi and Fe₂Ti. The intermetallic compound FeTi has been considered for many years to be promising hydrogen storage alloy because it has excellent hydrogen storage properties at room temperature provided that it has been pre-activated. FeTi-based AB alloys are based on an ordered body-centred-cubic structure.

![Fe-Ti binary alloy phase diagram](image)

**Figure 2.13** Fe-Ti binary alloy phase diagram [166].
In 1974, Reilly and Wiswall [5] explored the Fe-Ti-H system between the approximate limits, by weight, of 70% Fe-30% Ti and 37% Fe-63% Ti, corresponding to the atomic proportions Fe$_2$Ti and FeTi$_2$. At the iron-rich end shown in Figure 2.14, the composition of the unhydrided alloy, as determined by analysis, was 53.6% Fe and 46.7% Ti. The only metal phase present is that of FeTi. The shape of the isotherms were interpreted as follows: on the left, where the isotherms rise steeply as the hydrogen content of solid increases, is the region of solid solution of hydrogen in the Fe-Ti metal lattice. This solid solubility region may be designated as the $\alpha$ phase of the FeTi-H system. As the hydrogen content of the solid is further increased, the equilibrium pressure remains constant and forms, so to speak, a plateau. The composition at which plateau begins marks the point at which a new phase appears and also marks the maximum solubility of hydrogen in the $\alpha$ phase. At room temperature that composition corresponds to FeTiH$_{0.10}$ (H/M=0.05). The new phase is the monohydride or $\beta$ phase of the FeTi-H system. Both the $\alpha$ and $\beta$ phase co-exist until the solid composition corresponds to FeTiH$_{1.04}$ where the isotherms begin a steep ascent. At this point the $\alpha$ phase had disappeared. As the hydrogen content of the $\beta$ phase is increased, a new phase appears, the $\gamma$ or dihydride phase.

The reaction taking place in the lower plateau region (H/M=0.10 to H/M=0.52) was written as
Chapter Two  

Literature Review

\[ 2.13\text{FeTiH}_{0.10} + \text{H}_2 \rightleftharpoons 2.13\text{FeTiH}_{1.04} \]  \hspace{1cm} (2.4)

which is followed by

\[ 2.20\text{FeTiH}_{1.04} + \text{H}_2 \rightleftharpoons 2.20\text{FeTiH}_{1.95} \]  \hspace{1cm} (2.5)

Figure 2.14  Pressure-composition isotherms of FeTi-H system [5].

The \( P-C-T \) properties and cost of the FeTi alloy is listed in Table 2.4. FeTi alloy has good \( P-C-T \) properties, good H-capacities and low raw materials costs, but the
problems associated with activation, gaseous impurities and upper plateau instabilities.

Table 2.4  \( P-C-T \) properties and cost of FeTi alloy hydride at lower plateau

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta H )</td>
<td>-28.1 kJ mol(^{-1})H(_2)</td>
</tr>
<tr>
<td>( \Delta S )</td>
<td>-0.106 kJ mol(^{-1}) K(^{-1})</td>
</tr>
<tr>
<td>25°C ( P_d )</td>
<td>4.1 atm</td>
</tr>
<tr>
<td>( T ) for 1 atm ( P_d )</td>
<td>-8°C</td>
</tr>
<tr>
<td>Plateau: Hysteresis</td>
<td>0.64;</td>
</tr>
<tr>
<td>Slope</td>
<td>0.0</td>
</tr>
<tr>
<td>( (H/M)_{max} )</td>
<td>0.975</td>
</tr>
<tr>
<td>( (wt.%)_{max} )</td>
<td>1.86</td>
</tr>
<tr>
<td>( (\Delta H/M)_{r} )</td>
<td>0.79</td>
</tr>
<tr>
<td>( (\Delta wt.%)_{r} )</td>
<td>1.5</td>
</tr>
<tr>
<td>( (\Delta H/V)_{r} )</td>
<td>5.0×10(^{22}) H-atoms/cm(^3)</td>
</tr>
<tr>
<td>Alloy Raw Materials Cost</td>
<td>$4.68 kg(^{-1})</td>
</tr>
<tr>
<td>Alloy Raw Materials Cost</td>
<td>$0.31 g(^{-1}) H stored</td>
</tr>
</tbody>
</table>

2.4.4.2 Activation of FeTi alloy

The activation process and the reaction kinetics of hydrogenation of metals are of importance relative to their practical use as hydrogen storage materials. Activation of the FeTi system is particularly difficult. Activation (usually in powder form)
involves heating FeTi to higher temperature (about 450 °C) in vacuum and annealing in $H_2$ at a certain pressure (about 7 bars), followed by cooling down to room temperature and admission of hydrogen at pressure of 35-65 bars. After activation FeTi is readily poisoned by exposure to air or other gases and gas mixtures [5, 167]. The activation mechanism has been discussed by many researchers [168-172]. Although their results are not in agreement, they all conclude that the activation process is necessary because of the presence of an oxide film which obstructs hydrogen absorption. The samples are activated by performing a number of thermal and hydrogen absorption-desorption cycles. Thus the activation of FeTi hydrogen storage alloy is one of the fundamental problems that must be overcome.

2.4.4.3 *Amorphous and nanocrystalline FeTi alloys*

(a) *Preparation of amorphous and nanocrystalline FeTi alloys*

Mechanical alloying (MA) and mechanical milling (MM) by ball milling are very effective methods to achieve non-equilibrium FeTi alloys, especially amorphous and nanocrystalline FeTi alloys. For instance, an amorphous FeTi alloy can be synthesized by ball milling an elemental mixture of 50 at.% Fe and 50 at.% Ti powders using a vibrating frame high energy ball mill (Spex 8000) for 22 hours [173]. Also, a nanocrystalline FeTi alloy can be obtained by ball milling a polycrystalline FeTi alloy using a vibrating frame high energy ball mill (Spex 8000) [175,176].
Figure 2.15  Hydrogen absorption curves of the FeTi powders at 10 °C and 2 MPa H₂ after ball milling for 0, 1.8, 10.8 and 86.4 ks in an argon atmosphere and without exposure to the air [177,178].

(b) Hydrogenation characteristics of ball milled FeTi alloys

Ball milling can effectively improve the activation process and the reaction kinetics of hydrogenation of FeTi alloy. Aoki et al. [177,178] reported that ball milling in an argon gas atmosphere and in a vacuum, which give rise to the creation of fresh surfaces and cracks, is effective for the improvement of the initial hydrogen absorption rate of FeTi and Mg₂Ni alloys. Figure 2.15 shows the hydrogen
absorption curves of the FeTi powders at 10 °C and 2 MPa H₂ after ball milling for different periods in an argon atmosphere. The longitudinal axis represents the hydrogen contents, H/M, expressed by the number of hydrogen atoms per metal atoms. No hydrogen absorption is observed in as-pulverised FeTi, in agreement with the reference [5]. However, hydrogen is absorbed into FeTi after milling for 1.8 ks or more if it is not exposed to the air. As the milling time increases, hydrogen is absorbed more rapidly.

Figure 2.16 Pressure-concentration isotherms (for absorption) for amorphous FeTi (a), nanocrystalline FeTi alloy (b) and as-alloyed intermetallic compound FeTi (c) [173,183].
Activation of amorphous and nanocrystalline FeTi alloys is much easier than that of their polycrystalline counterpart. Ball-milled amorphous FeTi alloy can be readily activated after a single annealing at 300 °C under vacuum for 0.5 hours [173,179]. After activation, pressure-concentration isotherms for ball-milled amorphous FeTi alloy is shown in Figure 2.16a, which exhibits hydrogenation characteristics for amorphous materials: a monotonic increase of hydrogen content with the logarithm of applied pressure [180-182] with no plateau.

Nanocrystalline FeTi alloy with grain sizes of about 5 nm can be activated after a single annealing at 400 °C under vacuum for 0.5 hours [173]. After activation, pressure-concentration isotherms for nanocrystalline FeTi alloy are as shown in Figure 2.16b. In contrast to the crystalline FeTi alloys (Figure 2.16c), the nanocrystalline FeTi alloy showed a relatively large solubility region (up to 0.3H/FeTi) at low pressure.

Above all, amorphous and nanocrystalline FeTi alloys possess very different hydrogen storage properties compared with their crystalline counterparts. It is possible that they may have some useful electrochemical hydrogen storage properties for Ni-MH batteries.
2.4.5 Magnesium-based hydrogen storage alloys

2.4.5.1 Introduction

Magnesium is the lightest of the commercial structural materials and is the sixth most abundant element in the earth. Magnesium can also reversibly store about 7.65 wt. % hydrogen according to the reaction:

\[ \text{Mg} + \text{H}_2 \leftrightarrow \text{MgH}_2 \]  

(2.6)

\( \text{MgH}_2 \) contains much more hydrogen than other metal hydrides (see Table 2.5).

<table>
<thead>
<tr>
<th>Medium</th>
<th>Hydrogen content (wt.%)</th>
<th>Volumetric density (H atoms l(^{-1}) x 10(^{19})</th>
<th>Energy density (mJ kg(^{-1}))</th>
<th>Energy density (mJ l(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gaseous ( \text{H}_2 ) (150 atm)</td>
<td>100.00</td>
<td>0.5</td>
<td>141.90</td>
<td>1.02</td>
</tr>
<tr>
<td>Liquid ( \text{H}_2 ) (-253 °C)</td>
<td>100.00</td>
<td>4.2</td>
<td>141.90</td>
<td>9.92</td>
</tr>
<tr>
<td>( \text{MgH}_2 )</td>
<td>7.65</td>
<td>6.7</td>
<td>9.22</td>
<td>14.32</td>
</tr>
<tr>
<td>( \text{Mg}_2\text{NiH}_4 )</td>
<td>3.60</td>
<td>5.9</td>
<td>4.48</td>
<td>11.49</td>
</tr>
<tr>
<td>( \text{VH}_2 )</td>
<td>2.10</td>
<td>11.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{FeTiH}_{1.95} )</td>
<td>1.95</td>
<td>5.5</td>
<td>2.47</td>
<td>13.56</td>
</tr>
<tr>
<td>( \text{LaNi}<em>3\text{H}</em>{6.7} )</td>
<td>1.50</td>
<td>7.6</td>
<td>1.94</td>
<td>12.77</td>
</tr>
<tr>
<td>( \text{ZrMn}<em>2\text{H}</em>{3.6} )</td>
<td>1.75</td>
<td>6.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{ZrMn}<em>2\text{Fe}</em>{0.8}\text{H}_{3.4} )</td>
<td>1.38</td>
<td>4.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Unfortunately, the reaction (2.6) is generally difficult to nucleate because the surface is usually contaminated by magnesium oxide (MgO), or magnesium hydroxide (Mg(OH)$_2$) which either inhibits the dissociative adsorption of hydrogen or the transfer of hydrogen from the surface to bulk. Once nucleated, MgH$_2$ then grows slowly, the rate-limiting step being the diffusion of hydrogen through the growing MgH$_2$ layer [189-190]. Dissociative adsorption on the MgH$_2$ surface can also limit the growth rate [191]. It is known that the oxides and adsorbed gases at the surface of crystalline magnesium inhibit the hydriding of Mg [192]. Such surface layers also inhibit dehydriding [193]. Even if one eliminates the oxide layer formation, the reaction rates are still very low because of the protective layer problem. However, both the nucleation and growth kinetics of MgH$_2$ can be accelerated by the addition of a catalyst capable of promoting dissociative adsorption of hydrogen.

### 2.4.5.2 Mg-Ni hydrogen storage alloys

In order to eliminate the limitations of using Mg alone, studies of numerous metal additions to Mg (binary, ternary and multi-component) have been carried out in order to find the optimum alloy for hydrogen storage. Reilly and Wiswall [3, 194] reported a fairly rapid reaction of Mg$_2$Ni and Mg$_2$Cu with hydrogen at about 300 °C. They concluded that the presence of Ni or Cu has a catalytic effect on the hydrogenation of Mg. The catalytic effect of these elements is probably due to the formation of oxide-
free penetration sites on the surface of Mg particles, as reported for the Mg-Mg$_2$Cu system [189-191].

As shown in Figure 2.17, Mg forms two intermetallic compounds with Ni, namely, Mg$_2$Ni and MgNi$_2$. The latter does not react with hydrogen at pressures up to 540 atm in the temperature range -196 to 300°C. However, Mg$_2$Ni reacts with hydrogen to form a ternary hydride, Mg$_2$NiH$_4$,

$$\text{Mg}_2\text{Ni} + \text{H}_2 \rightleftharpoons \text{Mg}_2\text{NiH}_4$$  \hspace{1cm} (2.7)

Figure 2.17  Binary phase diagram of Mg-Ni system [196].
Figure 2.18 Desorption isotherms of Mg$_2$Ni-H$_2$ system. The initial composition is 45.9 wt.% Mg and 54.6 wt.% Ni [3].

even at room temperature. At 200°C and a pressure of 14 atm, it will react rapidly [3]. A series of pressure-composition isotherms for this system is shown in Fig. 2.18. The abrupt termination of the isotherms at a composition corresponding to Mg$_2$NiH$_4$ indicates that the hydride has a well-defined stoichiometry. The maximum solubility of hydrogen in the $\alpha$-phase corresponds to a composition of Mg$_2$NiH$_{0.3}$. The reaction starting with the hydrogen-saturated alloy may be written as:
1.08\text{Mg}_2\text{NiH}_{0.3} + 2\text{H}_2 \longleftrightarrow 1.08\text{Mg}_2\text{NiH}_4 \quad (2.8)

The hydrogen content in \text{Mg}_2\text{NiH}_4 is about 3.6 wt.\%, which is still a better value compared to other hydrogen storage materials, but it is less than one-half the amount, by weight, of hydrogen in MgH\textsubscript{2} (Table 2.5). The Mg\textsubscript{2}Ni-H\textsubscript{2} system is more unstable thermally than the corresponding Mg-H\textsubscript{2} system. As far as the reaction kinetics are concerned, the absorption process is faster, and the dissociation of the hydride is relatively rapid. Table 2.6 listed the \textit{P-C-T} properties and cost of Mg\textsubscript{2}Ni alloy.

<table>
<thead>
<tr>
<th>\textit{P-C-T} properties and cost of Mg\textsubscript{2}NiH\textsubscript{4} [161]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H = -64.5 \text{ kJ mol}^{-1}\text{H}_2$</td>
</tr>
<tr>
<td>$\Delta S = -0.122 \text{ kJ mol}^{-1} \text{K}^{-1}$</td>
</tr>
<tr>
<td>25°C $P_d = 10^{-5} \text{ atm (extrapolated)}$</td>
</tr>
<tr>
<td>$T$ for 1 atm $P_d = 255 \text{°C}$</td>
</tr>
<tr>
<td>$(H/M)_{\text{max}} = 1.33$</td>
</tr>
<tr>
<td>$(\text{wt.%})_{\text{max}} = 3.6$</td>
</tr>
<tr>
<td>$(\Delta H/M)_r = 1.23$</td>
</tr>
<tr>
<td>$(\Delta \text{wt.%})_r = 3.3$</td>
</tr>
<tr>
<td>$(\Delta H/V)_r = 5.2 \times 10^{22} \text{ H-atoms/cm}^3$</td>
</tr>
<tr>
<td>Alloy Raw Materials Cost = $6.26 \text{ kg}^{-1}$</td>
</tr>
<tr>
<td>Alloy Raw Materials Cost = $0.19 \text{ g}^{-1} \text{ H stored}$</td>
</tr>
</tbody>
</table>
2.4.5.3 **Substitution of Mg$_2$Ni alloys**

Substitution is one of the most widely used methods to control or improve the hydrogenation properties of the hydrogen storage alloys. Many substituted Mg$_2$Ni alloys have been investigated to improve their hydrogenation properties.

In the early 1980s, Oesterricher *et al.* [196] have suggested that the partial substitution of Mg in Mg$_2$Ni by an element of a more exothermic heat of hydride formation, such as Ca, Sc or Y, may result in a rise of equilibrium pressure for the substituted Mg$_2$Ni. This would bring Mg$_2$Ni into the range of reversible room temperature hydrogen sorption. Yvon *et al.* [197] suggested that the maximum hydrogen concentration of this compound is mainly limited by electronic factors, and that structurally related compounds having more than four hydrogen atoms per formula unit could possibly be stabilized by partially replacing Ni with a transition metal of lower valency, or Mg by a non-transition metal of higher valency.

Attempts have been made to prepare such compounds by partially replacing Ni by 3d elements [198-202], and Mg by non-transition elements [201] in the binary phase of Mg$_2$Ni. But the alloys obtained failed to yield hydrides having more than four H atoms per formula unit. On the other hand they show some interesting properties with respect to hydriding and dehydriding kinetics as well as the dissociation temperature of the hydride. It was also reported [203-205] that the partial
substitution of Mg by 3d metals on Mg-rich, rare-earth intermetallic compounds resulted in improved dehydriding kinetics.

In order to achieve partial substitution of Ni atoms in Mg$_2$Ni iron cobalt, some experiments were performed [198]. However, no significant amount of substitution occurred in the Mg$_2$Ni$_{1-x}$M$_x$ (M=Fe or Co) systems. The highest substituent concentrations of about 2 at. % were obtained for Co. The effects of these low-concentration additives on the stability of the corresponding hydrides were negligible. The same observation was made by Darnaudery et al. [200] for the addition of Mn or Ti. On the contrary, Lupu et al. [202] reported that there is no substitution in Mg$_2$Ni$_{1-x}$Fe$_x$ ($x \leq 0.37$) alloys. This was explained on the basis of Extended X-ray Absorption Fine Structure (EXAFS) measurements with Mössbauer spectral results. In this range of composition, multiphase alloys were obtained containing Mg$_2$Ni, Mg and more or less finely dispersed Fe in the form of isolated atoms or small clusters as proved by the EXAFS technique and Mössbauer spectroscopy. Thus they confirmed that there is no significant substitution of Ni by Fe atoms in the Mg$_2$Ni lattice, which is in agreement with the observation of Mintz et al. [198]. Stable hydrides are formed with Fe substituted Mg$_2$Ni alloys.

A study of the action of hydrogen on Mg$_2$Ni$_{1-x}$M$_x$ (M = V, Cr, Fe, Co, Cu, or Zn; $x = 0.25$) alloys has been carried out [200]. Hydriding of the alloys resulted in the formation of quaternary hydrides. The hydriding process leads to ternary alloys,
except in the case of Cu-containing alloy. This behaviour of \( \text{Mg}_2\text{Ni}_{0.75}\text{Cu}_{0.25} \) seems to be similar to that of \( \text{Mg}_2\text{Cu} \) due to the decomposition of the alloy during the hydriding reaction [194]. The thermal stabilities of these compounds are close to that of \( \text{Mg}_2\text{NiH}_4 \). In each case the hydrogen/alloy mole ratio is lower than the corresponding \( \text{Mg}_2\text{NiH}_4 \).

The replacement of Ni in \( \text{Mg}_2\text{Ni} \) by the 3d elements alters the dissociation temperature markedly. For example the dissociation temperature in 1 atm pressure for Cu-containing alloy significantly drops from 250 °C to 227 °C, whereas for the Co-containing alloy this temperature increases to 267 °C. The absorption and desorption rates for \( \text{Mg}_2\text{Ni}_{1-x}\text{M}_x \) alloys are close to those obtained with \( \text{Mg}_2\text{Ni} \) except for the Co-containing alloy. Because of the encouraging results obtained with the \( \text{Mg}_2\text{Ni}_{1-x}\text{Cu}_x \) system, Darnaudery et al. [206] continued their work on the same system by varying the \( x \) values from 0 to 0.85 in order to optimise the alloy. The absorption and desorption rates for these alloys are close to those obtained with \( \text{Mg}_2\text{Ni} \).

Au and co-workers [207] have investigated the hydrogen storage properties of multi-component Mg-based alloys and found that \( \text{Mg}_{0.833}\text{Ni}_{0.066}\text{Cu}_{0.095}\text{Ml}_{0.006} \) (Ml stands for La-rich misch-metal) has good hydriding/dehydriding properties. It can absorb 4.75 wt.% hydrogen at 330 °C under 0.1 MPa pressure in 0.5 hours. The alloying elements Ni, Cu and RE (rare earth metal) are identified to have positive effects on
the kinetic properties of Mg-based alloys. The intermetallic compound of Mg with Ni, Cu (and RE), namely Mg₂(Cu, Ni), plays the key role in improving the kinetic properties of the multi-component Mg-based alloy.

### 2.4.5.4 Amorphous and nanocrystalline Mg-Ni alloys

(a) Mg-based alloys prepared by ball milling (mechanical alloying and milling)

Because Mg and Mg-based alloys are some of the most promising hydrogen storage alloys, there has been extensive work on Mg-based hydrogen storage alloys for more than three decades, both from fundamental and applications points of view. In recent years, it was found that ball milling is an effective method of improving the hydriding/dehydriding kinetics and hydrogenation characteristics of Mg-based alloys.

In the late of 1980s, Khrussanova et al. reported that ball milling 90 wt.% Mg and 10 wt.% TiO₂ mixture in a planetary mill results in improving the absorption and desorption characteristics of magnesium [208], and ball milling is found to favour the appearance of a clean Mg surface without the usual thin oxide film [209]. Ball milled 90 wt.% Mg and 10 wt.% V₂O₅ mixture is activated quickly and has a high hydrogen capacity which is preserved after prolonged cycling. It also has good desorption characteristics [210]. Ball milling can also improve the hydrogen absorption rate of Mg₂Ni intermetallic compound greatly [177]. Song [211-213] investigated the hydriding and dehydriding characteristics of mechanical milled Mg and mechanical alloyed mixtures with the compositions Mg-x wt.% Ni (x= 5, 10, 25
and 55) using a planetary mill with an acceleration of about 60 ms^{-2} for only 5 min. The results indicated that the Mg-x wt.% Ni and Mg-25 wt.% Ni mixtures are activated easily, show much larger hydrogen storage capacities and much higher hydriding rates, and higher dehydriding rates, than other magnesium-based alloys or mixtures. Mechanical milled Mg-based composites, Mg-G (graphite) and Mg-Pd-G, were extremely active toward hydrogen absorption even at 27 °C and showed good reversibility for hydriding/dehydriding [214-217]. A ball milled MgNi alloy with graphite can also absorb hydrogen at 30 °C in much larger quantities than that prepared by induction melting [218]. Moreover, more and more work has been done by ball milling ternary hydrogen storage alloys, such as Mg_{2}Ni_{1-x}Zr_{x} (0< x <= 0.3) [219], and Mg-based composite [200-223], which lead to better hydriding/dehydriding kinetics and/or larger hydrogen absorption abilities of the materials.

(b) Hydrogenation characteristics of nanocrystalline and amorphous Mg-Ni alloys

Ball milling is also the most effective and simplest method to manufacture nanocrystalline and amorphous Mg-Ni alloys. In 1995, Zaluski et al. reported that ball-milled nanocrystalline Mg_{2}Ni shows hydrogen absorption characteristics superior to that of the conventional crystalline phase. The activation of nanocrystalline Mg_{2}Ni is much easier, or even unnecessary. At high temperatures (about 300 °C) the hydrogen absorption rate is very high, even for the as-made...
nanocrystalline samples. The absorption rate can be further improved by applying one hydrogenation cycle as a pre-treatment. Nanocrystalline Mg$_2$Ni exhibits also hydrogen absorption at lower temperatures (for instance at 200 °C, i.e. below the temperature of structural transformation of the Mg$_2$NiH$_4$ hydride) without any activation [224]. Tanaka et al. investigated the hydrogen absorbing rates and pressure-composition isotherms (P-C-T) of nanocrystalline Mg-Ni and Mg-Ni-Re (Re=La, Nd) alloys prepared by a melt-spinning and crystallisation method. These nanocrystalline alloys, particularly of the Mg-Ni-RE systems, exhibit excellent hydrogen absorbing kinetics and P-C-T characteristics in comparison with those of the corresponding as-cast alloys with a coarse eutectic structure [225].

Orimo et al. investigated the hydrogenation properties of amorphous Mg-Ni alloys prepared by ball milling under a hydrogen atmosphere [226,227]. The hydrogen pressure-composition isotherms in dehydriding processes of amorphous MgNi alloy is shown in Figure 2.19. Even at 160 °C, the dehydriding reaction proceeds below 0.1 MPa. The pressure dependence of the hydrogen content is small, compared to the other amorphous alloys with broad site energy distribution for hydrogen atoms, such as FeTi system [173,183]. This suggests that the energy distribution is narrower in amorphous MgNi alloy.

Funaki et al. [228] synthesized the amorphous MgNiC$_x$ ($x = 0-1.31$) by mechanical alloying of amorphous MgNi and graphite as starting materials. Upon hydrogenation
of MgNiC₃, the atomic ratio of hydrogen plus carbon to metal (H+C)/M remained a constant value of about 0.9.

Figure 2.19  P-C-T curves in dehydriding processes of completely hydrogenated amorphous MgNi alloy [227].

More recently, Tsushio and co-workers investigated the effect of elemental substitutions on the hydrogenation properties of amorphous MgNi₀.₈₆M₀.₀₃ (M=Cr, Fe, Co, Mn) alloys prepared by ball milling [229]. Most of the P-C-T curves were completely different from those of the crystalline Mg₂Ni-H₂, Mg-H₂ systems, and even amorphous MgNi alloy [227]. They show a monotonic increase of hydrogen content with the logarithm of applied pressure with no plateau. The synthesis and
hydriding/dehydriding properties of Mg$_2$Ni$_{1.9}$M$_{0.1}$ (M=none, Ni, Ca, La, Y, Al, Si, Cu and Mn) alloys mechanically alloyed from Mg$_2$Ni$_{1.9}$M$_{0.1}$ and Ni powder were also reported [230]. Figure 2.20 shows the pressure-composition isotherms of amorphous Mg$_2$Ni$_{1.9}$M$_{0.1}$ (M=none, Ca and Cu), which indicates the elemental substitution of amorphous Mg-Ni alloys can effectively change their hydriding/dehydriding properties.

![Figure 2.20 Pressure composition isotherms of amorphous Mg$_2$Ni$_{1.9}$M$_{0.1}$ (M=none, Ca and Cu) [230].](image)

Above all, the formation of amorphous or nanocrystalline Mg-based hydrogen storage alloys produced by ball-milling results in dramatic changes in hydrogen sorption properties, especially in the elimination of the need for activation and the improvement of hydriding/dehydriding kinetics.
2.5 Metal-hydride electrodes for Ni-MH batteries

2.5.1 Introduction

In 1963, Barton et al. first proposed the application of a hydrogen storage metal, Pd, in a rechargeable battery [231]. Because of its high cost, palladium electrode has only been utilised in limited areas such as a high purity hydrogen generator in which hydrogen produced by water electrolysis diffuses through the palladium, producing hydrogen with purity of more than 99.99%. In 1969, Zijlstra and Westendorp accidentally found that rare-earth intermetallic compounds absorbed large amounts of hydrogen during research on rare-earth magnets (SmCo5) [232], opening a new scientific and technical field — hydrogen storage alloys. Soon after this discovery, intermetallic compounds were applied as “hydrogen storage alloy electrodes”, for instance, TiNi-Ti2Ni [233], LaNi5 [234], and LaNi5-xMx (M=Al, Cr, Cu, Mn) [235-237]. Markin et al. constructed and evaluated the rechargeable nickel-metal hydride (Ni-MH) batteries composed of nickel hydroxide positive electrodes and metal hydride negative electrodes using LaNi5 [238,239].

After the oil crisis in 1974, hydrogen energy was proposed as the most promising clean energy system, creating a strong need for a light, compact and safe storage tank. Extensive research and development projects were carried out throughout the world.
on hydrogen storage alloys because they could store larger amounts of hydrogen (1000 cc/cc) per unit volume than liquid hydrogen (784 cc/cc at -273 °C) and high pressure tanks (200 cc/cc at 200 atm). Since 1985, a tremendous research and development effort has been conducted on the MH electrodes and the Ni-MH battery, leading to significant progress in every area of performance. The good combination of both metal hydride technology and battery technology resulted in the rapid commercialisation of the sealed Ni-MH battery in 1990 [160].

Since the invention of the Pb–acid battery in 1859 and the Ni–Cd battery in 1899, no successful rechargeable battery appeared for 90 years. The Ni–MH battery is the third practical secondary battery and is now a key component not only for advanced information and telecommunication systems, but also for the next generation of vehicles in which energy can be used efficiently with low emissions to the environment. The key materials for this high-tech battery are hydrogen storage alloys [1].

The hydrogen storage alloys used for the negative electrode materials of Ni-MH batteries must satisfy the following requirements [2,251]:

1. Large electrochemical hydrogen storage capacity.

2. High electrochemical catalytic activity.

3. High durability against oxidation in concentrated alkaline solution.

(5) Low cost.

2.5.2 Principles of Ni-MH batteries

A schematic structure of a cylindrical sealed Ni-MH cell is shown in Figure 2.21.

![Schematic structure of a cylindrical sealed Ni-MH cell](image)

**Figure 2.21** Schematic structure of a cylindrical sealed Ni-MH cell [240].

It is composed of a nickel hydroxide Ni(OH)$_2$ positive electrode, a polymeric separator (polyamide or hydrophilic polypropylene non-woven cloth), electrolyte solution (6-8 M KOH and 0.5-2 M LiOH aqueous) and a negative MH electrode.
The lithium ions are intercalated into layers of Ni(OH)$_2$, improving the durability of the electrode.

### 2.5.2.1 Charge-discharge mechanism

Figure 2.22 illustrates the charge-discharge mechanism of a Ni-MH battery. During charging, hydrogen is formed at the interface of electrode and electrolyte by an electrochemical reduction of water and is subsequently absorbed by the alloy.

![Diagram of charge-discharge mechanism](image)

**Figure 2.22**  Charge-discharge mechanism of a Ni-MH battery [1]
During discharging, the hydrogen in the MH is desorbed and oxidised electrochemically at the interface. The half-cell reactions and overall-cell reaction on charge and discharge of the battery can be written as:

at the nickel hydroxide positive electrode

\[
\begin{align*}
\text{charge} & : \quad \text{Ni(OH)}_2 + \text{OH}^- \leftrightarrow \text{NiOOH} + \text{H}_2\text{O} + \text{e}^- \quad (E^0 = +0.490\text{V}) \quad (2.9) \\
\text{discharge} & :
\end{align*}
\]

at the hydrogen storage alloy negative electrode

\[
\begin{align*}
\text{charge} & : \quad \text{M} + \text{H}_2\text{O} + \text{e}^- \leftrightarrow \text{MH} + \text{OH}^- \quad (E^0 = -0.828\text{V}) \quad (2.10) \\
\text{discharge} & :
\end{align*}
\]

the over all cell reaction is:

\[
\begin{align*}
\text{charge} & : \quad \text{Ni(OH)}_2 + \text{M} \leftrightarrow \text{NiOOH} + \text{MH} \quad (E^0 \approx 1.318\text{V}) \quad (2.11) \\
\text{discharge} & :
\end{align*}
\]

The mechanism of the Ni-MH battery is clearly distinguished from other batteries such as Ni-Cd, Ni-Zn, Ni-Fe, Pb-acid and Li batteries in which their is dissolution and precipitation of the active materials. The solid state transition mechanism allows the Ni-MH battery to have a more densely packed structure and a greater reliability [164].
2.5.2.2 Overcharge and overdischarge reactions

In the sealed cell, the MH has a higher capacity than the Ni(OH)$_2$ electrode, thus facilitating a gas recombination reaction. During overcharging, the oxygen gas generated from the nickel positive electrode is consumed by the hydrogen storage alloy negative electrode, \textit{i.e.}

\begin{equation}
\text{(Positive): } \quad 2\text{OH}^- \rightarrow \text{H}_2\text{O} + 1/2\text{O}_2 + 2e^- \quad (2.12)
\end{equation}

\begin{equation}
\text{(Negative): } \quad 2\text{MH} + 1/2\text{O}_2 \rightarrow 2\text{M} + \text{H}_2\text{O} \quad (2.13)
\end{equation}

\begin{equation}
2\text{M} + 2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{MH} + 2\text{OH}^- \quad (2.14)
\end{equation}

During overdischarging, the hydrogen generated from the polarity-reversed nickel positive electrode is oxidized into water at the hydrogen storage alloy negative electrode according to the following reactions:

\begin{equation}
\text{(Positive): } \quad 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad (2.15)
\end{equation}

\begin{equation}
\text{(Negative): } \quad \text{H}_2 + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 2e^- \quad (2.16)
\end{equation}

\begin{equation}
2\text{OH}^- + 2\text{MH} \rightarrow 2\text{H}_2\text{O} + 2\text{M} + 2e^- \quad (2.17)
\end{equation}
Thus, for both overcharge and overdischarge reactions, no net change occurs. The unique protective function of the Ni-MH battery against overcharging or discharging allows a completely hermetic design of the battery to be achieved.

### 2.5.3 Equilibrium potential of metal hydride electrodes

*(Electrochemical P-C isotherms)*

In the equilibrium state, the hydrogen partial pressure $P(\text{H}_2)$ on the electrode can be equal to the hydrogen equilibrium pressure $P_{\text{equ}}(\text{H})$ of the MH. According to the Nernst equation, the potential of the anode corresponds to a pressure of hydrogen gas on the surface which is equilibrated with atomic hydrogen in the hydride ($\text{H}_2 \leftrightarrow 2\text{H}$) as follows [241,242]:

$$E(\text{H}) - E(\text{HgO/Hg}) = [E(\text{H})^0 - E(\text{HgO/Hg})^0] + \left(\frac{RT}{2F}\right) \ln \left[\frac{a(\text{H}_2\text{O})}{a(\text{H}_2)}\right]$$

$$= [E(\text{H})^0 - E(\text{HgO/Hg})^0] + \left(\frac{RT}{2F}\right) \ln \left[\frac{a(\text{H}_2\text{O})}{a(\text{H}_2)}\frac{\gamma(\text{H}_2)}{P(\text{H}_2)}\right] \quad (2.18)$$

where $E(\text{H})^0$ and $E(\text{HgO/Hg})^0$ are the standard potentials of the $\text{H}_2\text{O}/\text{H}$ couple and the $\text{HgO/Hg}$ couple, respectively; $a(\text{H}_2\text{O})$ is the activity of water; $a(\text{H}_2)$ is the activity of hydrogen; $\gamma(\text{H}_2)$ is the fugacity coefficient, $P(\text{H}_2)$ is the hydrogen partial pressure. Wakao and Yonemura reported that the plateau pressures obtained from
electrochemical measurement for LaNi$_{5-x}$M$_x$ (M=Cu, Cr, Mn, Al) electrodes showed excellent agreement with those obtained by the conventional Sieverts’ method [243].

Sakai and co-workers [20,242] obtained the electrochemical pressure-composition isotherms at different temperatures for various LaNi-based alloys to evaluate the charged and discharged pressures of the electrodes. This technique was also applied for evaluating electrochemical hydrogen desorption behaviours in thin films of alloys [244, 245] and amorphous MNi$_2$ (M=La, Ce, Pr, Mm) alloys [246, 247].

2.5.4 Kinetic properties of metal hydride electrodes

The mechanism for charging-discharging the MH electrode is shown in Figure 2.23. First, charge transfer reaction produces adsorbed atomic hydrogen (H$_{ad}$) and OH$^-$ on the electrode surface (Volmer process; eq. 2.19). If the diffusion rate of the atomic hydrogen can not follow the production rate, the hydrogen evolution reaction occurs (Tafel process; eq. 2.20). The atomic hydrogen has to diffuse from the surface to the bulk through the surface layer and grain boundaries before hydride formation in eq. (2.21):

\[
\begin{align*}
H_2O + e^- & = H_{ad} + OH^- \quad \text{(Volmer process)} , \\
2H_{ad} & = H_2 \quad \text{(Tafel process)} , \\
H_{ad-surface} & = MH \quad \text{(Hydride)} .
\end{align*}
\]
The rate of the charge-discharge reaction is expected to depend on [164]:

1. surface conductivity of the alloy particles,
2. effective surface area per unit weight of alloy or per unit area of electrode which is always changing by decrepitation, surface oxidation and dissolution of component elements,
3. diffusivity of hydrogen from the surface to the bulk alloy,
4. diffusivity of OH$^{-}$ ion and H$_2$O to/from reaction surface,
5. contact resistance between alloy and current collector.

![Mechanism for charging-discharging the MH electrode](image)

**Figure 2.23** Mechanism for charging-discharging the MH electrode [164].
2.5.5 Electrochemical impedance analysis of MH electrodes

Electrochemical impedance spectroscopy (EIS) is an effective technique for analysing the mechanisms of interfacial electrochemical reactions. Kuriyama et al. [248-250] have conducted systematic analyses of the electrode reaction using electrochemical impedance spectroscopy. A Cole-Cole plot of the impedance of an MH electrode using a copper-coated MnNi3.5Co0.7Al0.8 alloy was well fitted by the equivalent circuit shown in Figure 2.24. $R_1$ was assigned to the electrolyte resistance. $R_2$ was ascribed to the contact resistance between current collector and alloy. $R_3$ was considered to be due to the contact resistance between alloy particles. $R_4$ was ascribed to the reaction resistance on the alloy surface. During 440 cycles, $R_2$ and $R_3$ did not change, showing that the copper layer on the alloy could preserve good electrical conductivity in the electrode, while $R_4$ increased significantly because of the degradation of the alloy surface. Even storage of the copper coated alloy in air for 6 months caused an increase in the $R_4$. The Warburg impedance ($W_4$) was related to the diffusion of hydrogen and electrolyte solution. When the electrode was made without copper coating, the contact resistances ($R_2$ and $R_3$) significantly increased with increasing discharge depth, and with increasing cycles. This result shows that a suitable electrode structure for giving the alloy powder a good conductivity, is important in order to test the electrode performance of the alloys.
Figure 2.24  Schematic representation of (a) a Cole-Cole plot of impedance and (b) an equivalent circuit for metal hydride electrodes. $R_n$, resistive components; normal capacitive component; $Q_n$, capacitive components in order to describe a depressed semicircle; $W_4$, Warburg impedance; $Q_b Q_i(\omega) = [Y_{i0} (j\omega)^n]^{-1}, (1<n<1)$ [248].
2.6 Summary

Commercial nickel-metal hydride rechargeable batteries using a hydrogen storage alloy as the negative electrode have been replacing the environmentally dangerous Ni-Cd batteries. Because of their advantages in terms of rate capabilities, volumetric energy densities, and long life cycle, they are widely used in mobile phones, lap-computers, camcorders, shavers, and military applications. Also they are considered a viable alternative for electric vehicle applications. Although many hydrogen storage alloys will react directly and reversibly with hydrogen to form hydrides, few can satisfy all of the criteria required for wide use as negative materials for Ni-MH batteries. Only the AB$_5$-type (rare-earth system) and AB$_2$ Laves phase-type (zirconium-based system) hydrogen storage alloys have been well studied and are used as negative materials for the commercial production of Ni-MH battery. However, major problems still lie in the capacity and the cost of the negative materials — hydrogen storage alloys.

Magnesium-based alloys, as previously mentioned, are promising materials for technological applications of hydrogen storage because of their capacities to store large amounts of hydrogen and their low cost. Iron-titanium-based alloys are also the cheapest of the promising hydrogen conversion and storage materials. However, crystalline Mg-based and Fe-Ti type hydrogen storage alloys have very poor
discharge capacities as Ni-MH electrodes because of their slow hydriding/dehydriding kinetics at ambient temperature in alkaline solution.

This literature review has shown that amorphous and nanocrystalline metals and alloys are novel materials which attract much attention from materials scientists because of their excellent properties compared with their crystalline counterparts. The amorphous and nanocrystalline Mg-based and FeTi-type alloys produced by ball-milling results in dramatic changes in gas phase hydrogen sorption properties, especially by elimination of the need for activation and improvement of hydriding/dehydriding kinetics.

Therefore, there appear to be some possibilities to achieve high discharge capacities for amorphous and nanocrystalline Mg-based and FeTi-type alloy negative electrodes. The main purpose of this study is to investigate the formation of the amorphous and nanocrystalline Mg-based and FeTi-type alloys produced by mechanical milling and mechanical alloying methods, and to examine their electrochemical hydriding/dehydriding properties as negative electrode materials for the Ni-MH secondary battery.
CHAPTER 3 EXPERIMENTAL DETAILS

3.1 Metals and chemicals

Most metals and chemicals used in this work were supplied by the Aldrich Chemical Company Pty. Ltd. They are detailed in Table 3.1.

The high purity argon gas (99.999 %) used for the preparation and processing of iron-titanium and magnesium-based alloys was supplied by BOC GASES Company Limited.

3.2 Preparation of alloys

3.2.1 Fe-Ti Alloys

The intermetallic compound FeTi was fabricated by electric arc melting with the required proportions of iron and titanium under an argon atmosphere. Both iron and titanium were cut into small pieces before the electric arc melting. After melting, the molten solution of iron-titanium was poured into a copper mould cooled by flowing
water. To ensure the homogeneity of the alloy, the alloy ingot was re-melted several times. After repeated melting, the alloy ingot was quite brittle and could very easily be broken into pieces. The as-cast ingot was crushed and mechanically ground to powders for further preparation of samples.

**Table 3.1** Descriptions of metals and chemicals

<table>
<thead>
<tr>
<th>Product</th>
<th>Purity (%), shape and particle size (mesh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium</td>
<td>99.8 (powder), 50 (μm)</td>
</tr>
<tr>
<td>Nickel</td>
<td>99.7 (powder), 100 (μm)</td>
</tr>
<tr>
<td>Iron</td>
<td>99.9 (powder), 80 (μm)</td>
</tr>
<tr>
<td>Iron</td>
<td>99.9 (pieces)</td>
</tr>
<tr>
<td>Vanadium</td>
<td>99.5 (powder), 325</td>
</tr>
<tr>
<td>Cobalt</td>
<td>99.9 (powder), 100</td>
</tr>
<tr>
<td>Cobalt</td>
<td>99.9 (pieces)</td>
</tr>
<tr>
<td>Titanium</td>
<td>99.9 (powder), 10 (μm)</td>
</tr>
<tr>
<td>Titanium</td>
<td>99.7 (rod)</td>
</tr>
<tr>
<td>Potassium Hydroxide (KOH)</td>
<td>85+</td>
</tr>
<tr>
<td>Poly(vinyl alcohol) hydrolysed (PVA[-CH₂CH(OH)ₙ])</td>
<td>99</td>
</tr>
</tbody>
</table>
3.2.2 Magnesium-based alloys

3.2.2.1 Sintered Mg-based alloys

The sintered Mg-based alloys were manufactured by a powder metallurgical method from chemically pure metal powders. The metal powders were well mixed in the required proportions and sintered under an argon atmosphere at 620 °C or 700 °C for 9 to 10 hours.

All as supplied powders were carefully opened in a glove box filled by an argon atmosphere to prevent oxidation. The metal powders prepared according to the required stoichiometric ratios were thoroughly mixed under an argon gas atmosphere using a planetary mill (Fritsch Pulverisette 5). The well-mixed metal powders were compressed into pellets at a pressure of 5×10^3 kgf cm^-2, transferred into sintered alumina boats, and then put in a vacuum tube furnace. After flushing the vacuum chamber of the tube furnace with argon gas several times, the pellets were sintered in the tube furnace under an argon atmosphere at different temperature for certain hours, then finally cooled to room temperature in the furnace to obtain the sintered Mg-based alloys.

3.2.2.2 Induction melted Mg_2Ni alloy

The induction melted (IM) Mg_2Ni alloy was supplied by the Santoku Metal Industry Co., Japan. The composition of the IM Mg_2Ni alloy was analysed by the Santoku
Metal Industry Company using an inductively coupled plasma (ICP) method and is shown in Table 3.2.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium</td>
<td>46.58</td>
</tr>
<tr>
<td>Nickel</td>
<td>Balance</td>
</tr>
<tr>
<td>Aluminium</td>
<td>0.07</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.03</td>
</tr>
<tr>
<td>Iron</td>
<td>0.09</td>
</tr>
<tr>
<td>Calcium</td>
<td>&lt; 0.01</td>
</tr>
</tbody>
</table>

### 3.3 Mechanical milling and alloying

All the mechanical milling and alloying work was performed with a Fritsch (Pulverisette 5) planetary ball mill. The vial and balls were made from stainless steel and hardened steel, respectively. To avoid the oxidation of the samples, the ball mill vials were degassed using a vacuum pump, and filled with high pure argon gas.
several times. Then the ball mill vials were well sealed and filled argon gas at a pressure of about 2 kgf cm⁻².

3.3.1 Ball milled Fe-Ti alloys

The starting material was in two forms: the intermetallic compound FeTi, or mixture of the iron and titanium powders.

For the mechanical milling of the intermetallic compound FeTi, the crushed FeTi alloy was ball milled at 160 rpm in an argon atmosphere. The weight ratio of ball to sample was 30:1. After several hours of milling, the milled powders were examined by X-ray diffraction (XRD). Mechanical alloying was completed using the same equipment but using pure iron powder and pure titanium powder. The experimental conditions were the same as for the mechanical milling.

3.3.2 Ball milled sintered Mg-based alloys

To obtain more active alloy powders, the sintered Mg-based alloys and pure metal powder (nickel or cobalt) were mixed at an atomic ratio of 1:1. Then the sintered Mg-based alloys and pure metal powder were ball milled in an argon atmosphere for various periods of time at 150 rpm in an argon atmosphere. The weight ratios of ball to sample were 30:1 and 100:1, respectively. After each specified number of hours of milling, the milled powders were examined by X-ray diffraction.
3.3.3 Ball milling of induction melted Mg-based alloys

For the preparation of nanocrystalline Mg$_2$Ni, the induction melted Mg$_2$Ni alloy was ball milled for a period of 70 hours at 200 rpm under the protection of an argon atmosphere. The weight ratio of ball to sample was 30:1.

The induction melted Mg$_2$Ni alloy was mixed and ball-milled with Ni and V powders for a period of 70 hours at 200 rpm in an argon atmosphere. The starting alloy compositions are listed in Table 3.3. After milling, the powders were examined by X-ray diffraction.

<table>
<thead>
<tr>
<th>Mg$_2$Ni, Ni and V ratio (molar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$_2$Ni + Ni</td>
</tr>
<tr>
<td>Mg$_2$Ni + 1.28 Ni</td>
</tr>
<tr>
<td>Mg$_2$Ni + Ni + 0.1V</td>
</tr>
<tr>
<td>Mg$_2$Ni + Ni + 0.2V</td>
</tr>
<tr>
<td>Mg$_2$Ni + Ni + 0.4V</td>
</tr>
<tr>
<td>Mg$_2$Ni + 1.28 Ni + 0.1V</td>
</tr>
</tbody>
</table>

Table 3.3 Compositions of ball milled Mg-based alloys
3.4 Electrode fabrication

The as-produced hydrogen storage alloy was crushed into powder and mixed with Ni powder in the weight ratio of 1:1 to make the electrodes. The addition of the nickel powder is designed to enhance the electronic conductivity. The hydrogen storage alloy powders obtained from mechanical milling and mechanical alloying were also mixed with Ni powder in the weight ratio of 1:1 for electrode preparation. The polyvinyl alcohol (PVA, 3 \% wt.) solution, which was used as a binder, was prepared by mixing pure polyvinyl alcohol with distilled water at the temperature of 80 °C for more than 6 hours.

The hydrogen storage alloy electrodes were fabricated by mixing the powders with the polyvinyl alcohol solution and pasting them into a foamed nickel matrix, which acted as the current collector for the electrode. The foamed nickel was spot-welded to a nickel wire for the connection. The alloy electrodes were put into a glove box filled with argon until they were fully dried. After being compressed at a pressure of 1000 kgf cm\(^{-2}\), each electrode was impregnated with the electrolyte for at least 2 hours prior to the charge-discharge cycle tests, in order to fully soak the test electrode. The alloy electrodes were then ready for the measurement of the electrochemical properties.
3.5 Charge/discharge properties

Electrochemical charge-discharge cycle tests of the hydrogen storage alloy electrodes were conducted in a double compartment cell which were separated from each other by a porous glass plate. The hydrogen storage alloy electrodes were immersed as the anodes in the test cell. The test anode was set in one compartment with a sintered NiOOH/Ni(OH)$_2$ counter electrode in other compartment. The total capacity of the sintered NiOOH/Ni(OH)$_2$ cathode electrode used was much larger than that of the anode electrode. The test cell was filled with a 6 M KOH electrolyte solution. A mercury oxide electrode (Hg/HgO) was used as the reference electrode.

The electrochemical charge-discharge properties of the alloy electrodes were measured by using an automatic battery test unit, which monitored the potential of the alloy electrode with respect to an Hg/HgO reference electrode. The battery test unit was controlled by a microcomputer. The measurement was performed at ambient temperature. In the charge-discharge cycle tests, the charge cycle was commenced using a current density of 100 mA per gram of hydrogen storage alloy for 10 hours. Then, after one minute rest, the discharge was continued using a current density of 50 mA/g until the voltage of the negative electrode against the mercury oxide electrode reached -0.5 or -0.6 V. The discharge capacities of the alloy electrodes were calculated based on the total weight of the hydrogen storage alloys.
3.6 Physical analyses

3.6.1 X-ray diffraction and thermal analysis measurements

The phase structure of all the alloys used in this study was identified by an X-ray diffraction (XRD) method. The X-ray diffraction measurements were conducted in a Philips PW1010 X-ray diffractometer with Cu $K_\alpha$ ($\lambda = 1.540562 \text{ Å}$) radiation. The voltage and current were 40 kV and 20 mA, respectively. The average grain size of nanocrystalline alloys was calculated from the X-ray diffraction data using the Scherrer equation [257]:

$$d = \frac{0.89 \lambda}{\beta \cos \theta}$$

(3.1)

where $\lambda$ is the X-ray wavelength, $\beta$ is the full width at half height and $\theta$ is the position of the selected Bragg angle. After subtracting the instrumental broadening and microstress broadening, the $\beta$ value was used in the equation.

Thermal analysis was performed using a Setaram differential thermal (DTA) and thermogravimetric (TG) analyser at a heating rate of 10 °C/min under the protection of a pure argon atmosphere. The weight of the samples for the thermal analyses was approximately 0.03 g.
Chapter Three

Experimental Details

3.6.2 Particle size, morphology and microstructural examination

Particle distribution and specific surface area analysis of the metal and alloy powders were determined by a Malvern particle analyser (300 Rfmm range and 2.40 mm beam).

Morphologies, energy dispersive X-ray spectra (EDS) and X-ray mapping analyses of the alloy powders were carried out using a Leica Stereoscan 440 scanning electronic microscope (SEM), Oxford ISIS system and an OXFORD Link Pentatet detector. The ball milled powders were pressed on electric conducting sticky tapes. The tapes were adhered to the SEM sample holders. Then, the ball milled powders were put into the chamber and ready to be examined by SEM and EDS.

The morphology and diffraction patterns of the powders of ball milled hydrogen storage alloys were examined using a JEOL 2000 FX transmission electron microscope (TEM). The accelerating voltage was 120 kV. The ball milled powders were added into an acetone solution and treated in an ultrasonic cleaner for ten minutes. After the treatment, the powders were dried and ready to be examined by TEM.
Chapter Four  
Formation and Electrode Properties of Amorphous and Nanocrystalline FeTi Alloys

CHAPTER 4  FORMATION AND ELECTRODE PROPERTIES OF AMORPHOUS AND NANOCRYSTALLINE FeTi ALLOYS

4.1 Introduction

FeTi alloy is one of the prime candidates for hydrogen storage systems [5]. It is also a typical hydrogen storage alloy of the AB-type. However, the intermetallic FeTi does not absorb hydrogen under normal conditions and has to be activated before the hydrogen is readily absorbed. Activation (usually in powder form) involves heating FeTi to higher temperature (about 450 °C) in vacuum and annealing in H₂ at a certain pressure (about 7 bar), followed by cooling down to room temperature and admission of hydrogen at a pressure of 35-65 bars. Many research results indicate that the activation process is necessary because of the presence of an oxide film, which obstructs hydrogen absorption [168-172]. The activation of FeTi hydrogen storage alloy is one of the fundamental problems that must be solved. In addition, after activation FeTi is readily poisoned by exposure to air or other gases and gas mixtures [5,167].
The lowest free energy state of a solid at low temperature is the perfect crystal. However, it is well known that solids deviating from this perfectly ordered structure exhibit attractive features. In recent years nanocrystalline and amorphous alloys have been developed for hydrogen storage. For instance, Zaluski et al. reported that the activation of nanocrystalline and amorphous FeTi alloys was found to be much easier than their crystalline counterpart [183]. Up to the present, however, there is no literature reported the research work on the FeTi-type hydrogen storage alloys used for the negative electrode of the Ni-MH battery at room temperature.

In this chapter, the nanocrystalline and amorphous FeTi alloys were fabricated by ball milling using a planetary ball mill. Their grain size and particle distribution were determined. Small amounts of oxygen were found to have a significant effect on the formation of the FeTi alloy during the mechanical alloying process. Both amorphous and nanocrystalline FeTi alloys exhibited much higher discharge capacities as metal hydride electrodes in comparison with crystalline FeTi alloy.
4.2 Formation of nanocrystalline and amorphous FeTi alloys

4.2.1 FeTi alloy by mechanical milling

After mechanical milling, the structure of intermetallic compound could be nanocrystalline [109,116,156,174,252] or amorphous [73,74,90,98,253-256].

Figure 4.1 shows the X-ray diffraction patterns of the FeTi alloy with different milling times. During the MM process, the peaks of the FeTi phase gradually broadened with increasing ball milling time. The grain size of the FeTi phase decreases with ball milling time. By measuring the half-maximum width of the broadening XRD lines, the average grain size $d$ can be calculated by using the Scherrer equation: $d = \frac{0.89\lambda}{\beta \cos \theta}$, where $\lambda$ is the X-ray wavelength, $\beta$ is the full width at half height and $\theta$ is the position of the selected Bragg angle [257].

The reduction of the average grain size of the FeTi phase with increasing ball milling time is shown in Figure 4.2. The average grain size of FeTi alloy is about 8 nm after 40 hours of ball milling. Hellstern et al. [130] have studied the structure evolution of the intermetallic compound AlRu with ball milling time in a Spex shaker mill. They used measurements of X-ray diffraction line broadening to estimate the crystallite size and studied the microstructural evolution by transmission electron microscopy.
(TEM) and high resolution electron microscopy (HREM). They had observed that at the early stages of milling the deformation was localized with shear bands approximately 0.5 to 1μm wide. Small grains, 8-12 nm diameter, were seen within the shear bands and the misorientation angles between the grains were relatively small. The grain size decreased steadily and the shear bands coalesced for longer milling times. The small angle boundaries were replaced by higher angle boundaries, implying grain rotation. Fecht et al. [252,258] studied the formation of nanocrystalline structures by ball milling several intermetallic compounds with the CsCl structure. They observed decreases in grain size as a function of milling time by using both X-ray diffraction line broadening and TEM measurements. The intermetallic compound FeTi also has the CsCl structure. It therefore seems likely that it also should have the same mechanism of nanocrystalline structure formation by ball milling.

The differential thermal analysis (DTA) and thermogravimetric analysis (TG) traces for the MM FeTi alloy after 40 hours milling (Figure 4.3 (b)) are compared with those for an empty crucible in Figure 4.3 (a). It may be seen that there are some small exothermic peaks for the MM FeTi alloy above 300 °C, but no weight change during the heating process from room temperature to 1000 °C in an argon atmosphere. The results in Figure 4.3 (b) suggest that there is recrystallisation and grain growth during the heating process.
Figure 4.1  X-ray diffraction patterns of the FeTi alloy at different ball milling times.
Figure 4.2  Average grain size of the FeTi phase of the milled FeTi alloy in relation to the ball milling time.
Figure 4.3 DTA and TG traces of the empty crucible (a) and MM FeTi alloy after milling 40 hours (b) at a heating rate of 10 °C min⁻¹.
4.2.2 FeTi alloy by mechanical alloying

In mechanical alloying the resultant powder develops by the repeated cold welding and fracture of the powder particles until the final composition of the powders corresponds to the percentages of the respective constituents in the initial charge. While the primary application of MA has been the production of oxide dispersion strengthened alloys, in recent years this technique has been used to make a wide range of materials including many metastable structures such as amorphous [35,41,42, 89-101], nanocrystalline [259-261] and quasicrystalline materials [262].

As shown in Figure 4.4, the X-ray diffraction patterns of the Fe and Ti powders have an atomic ratio of 1:1 after milling for 0, 10, 20, and 40 hours. The peak of amorphous FeTi phase appears after milling for 20 hours. The resultant powders become a single amorphous FeTi phase after milling for 40 hours. Figure 4.5 shows the traces of DTA and TG of the MA FeTi alloy after 40 hours of milling. It is seen that there is an amorphous exothermic peak from 436 °C to 576 °C. The crystallization temperature of the amorphous FeTi alloy is about 464 °C.
Figure 4.4  X-ray diffraction patterns of the Fe and Ti powders after milling for 0, 10, 20, and 40 hours.
Figure 4.5  DTA and TG traces of the Fe and Ti powders after milling 40 hours at a heating rate of 10 °C min⁻¹.

4.3  Particle distribution and morphologies of FeTi alloys

Figure 4.6 shows the analysis of the particle distribution of (a) the Fe, Ti powders, (b) amorphous FeTi alloy and (c) nanocrystalline FeTi alloy. Before milling, the Ti and Fe powders were about 8 μm and 70 μm respectively. After milling 40 hours, the Fe and Ti powders alloyed to form the amorphous FeTi alloy with particle size
between 2-50 \( \mu m \). Most of the particles of the amorphous FeTi powders are around 10 \( \mu m \). The particle size of the nanocrystalline FeTi alloy is in the range of 3-30 \( \mu m \). Most of particle sizes of the nanocrystalline FeTi powders are about 13 \( \mu m \), only a little larger than that of the MA FeTi powders.

**Figure 4.6** Particle distribution of the (a) Fe and Ti powders, (b) amorphous FeTi alloy powders and (c) nanocrystalline FeTi alloy powders.
Table 4.1 lists the specific surface areas of the MA and MM FeTi alloys after milling 40 hours. It is seen that the specific surface area of the MA FeTi alloy is more than twice that of the MM FeTi alloy although the particle size of MA FeTi alloy is only a little smaller than that of the MM FeTi alloy.

Table 4.1  Specific surface area of MM and MA FeTi alloys

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific surface area (m²g⁻¹)</th>
<th>Microstructure</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeTi alloy by MM 40 h</td>
<td>1.18</td>
<td>Nanocrystalline</td>
</tr>
<tr>
<td>FeTi alloy by MA 40 h</td>
<td>2.49</td>
<td>Amorphous</td>
</tr>
</tbody>
</table>

The particle size and morphologies of the FeTi alloys can also be determined by SEM. Figure 4.7 shows the SEM images of the (a) Fe and Ti powders before milling, (b) after milling 40 hours and (c) FeTi alloy powder after ball milling 40 hours. The SEM results of the Fe and Ti powders, amorphous FeTi alloys and nanocrystalline FeTi alloy powders are consistent with the results of the particle distribution. In Figure 4.7 (a), the small particles are Ti and the large particles are Fe. The MA and MM FeTi alloys have very rough surfaces that should be favourable for hydrogen absorption.
Figure 4.7 (continues)
4.4 Effect of small amounts of oxygen on the mechanical alloying

Figure 4.8 shows the X-ray diffraction pattern of the mechanically alloyed Fe and Ti powders when there was a small amount of air in the protecting argon atmosphere. After milling for 100 hours, the peaks of Ti disappear and the peak of TiO$_2$ appears. This means that the most of the Ti powder was oxidized to form amorphous titanium.
oxide. Figure 4.9 shows the DTA and TG traces of the Fe and Ti powders after milling 100 hours. The peak 1-2 is the FeTi alloy melting enthalpy and the peak 3-4 is the melting enthalpy of the Fe element. Only a small amount of the Ti appears to have combined with the Fe to produce the FeTi alloy. During the heating from 45 °C to 1600 °C, no weight change occurred for the sample. That means no phases oxidized during the heating. From the EDS spectra of the Fe and Ti powders after milling 100 hours, it is seen that there is a certain amount of oxygen in the sample.

It can be concluded that oxygen combined with Ti powders to form amorphous titanium oxide and unoxidized Ti powders reacted with Fe powders to form a small amount of FeTi alloy. This was too small to be seen in the X-ray pattern. The results show that small amounts of oxygen present during the mechanical alloying have a significant effect on the formation of the FeTi alloy.
Figure 4.8  X-ray diffraction pattern of the mechanical alloying Fe and Ti powders when there was a small amount of air in the protective argon atmosphere.
**Figure 4.9** DTA and TG traces of the Fe and Ti powders after ball milling for 100 hours.
4.5 FeTi alloy electrodes

4.5.1 Charge/discharge performance

Based on the electrochemical reversible storage of hydrogen, the hydrogen storage alloy electrode acts as a rechargeable electrode in an alkaline aqueous solution. The charge/discharge reactions which occur during the charging and discharging of a hydrogen storage alloy electrode (M) in an alkaline electrolytes can be represented as follows:

(i) charge:

\[ M + x H_2O + x e^- \rightarrow MH_x + x OH^- \]  \hspace{1cm} (4.1)

(ii) discharge:

\[ MH_x + x OH^- \rightarrow M + x H_2O + x e^- \]  \hspace{1cm} (4.2)

when \( x = 1 \), \( E^0 = -0.828 \) V vs. standard hydrogen electrode. Equation (4.1) indicates that on charging, the hydrogen storage alloy (M) will react with \( H_2O \) at the interface with the electrolyte and the incoming electrons (\( e^- \)) to absorb hydrogen within its structure metal hydride (MH). The hydroxyl ions (\( OH^- \)) produced are released to the electrolyte. Equation (4.2) shows the reaction which proceeds on discharging. The hydrogen charged alloy reacts with hydroxyl ions producing water,
releasing electrons to the external circuit and becomes depleted of its stored hydrogen. Each absorbed/desorbed hydrogen atom corresponds to the storage of one electron. Therefore, the theoretical electrochemical capacity of a metal hydride electrode may be calculated using Faraday’s law:

\[ C_{th} = \frac{xF}{(3.6M)} \quad (\text{mAh g}^{-1}) \quad (4.3) \]

where \( C_{th} \) is the alloy’s theoretical electrochemical capacity, \( x \) is the number of hydrogen atoms per alloy unit, \( F \) is the Faraday constant and \( M \) is the molecular weight of the alloy. Table 4.1 lists the calculated values of the theoretical electrochemical capacities of some typical hydrogen storage alloy electrodes.

**Table 4.2** Theoretical capacities of LaNi\(_5\)H\(_6\), FeTiH\(_{1.95}\) and Mg\(_2\)NiH\(_4\) hydride electrodes.

<table>
<thead>
<tr>
<th>Hydride electrode</th>
<th>Theoretical capacity (mAh g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaNi(_5)H(_6)</td>
<td>372</td>
</tr>
<tr>
<td>FeTiH(_{1.95})</td>
<td>504</td>
</tr>
<tr>
<td>Mg(_2)NiH(_4)</td>
<td>999</td>
</tr>
</tbody>
</table>
Theoretically, either FeTiH\textsubscript{1.95} hydride electrode or Mg\textsubscript{2}NiH\textsubscript{4} hydride electrode has a much higher electrochemical capacity than that of well known commercialised AB\textsubscript{5}-type hydride electrode. However, there is no literature reporting the FeTi-type hydrogen storage alloys being used for the negative electrodes of Ni-MH batteries, and it is known that coarse grained polycrystalline Mg-based hydrogen storage alloys have very poor discharge capacities as Ni-MH electrodes because of their slow hydriding/dehydriding kinetics at ambient temperature [7,8,108].

Figure 4.10 shows the galvanostatic discharge curves of the crystalline, nanocrystalline and amorphous FeTi alloy electrodes at the first charge-discharge cycle in 6M KOH aqueous solution at 25 °C. The charge cycle was commenced using a current density of 100 mA per gram of FeTi alloy for 5 hours, then after one minute rest, the discharge was continued using a current density of 50 mA g\textsuperscript{-1} until the voltage of the negative electrode against the mercury oxide electrode reached -0.5 V. The common induction melted crystalline FeTi alloy has an extremely low discharge capacity of only 3 mAh g\textsuperscript{-1} which is much less than the capacity obtained by converting the capacity in the gas-phase reaction into electrochemical units. This indicates that the crystalline FeTi alloy has very poor electrochemical hydriding/dehydriding behaviour in the electrolyte, so that the amount of the electrochemically absorbed hydrogen is much less than that in the gas-phase. Therefore, it is considered that the common crystalline FeTi alloy is not suitable for use as a rechargeable anode material in an alkaline solution at room temperature.
The nanocrystalline FeTi alloy has an improved discharge capacity of 54 mAh g$^{-1}$ at the first discharge, which is much higher than that of crystalline FeTi alloy, but is only around 10% of the calculated theoretical electrochemical capacity of FeTi alloy. Because the average grain size of the nanocrystalline FeTi alloy is around 8 nm, the atoms in its grain boundaries could be estimated [141] (also see Chapter 2, Figure 2.8) and should be about 20%. Due to the good catalytic activity [109,110] and electrocatalytic activity [263-265] of nanocrystalline materials, it can be inferred that the atoms in the grain boundaries of the nanocrystalline FeTi alloy were electrochemically reacted with hydrogen to form the hydride in the first charge-discharge cycle.

The amorphous FeTi alloy has the highest discharge capacity of 220 mAh g$^{-1}$ at the first charge-discharge cycle, even higher than that of the nanocrystalline FeTi alloy. This is because the amorphous alloys have no long range ordering, their surfaces are much richer in low-coordination sites and defects which play important roles in the catalytic activity of materials [266].

The galvanostatic charge-discharge curves of the amorphous FeTi alloy electrode on the first cycle are shown in Figure 4.11. The charge curve is a typical charge curve of the FeTi alloy in which the charge voltage goes up quickly. For the amorphous FeTi alloy, its charge voltage goes up to the maximum after charging for about 30 minutes at a charge current density of 100 mA g$^{-1}$. During the discharge process, the discharge curve has a plateau region at around −0.87 V vs. Hg-HgO electrode.
Figure 4.10  Galvanostatic discharge curves of the crystalline, nanocrystalline and amorphous FeTi alloy electrodes at first charge-discharge cycle in 6M KOH aqueous solution at 25 °C.
Figure 4.11 Charge-discharge curves of the amorphous FeTi alloy electrode on the first cycle in 6M KOH aqueous solution at 25 °C. The amorphous FeTi alloy was obtained by ball milling Fe, Ti powders for 40 hours.
Figure 4.12 shows the charge-discharge curves of the amorphous FeTi alloy electrode from the first to the tenth cycles at a discharge current density of 50 mA g$^{-1}$. It can be seen that the discharge capacity of the amorphous FeTi alloy electrode decreases quickly with increasing cycle number, the discharge plateau region becomes small and the mean discharge potential is gradually reduced.

4.5.2 Cycle lives of the FeTi alloy electrodes

Figure 4.13 shows the discharge capacities of the crystalline, nanocrystalline and amorphous FeTi alloy electrodes after repeated charge-discharge cycles at a discharge current density of 50 mA g$^{-1}$. After 20 cycles, the discharge capacity of the crystalline FeTi alloy is still very poor, which means that repeated charging-discharging did not alter the electrochemical hydriding/dehydriding kinetics of the alloy in the alkaline solution. After 20 cycles, the discharge capacity of the nanocrystalline FeTi alloy shows almost no change, although it is not very high.
Figure 4.12  Discharge curves of the amorphous FeTi alloy electrode on first to tenth cycles.
Figure 4.13  Discharge capacities of the crystalline, nanocrystalline and amorphous FeTi alloy electrodes after repeated charge-discharge cycles at a discharge current density of 50 mA g\(^{-1}\) at 25 °C.
Generally, the most commonly used AB\textsubscript{5}-type alloys hydrogen storage alloy electrodes reach their maximum values of discharge capacity after a certain number of charge-discharge cycles [20,267-272]. By contrast, the amorphous FeTi alloy achieves its highest discharge capacity of 220 mAh g\textsuperscript{-1} on the first charge-discharge cycle because the amorphous alloy has high electrocatalytic activity [273]. This discharge capacity is comparable with the capacities of commercial alloys. Unfortunately, due to the oxidation of the amorphous FeTi alloy in the alkaline solution, its discharge capacity decreases rapidly with increasing the charge-discharge cycles, but it still has a discharge capacity of 78 mAh g\textsuperscript{-1} at the twentieth cycle.

4.6 Conclusions

In this chapter, the formation of nanocrystalline and amorphous FeTi alloys were investigated, and the charge-discharge properties of the nanocrystalline and amorphous FeTi alloys were explored in 6M KOH aqueous solution at room temperature. It can be concluded that:

- Nanocrystalline and amorphous FeTi alloys can be obtained by ball milling using a planetary ball mill with an argon atmosphere.

- FeTi alloy after mechanical milling 40 hours became nanostructured powders with an average grain size of about 8 nm, a particle size of about 13 μm and a...
specific surface area of 1.18 m²g⁻¹. Fe and Ti powders after mechanical alloying for 40 hours became amorphous powders with a particle size of about 10 μm and a specific surface area of 2.49 m²g⁻¹. Small amounts of oxygen present during the mechanical alloying process have a significant effect on the formation of the FeTi alloy.

- The induction melted crystalline FeTi alloy has an extremely low discharge capacity of only 3 mAh g⁻¹ at a discharge current density of 50 mA g⁻¹, which is negligibly small compared with its theoretical discharge capacity. Therefore, the common crystalline FeTi alloy is not suitable for use as a rechargeable anode material in an alkaline solution at room temperature.

- The nanocrystalline FeTi alloy has an improved discharge capacity of 54 mAh g⁻¹ on the first discharge, which is much higher than that of crystalline FeTi alloy, but is only around 10 % of the calculated theoretical electrochemical capacity of the FeTi alloy. Due to its good discharge capacity during the first twenty cycles, it may be possible to improve the electrochemical discharge capacity of FeTi-type alloy with good cycle life by achieving a nanocrystalline structure.

- Unlike commercial AB₅-type hydrogen storage alloy electrodes, the amorphous FeTi alloy achieves its highest discharge capacity of 220 mAh g⁻¹ on the first
charge-discharge cycle at a discharge current density of 50 mA g$^{-1}$. This discharge capacity is comparable with the capacities of commercial alloys. Although the discharge capacity of the amorphous FeTi alloy decreases rapidly on further charge-discharge cycles, it still has a discharge capacity of 78 mAh g$^{-1}$ on the twentieth cycle. Thus, ball milling is an effective method for the FeTi-type alloy to achieve high discharge capacity as an anode material in the Ni-MH battery.
CHAPTER 5 Mg-Ni ALLOY ELECTRODES
PREPARED BY SINTERING AND SUBSEQUENT BALL MILLING WITH NICKEL POWDERS

5.1 Introduction

Mg-based hydrogen storage alloys possess very high hydrogen absorption capacity. Magnesium is also abundant in nature, light in weight and low in cost. As a result, Mg₂Ni-type hydrogen storage alloys are promising energy conversion and storage materials. For a long period, it has been thought that Mg₂Ni-type hydrogen storage alloys, unlike LaNi₅-type hydrogen storage alloys, were unsuitable for Ni-MH negative electrodes because of their slow hydriding/dehydriding kinetics at ambient temperature and their oxidation in alkaline solution. In recent years, some research work on the properties of Mg₂Ni-type alloys has shown that they are promising materials for increasing the negative electrode capacity of Ni-MH batteries. The theoretical discharge capacity of Mg₂Ni alloy is approximately 1000 mAh/g, much higher than that of the main commercial LaNi₅ alloy (which has a capacity of only about 370 mAh/g).
The addition of other elements can increase the discharge capacities of Mg$_2$Ni electrodes. Cui and co-workers reported a discharge capacity of 150 mAh/g for Mg$_{1.9}$Al$_{0.1}$Ni$_{0.9}$Y$_{0.1}$ alloy [7,274] and 90 mAh/g for Mg$_{1.8}$Ti$_{0.2}$Ni$_{0.75}$Fe$_{0.25}$ alloy [275] compared with only 8 mAh/g for Mg$_2$Ni alloy at a discharge current density of 5 mA/g. Microencapsulation of Mg$_2$Ni-type alloys by metal and alloy coatings can also improve the electrode performance. Luo and Cui [276] increased the discharge capacity of Mg$_{1.9}$Al$_{0.1}$Ni$_{0.9}$Y$_{0.1}$ alloy to about 175, 200 and 230 mAh/g at a current density of 10 mA/g by microencapsulation with Ni-B, Ni-P, and Ni-Pd-P respectively. The discharge capacity of the bare Mg$_{1.9}$Al$_{0.1}$Ni$_{0.9}$Y$_{0.1}$ alloy was only 140 mAh/g at the same discharge current density.

Lei et al. obtained improved discharge capacities of around 500 mAh/g for Mg-Ni alloys prepared by mechanical alloying (MA) at a current density of 20 mA/g [14,277]. Iwakura et al. [15] have also improved the discharge capacity of MA Mg-based alloy with graphite surface modification by ball milling (BM). After ball milling Mg$_2$Ni alloys with Ni powders, Kohno et al. have obtained large discharge capacities at a discharge current density of 20 mA/g [16,278]. A Mg$_{1.9}$Al$_{0.1}$Ni$_{0.8}$Co$_{0.1}$Mn$_{0.1}$ alloy was fabricated by ball milling with Ni powder and good discharge capacity was obtained at a discharge current density of 50 mAh/g [17].
Mechanical alloying and milling appear to be effective ways to achieve very high discharge capacities for Mg-based hydrogen storage alloys. The preparation processes of mechanical alloying and/or milling are very flexible, allowing different preparation conditions to affect the alloy structure and electrode properties. In this chapter, I have tried to find a relationship between some of these factors and the properties of the Mg-Ni alloy electrodes prepared by ball milling the sintered Mg$_2$Ni alloys with Ni powders.

### 5.2 Effect of sintering process on properties of Mg-Ni alloy electrodes

#### 5.2.1 Structures of sintered Mg$_2$Ni alloys before and after ball milling

The Mg$_2$Ni alloys were prepared by sintering Mg and Ni powders in their required proportions under an argon atmosphere at 700 °C for 10 hours (alloy I) and 700 °C for 10 hours plus 900 °C for 0.5 hours (alloy II). Table 5.1 lists the sintering processes for two Mg$_2$Ni alloy samples.

The X-ray diffraction patterns of Mg$_2$Ni alloys I and II are shown in Figure 5.1. The Mg$_2$Ni alloy I has a single Mg$_2$Ni phase but the alloy II has mainly Mg$_2$Ni phase and a small amount of an unknown phase. This is probably due to the high temperature
of 900 °C used in the sintering of alloy II, resulting in the vaporisation of a small amount of magnesium. Figure 5.2 shows the X-ray diffraction patterns of Mg$_2$Ni alloys I and II after ball milling with Ni powders in a molar ratio of 1:1 for 50 and 60 hours at 150 rpm, respectively. The ratio of ball to sample weight was 30:1. Mg$_2$Ni alloy II after ball milling with Ni powder for 60 h has mainly an amorphous structure while Mg$_2$Ni alloy I after ball milling with Ni powder for 50 h still shows some Ni phase. This suggests that the longer the ball milling time, the more amorphous phase will be formed. In order to obtain a completely amorphous structure of Mg-Ni alloy prepared by ball milling Mg$_2$Ni with Ni powders using a planetary ball mill, the ball milling time should be more than 60 hours. Figure 5.3 shows the TEM image and corresponding electron diffraction pattern of Mg$_2$Ni alloy II after ball milling which are typical amorphous morphology and diffraction patterns. In Figure 5.3 (a), a marker indicates a particle which has amorphous structure.

**Table 5.1** Sintering processes of two Mg$_2$Ni alloy samples.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Sintering conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$_2$Ni alloy I</td>
<td>700 °C for 10 hours</td>
</tr>
<tr>
<td>Mg$_2$Ni alloy II</td>
<td>700 °C for 10 hours plus 900 °C for 0.5 hours</td>
</tr>
</tbody>
</table>
Figure 5.1  X-ray diffraction patterns of sintered Mg$_2$Ni alloys.
Figure 5.2  X-ray diffraction patterns of sintered Mg$_2$Ni alloys after ball milling with Ni powders.
Figure 5.3  (a) TEM micrograph and (b) corresponding electron diffraction of Mg$_2$Ni alloy II after ball milling for 60 hours.
5.2.2 Discharge capacities of ball milled sintering Mg-Ni alloy electrodes

After ball milling, the most important change in the high discharge capacity Mg-based alloys is that they have completely or mainly amorphous structures. This has been demonstrated by X-ray diffraction analysis [14,16,17,77,277-286], electron diffraction and transmission electron microscopy [16,77,280-282,284,285]. After ball milling the Mg-based hydrogen storage alloys with Ni powders [16,278,281,282,284-286], the composition has the formula MgNi because the reaction during the ball milling process can be expressed by the equation:

\[
\text{Mg}_2\text{Ni} + \text{Ni} \rightarrow 2\text{MgNi}
\]  

Thus, all the discharge capacities of the hydrogen storage alloys in this thesis were calculated based on the total weight of the alloys (\text{Mg}_2\text{Ni}+\text{Ni}), rather than only the \text{Mg}_2\text{Ni}.

The discharge capacities as a function of cycle number for the \text{Mg}_2\text{Ni} alloy I, \text{Mg}_2\text{Ni} alloy II, \text{Mg}_2\text{Ni} alloy I after BM for 50 h and \text{Mg}_2\text{Ni} alloy II after BM for 60 h are presented in Figure 5.4. At a discharge current density of 50 mA/g, the initial discharge capacity of BM alloy I (273 mAh/g) is larger than that of BM alloy II (209 mAh/g). Both discharge capacities are much larger than that of the crystalline \text{Mg}_2\text{Ni} alloy I (about 18 mAh/g) and \text{Mg}_2\text{Ni} alloy II (about 15 mAh/g). These results...
suggest that ball milling is a very powerful method for Mg-based alloy electrodes to achieve high discharge capacities. For sintered Mg$_2$Ni alloys it is better to select the lower sintering temperature for achieving high discharge capacities. Even at a much larger discharge current density of 50 mA/g, the initial discharge capacity of the Mg$_2$Ni alloy I ball-milled with Ni powder is still larger than that of the previously reported bare Mg-based alloys [7,274,275], Mg$_2$Ni-10wt.%Ti$_2$Ni composite [275] and microencapsulated Mg$_{1.9}$Al$_{0.1}$Ni$_{0.9}$Y$_{0.1}$ alloys [276]. It is known that amorphous alloys have excellent catalytic and electrocatalytic activity [11,273]. Thus the amorphous structure of Mg-based alloy is a key factor to achieve a large discharge capacity.

5.3 Effects of ball milling time on discharge capacity

In order to know the effects of the ball milling time on the discharge capacities of Mg-Ni alloys, the Mg$_2$Ni alloy II was chosen for long time ball milling with nickel. The discharge capacities of alloy II after BM for 60 h, 120 h and 240 h with Ni powders are shown in Figure 5.5 as a function of cycle number at a ratio of ball to sample weight of 30:1. The discharge capacities of the samples after BM for 60 h and 120 h are almost identical (initial discharge capacity of the sample ball-milled 120 h was 213 mAh/g). The discharge capacity after BM 240 h is higher than that of the other two samples. Figure 5.6 shows the X-ray diffraction patterns of alloy II after ball milling for 0 h, 60 h, 120 h and 240 h. After ball milling for 60 hours, it
was seen from Figure 5.3 that the structure of Mg$_2$Ni alloy II is already mainly amorphous. After additional milling, the alloy structures after BM 120 h and BM 240 h were not obviously altered, but the discharge capacity of the BM 240 h alloy was higher than that of the others (its initial discharge capacity was about 271 mAh/g). This could be due to the amorphous structure of the sample ball milled for 240 h alloy becoming more uniform with the additional ball milling and the quantity of amorphous phase increasing.

5.4 Effects of ratio of ball to sample weight during ball milling

One of the most important parameters in the BM process is the ratio of the ball to sample weight. Figure 5.7 shows the discharge curves of Mg$_2$Ni alloy II after BM for 60 hours for ratios of ball to sample weight of 30:1 and 100:1. The 100:1 sample has a larger initial discharge capacity of 303 mAh/g and longer cycle life (the discharge capacity is ca. 126 mAh/g at the 6th cycle). The discharge capacity is much higher than the initial discharge capacity of the corresponding sample where the ratio was 30:1 (209 mAh/g). This probably means that the higher ratio of ball to sample results in faster milling, so that a uniform amorphous structure is achieved more quickly.

In summary, all the ball milled Mg$_2$Ni alloy electrodes studied have shown improved initial discharge capacity but they degrade quickly upon cycling even when an amorphous structure is achieved. It was known that alloy degradation can be reduced
by adding other elements [17, 278]. A combination of elemental addition and ball milling appears to offer the prospect of further improvement in electrode performance.

Figure 5.4  Discharge capacities of the Mg$_2$Ni alloy I, Mg$_2$Ni alloy II, Mg$_2$Ni alloy I after BM for 50 h and Mg$_2$Ni alloy II after BM for 60 h electrodes after repeated charge-discharge cycles at a discharge current density of 50 mA g$^{-1}$ at 25 °C.
Chapter Five  Mg-Ni alloy Electrodes Prepared by Sintering and Subsequent Ball Milling with Ni Powders

Figure 5.5  Discharge capacities as a function of cycle number for Mg$_2$Ni alloy II ball milled with Ni powder for 60 h, 120 h and 240 h. The ratio of ball to sample weight was 30:1.
Figure 5.6  X-ray diffraction patterns of the Mg$_2$Ni alloy II after ball milling time for: 0 h; 60 h; 120 h; and 240 h.
Figure 5.7 Discharge curves of Mg$_2$Ni alloy II after ball milling for 60 hours at a ratio of ball to sample weight of 30:1 and 100:1.
5.5 Discharge performance of ball milled Mg-Ni alloys

Figure 5.8 shows galvanostatic discharge curves of the Mg$_2$Ni alloy II electrodes at first to fourth cycles in 6M KOH aqueous solution at 25 °C. The charge current density is 100 mA/g, the discharge current density is 50 mA/g. At the first discharge process, the discharge curve has a plateau region at around -0.80 V vs. Hg-HgO electrode. During the four discharge cycles, the potential plateau regions have almost same value even though the discharge capacities decrease rapidly.

The galvanostatic discharge curves of the Mg$_2$Ni alloy II electrodes after 60 h, 120 h and 240 h at first discharge cycle are shown in Figure 5.9. It can be seen that the potential plateau regions of the Mg$_2$Ni alloy II electrodes after 60 h and 120 h are the same value, but the potential plateau regions of the Mg$_2$Ni alloy II electrodes after 240 h increase. Figure 5.10 shows the galvanostatic discharge curves of the electrodes of the Mg$_2$Ni alloy II after BM for 60 h for ratios of ball to sample weight of 30:1 and 100:1. Increasing the ratios of ball to sample weight results in the increase of the potential plateau regions of the Mg$_2$Ni alloy II electrode. Because a plateau of the potential in the discharge process of a hydrogen storage alloy is based on the oxidation of absorbed hydrogen [280], both increasing the ball milling time and the ratios of ball to sample weight in fabricating the Mg-Ni alloy electrodes can increase their electrochemical equilibrium pressure of hydrogen.
Figure 5.8  Galvanostatic discharge curves of the BM Mg$_2$Ni alloy II electrodes at first to fourth cycles in 6M KOH aqueous solution at 25 °C. The charge current density is 100 mA/g; the discharge current density is 50 mA/g. The ball to sample is 30:1.
Figure 5.9 Galvanostatic discharge curves of the Mg$_2$Ni alloy II electrodes after ball milling for 60 h, 120 h and 240 h at first discharge cycle in 6M KOH aqueous solution at 25 °C.
Figure 5.10  Galvanostatic discharge curves of the electrodes of the Mg$_2$Ni alloy II after BM for 60 h at the ratios of ball to sample weight of 30:1 and 100:1.
5.6 Conclusions

The Mg-Ni hydrogen storage alloy electrodes described in this chapter were manufactured by sintering and subsequent ball milling with Ni powders using a planetary ball mill and their electrode properties as a rechargeable anode electrode in the Ni-MH battery were investigated at room temperature. The conclusions are:

- Crystalline Mg$_2$Ni alloys can be prepared by sintering Mg and Ni powders in their required proportions under an argon atmosphere. The sintered crystalline Mg$_2$Ni alloys have extremely low discharge capacities of only 15 or 18 mAh g$^{-1}$ at a discharge current density of 50 mA g$^{-1}$, which is negligibly small in comparison with their theoretical discharge capacity. Thus, the common crystalline Mg$_2$Ni alloy is not suitable for use as a rechargeable anode material in an alkaline solution at room temperature.

- Although conventional metallurgical techniques can be used to manufacture Mg$_2$Ni alloy electrodes, ball milling improves the discharge capacities of the electrodes significantly. For sintered Mg$_2$Ni alloys followed by ball milling with Ni powders, it is better to select the lower sintering temperature for achieving high discharge capacities of the Mg-Ni alloys.
• All the ball milled Mg-Ni alloy electrodes studied have completely or mainly amorphous structures, showing very high initial discharge capacity compared with their crystalline counterparts. The amorphous structure is a key factor in order to obtain high initial discharge capacities for Mg-Ni alloy electrodes.

• In the ball milling process using a planetary ball mill, the ball milling parameters have significant effects on the discharge capacities of the Mg-Ni alloy electrodes. Increasing the ball milling time and the ratio of ball to sample weight are effective methods to further improve the discharge capacity for Mg-Ni alloy electrodes.
CHAPTER 6  EFFECT OF Co ADDITION ON Mg-Ni ALLOY ELECTRODES PREPARED BY SINTERING FOLLOWED BY BALL MILLING

6.1 Introduction

Cobalt is a very important element in metal hydride electrodes. Early in 1973, Van Mal et al. [288] reported that the partial substitution of cobalt for nickel results in a considerable reduction of the volume expansion on hydrogen absorption. In 1984, Willems [18] examined the LaNi$_{5-x}$Co$_x$ system in order to confirm a hypothesis that a reduction of the lattice expansion during hydriding should lead to a more stable hydride electrode. Sakai and co-workers [267] found that the decrepitation rate decreased with decreasing Vickers hardness in the order of $M = Mn > Cu > Cr > Al > Co$ for LaNi$_{5-x}M_x$, therefore increasing the cycle life of the alloys. With increasing cobalt content in $MmNi_{4.2-x}Co_xAl_{0.8}$ the cycle life of the electrodes was much improved [289].
The Co addition in a battery can also increase its cycle life. Ogama et al. [290] tested MmNi₄.₃₋ₓCoₓAl₀.₃Mn₀.₄ in a sealed cell and found that the cycle life of the battery was improved by increasing the cobalt content, developing a practical alloy MmNi₃.₅₅Co₀.₇₅Al₀.₃Mn₀.₄. Cobalt seems to be indispensable in commercial alloys of the AB₅-type hydride electrode, because with only a partial substitution of nickel by cobalt, the cycling stability can be improved to a competitive level in comparison with other types of batteries.

In order to improve the cycling stability of ball milled Mg-Ni alloy electrodes, the effect of Co addition on BM Mg-Ni alloy hydride electrodes was investigated. The Mg-Ni-Co alloy hydride electrodes were prepared in two different ways: 1) by ball milling the Mg₂Ni alloy prepared by sintering a mixture of Mg and Ni powders with Ni or Co powders; and 2) by ball milling Mg₂Ni₀.₆Co₀.₄ alloy prepared by sintering a mixture of Mg, Ni and Co powders with Ni powders. The results show that as a negative electrode, a Mg₂Ni₀.₆Co₀.₄ alloy ball-milled with Ni powders for 60 hours possesses the highest discharge capacity. Its initial discharge capacity is 327 mAh g⁻¹ at a discharge current density of 50 mA g⁻¹, while the Mg₂Ni alloy ball-milled with Ni powders has an initial discharge capacity of 303 mAh g⁻¹. Both of these initial discharge capacities are much higher than that of the Mg₂Ni alloy ball-milled with Co powders, which has an initial discharge capacity of only 219 mAh g⁻¹.
6.2 Preparation and structure of the alloys

Following the experimental results in chapter 5, to achieve high discharge capacities, lower sintering temperatures and higher ratios of ball to sample weight were applied in these experiments.

The Mg, Ni and Co powders in their required proportions were well mixed and pressed into pellets at a pressure of $5 \times 10^3$ kgf cm$^{-2}$. The pellets were sintered in a tube furnace under an argon atmosphere at 620 °C for 9 hours to obtain the Mg$_2$Ni and Mg$_2$Ni$_{0.6}$Co$_{0.4}$ alloys. To obtain more active alloy powders, 1 mole of sintered Mg$_2$Ni alloy was mixed and ball-milled with 1 mole of Ni or Co powder for various periods of time at 150 rpm in an argon atmosphere. The weight ratio of ball to sample was 100:1. One mole of sintered Mg$_2$Ni$_{0.6}$Co$_{0.4}$ alloy was also mixed and ball-milled with one mole of Ni powder under the same conditions.

The alloys used in this chapter are: (1) sintered Mg$_2$Ni alloy; (2) sintered Mg$_2$Ni alloy ball-milled with Ni powder for 60 hours (MgNi); (3) sintered Mg$_2$Ni ball-milled with Co powder for 60 hours (Mg$_2$NiCo-60); (4) sintered Mg$_2$Ni$_{0.6}$Co$_{0.4}$ alloy ball-milled with Ni powder for 60 hours (Mg$_2$Ni$_{1.6}$Co$_{0.4}$); and (5) sintered Mg$_2$Ni alloy ball-milled with Co powder for 120 hours (Mg$_2$NiCo-120). The X-ray diffraction patterns of the alloys are shown in Figure 6.1. The pattern (a) is the X-ray diffraction pattern of a sintered Mg$_2$Ni alloy indicating that a crystalline Mg$_2$Ni phase was formed. All
the X-ray diffraction patterns of (b), (c), (d) and (e) show that the microstructures of
the alloys were completely amorphous. This was also confirmed by the DTA traces
illustrated in the following section. Thus, the alloying reactions occurred during the
ball milling processes may be represented by the equations:

\[
\begin{align*}
Mg_2Ni + Ni & \rightarrow 2MgNi \text{ (amorphous)} \quad (6.1) \\
Mg_2Ni + Co & \rightarrow Mg_2NiCo \text{ (amorphous)} \quad (6.2) \\
Mg_2Ni_{0.6}Co_{0.4} + Ni & \rightarrow Mg_2Ni_{1.6}Co_{0.4} \text{ (amorphous)} \quad (6.3)
\end{align*}
\]

and the longer time of ball milling (120 hours) does not alter the structure of sintered
Mg$_2$Ni alloy ball-milled with Co powder for 60 hours.

### 6.3 Differential thermal analysis

Amorphous alloys are in a non-equilibrium state and possess high internal energy.
Therefore, amorphous alloys will release energy to change to a more stable state
when they are being heated. The thermal stability of the milled amorphous samples
is similar to the results reported for melt-spun and slowly cooled samples of
comparable composition [36,291-295]. Figure 6.2 shows the differential thermal
analysis (DTA) traces of (a) the ball milled MgNi, (b) Mg$_2$NiCo-60 and (c)
Mg$_2$NiCo-120 alloys. The differential gravity analysis (TG) traces of the three alloys
show straight lines that indicate that there are no chemical reactions during the heating process. The TG results are same as the FeTi alloys in Chapter 4 (see Section 4.2). But, the DTA trace of the MgNi alloy has two obvious exothermic crystallisation peaks around 337 °C and 446 °C. These peaks correspond to the crystallising reaction to Mg$_2$Ni and MgNi$_2$ phase, respectively [226,296]. The Mg$_2$NiCo-60 alloy has two exothermic crystallisation peaks around 393 °C and 475 °C corresponding to the Mg$_2$Ni-type and MgNi$_2$-type phases, which means Co substitution increases the two crystallisation temperatures about 50 °C. The two crystallisation temperatures for Mg$_2$NiCo-120 alloy were decreased to 375 °C and 456 °C, which means its stability decreased. It seems that there is a very small peak (around 330 °C) in the DTA trace of Mg$_2$NiCo-120 alloy before their crystallisation temperatures, which may correspond to the structure release of amorphous Mg$_2$NiCo-120 alloy, resulting from the longer time milling.

Recently, Ikeda et al. [297] reported the formation and crystallisation of amorphous MgNi$_{1-x}$T$_x$ (T = Co and Cu) in a position range of $x = 0-0.5$ prepared by mechanical alloying. By means of measuring the resultants of some MgNi$_{1-x}$T$_x$ alloys after DTA measurement, they confirmed that the crystallisation of the MgNi$_{1-x}$T$_x$ alloys proceeds in two steps, forming the Mg$_2$Ni-type and MgNi$_2$-type phases. The crystallisation temperatures increase/decrease by Co/Cu substitution. Also, the enthalpies of the amorphous alloy formation of the alloys are little changed by substitution. The $P$-$C$ isotherms indicate that the hydrogen-site energies become
Chapter Six  Effect of Co Addition on Mg-Ni Alloy Electrodes Prepared by Sintering Followed by Ball Milling

139

partially unstable with substitution.

Above all, the DTA results indicate that the addition of Co increases the stability of amorphous Mg-based alloys. Increasing the BM time therefore can decrease the stability of amorphous Mg-based alloys.

6.4 SEM morphologies and X-ray mapping analysis

Figure 6.3 shows the SEM micrographs of (a) the Mg$_2$Ni$_{1.6}$Co$_{0.4}$ and (b) Mg$_2$NiCo-60 alloys. We can see that both Mg$_2$Ni$_{1.6}$Co$_{0.4}$ and Mg$_2$NiCo-60 have very similar surfaces and particle sizes, around 3~10 µm similar to the nanocrystalline and amorphous FeTi hydrogen storage alloys prepared by ball milling [174].

The X-ray mapping analysis of all the ball-milled alloys indicates that they possess uniform compositions on their surface. Figure 6.4 is an example which shows the X-ray mapping of the Mg$_2$NiCo-60 alloy. Figure 6.4, (a) shows the morphology of Mg$_2$NiCo-60 alloy by SEM while Figures 6.4 (b), (c) and (d) are X-ray maps in the same field of Mg, Co and Ni, respectively. The Mg, Co and Ni concentrations in Mg$_2$NiCo-60 alloy are fairly evenly distributed.
Figure 6.1 XRD patterns of the sintered Mg$_2$Ni alloy (a), sintered Mg$_2$Ni alloy ball-milled with Ni powders for 60 hours (b), sintered Mg$_2$Ni ball-milled with Co powders for 60 hours (c), sintered Mg$_2$Ni$_{0.6}$Co$_{0.4}$ alloy ball-milled with Ni powders for 60 hours (d) and sintered Mg$_2$Ni alloy ball-milled with Co powders for 120 hours (e).
Figure 6.2  DTA traces of (a) the ball milled MgNi, (b) Mg₂NiCo-60 and (c) Mg₂NiCo-120 alloys at a heating rate of 10 °C min⁻¹ under the protection of a pure argon atmosphere.
Chapter Six  Effect of Co Addition on Mg-Ni Alloy Electrodes Prepared by Sintering Followed by Ball Milling

Figure 6.3  SEM micrographs of (a) ball milled Mg$_2$Ni$_{1.6}$Co$_{0.4}$ alloy and (b) Mg$_2$NiCo-60 alloy.
Figure 6.4  SEM morphology of Mg$_2$NiCo-60 alloy (a) and X-ray mapping of Mg (b), Co (c) and Ni (d) of Mg$_2$NiCo-60 alloy in the same field, respectively.
6.5 Electrochemical discharge ability of the alloys

Figure 6.5 shows the discharge capacities of (a) Mg$_2$Ni, (b) Mg$_2$Ni$_{0.6}$Co$_{0.4}$, (c) Mg$_2$NiCo-60, (d) MgNi and (e) Mg$_2$Ni$_{1.6}$Co$_{0.4}$ after repeated charge-discharge cycles at 25 °C. The discharge capacities of the sintered Mg$_2$Ni and Mg$_2$Ni$_{0.6}$Co$_{0.4}$ alloys are very poor (around 19 mAh/g and 20 mAh/g, respectively). The cobalt addition does not alter the discharge capacity of sintered Mg-Ni alloys. This could be attributed to their poor electrochemical hydriding/dehydriding behaviour in alkaline solution, resulting from the incompleted hydriding reaction and oxidation of Mg-based alloys. However, all the alloys after ball milling for 60 hours with Ni, Co powders achieved very high discharge capacities compared with crystalline Mg$_2$Ni and Mg$_2$Ni$_{0.6}$Co$_{0.4}$ alloys. The capacities were also much higher than other Mg-based alloys prepared by the addition of other elements [7] or microencapsulated by metal and alloy coatings [276]. These high discharge capacities are ascribed to the amorphous structure of the ball-milled alloys.

The Mg$_2$Ni$_{0.6}$Co$_{0.4}$ alloy ball-milled with Ni powders (Mg$_2$Ni$_{1.6}$Co$_{0.4}$) possessed the highest discharge capacity: its initial discharge capacity was 327 mAh g$^{-1}$ which was higher than that of Mg$_2$Ni alloy ball-milled with Ni powder (MgNi) which had an initial discharge capacity of 303 mAh g$^{-1}$. It also has improved cycle life in comparison with the amorphous MgNi alloy. This might have been due to the
addition and homogeneous distribution of cobalt. Both of their initial discharge capacities were much higher than that of the Mg$_2$Ni alloy ball milled with Co powders (Mg$_2$NiCo), which had an initial discharge capacity of only 219 mAh g$^{-1}$. However, the Mg$_2$NiCo alloy also exhibits better cycle life. Thus the higher Co addition in the amorphous Mg-Ni alloy results in a lower initial discharge capacity but better cycle life.

The effect of BM time on the discharge capacity of the Mg$_2$NiCo alloy is shown in Figure 6.6. After BM for 120 hours, the initial discharge capacity of the Mg$_2$NiCo-120 alloy is 260 mAh g$^{-1}$, much higher than that of the alloy after BM for 60 hours which is only 219 mAh g$^{-1}$. This is because the Mg$_2$NiCo-120 alloy has higher surface energy which results in a higher electrocatalytic activity. However, at about the sixth cycle, the discharge capacities of both alloys are nearly the same; after about the seventh cycle, discharge capacities of the Mg$_2$NiCo-120 alloy decrease slightly faster. This is probably due to the high internal energy of the Mg$_2$NiCo-120 alloy resulting in a high corrosion rate in the alkaline solution.

Figure 6.7 shows the discharge curves of amorphous MgNi, Mg$_2$NiCo-60, Mg$_2$NiCo-120 and Mg$_2$Ni$_{1.6}$Co$_{0.4}$ alloys at the first charge-discharge cycle. They have almost same plateau regions at around -0.79 V vs. Hg/HgO electrode, but their capacities are very different: MgNi alloy, 303 mAh g$^{-1}$; Mg$_2$NiCo-60, 219 mAh g$^{-1}$; Mg$_2$NiCo-120, 260 mAh g$^{-1}$; and Mg$_2$Ni$_{1.6}$Co$_{0.4}$, 327 mA g$^{-1}$. 
Figure 6.5  Discharge capacities of (a) Mg$_2$Ni, (b) Mg$_2$Ni$_{0.6}$Co$_{0.4}$, (c) Mg$_2$NiCo$_{60}$, (d) MgNi and (e) Mg$_2$Ni$_{1.6}$Co$_{0.4}$ after repeated charge-discharge cycles.
Figure 6.6  Discharge capacities of the Mg$_2$NiCo-60 and Mg$_2$NiCo-120 alloys as a function of cycle number.
Figure 6.7  Discharge curves of amorphous MgNi, Mg$_2$NiCo-60, Mg$_2$NiCo-120 and Mg$_2$Ni$_{1.6}$Co$_{0.4}$ alloys at first charge-discharge cycle.
6.6 Conclusions

An investigation of the effect of Co additions on ball milled amorphous Mg-Ni alloy hydride electrodes is described in this chapter. The Mg-Ni-Co alloy hydride electrodes were prepared in two different ways: 1) by ball milling the Mg$_2$Ni alloy prepared by sintering a mixture of Mg and Ni powders with Ni or Co powders; and 2) by ball milling Mg$_2$Ni$_{0.6}$Co$_{0.4}$ alloy prepared by sintering a mixture of Mg, Ni and Co powders with Ni powders. It can be concluded that:

- The sintered Mg$_2$Ni alloy ball-milled with Ni or Co powders in a molar ratio of 1:1 for extended times can achieve an amorphous structure. The sintered Mg$_2$Ni$_{0.6}$Co$_{0.4}$ alloy ball-milled with Ni powders for 60 hours can also achieve an amorphous structure. In both methods, homogenous amorphous Mg-Ni-Co alloys can be obtained by ball milling.

- The discharge capacity of the sintered crystalline Mg$_2$Ni$_{0.6}$Co$_{0.4}$ alloy is still very poor (20 mAh/g), demonstrating that this alloy is not suitable for use as a rechargeable anode material in an alkaline solution at room temperature. The cobalt addition does not alter the discharge capacity of sintered Mg-Ni alloys.
- All the ball milled alloy electrodes studied have shown improved initial discharge capacity but they degrade quickly upon cycling. The amorphous structure of Mg-Ni-Co alloys is also a key factor in obtaining high initial discharge capacities. The addition of a small amount of Co to amorphous MgNi alloys can increase their initial discharge capacities and increase their cycle lives. Increasing the Co addition in the amorphous Mg-Ni alloy results in a lower initial discharge capacity but a slightly better cycle life.

- Like ball milled amorphous Mg-Ni alloys, increasing the ball milling time is an effective method of obtaining further improvements in the initial discharge capacities of amorphous Mg-Ni-Co alloys.
CHAPTER 7  SYNTHESIS AND ELECTRODE PROPERTIES OF NON-STOICHIOMETRIC AMORPHOUS Mg-BASED ALLOYS MADE BY BALL MILLING

7.1 Introduction

In recent years, it has been shown that the most effective way for Mg-based hydrogen storage alloy electrodes to achieve high discharge capacities is by mechanical alloying (MA) [14,277,279,280]: \( \text{Mg} + \text{Ni} \rightarrow \text{MgNi} \) and mechanical milling (MM) the Mg-based hydrogen storage alloys with Ni powders [16,17,77,278,281-283].

After mechanical milling, the most important change in the high discharge capacity Mg-based alloys is that they have completely or mainly amorphous structures. This has been demonstrated by X-ray diffraction (XRD) analysis [14,16,17,77,277-286], electron diffraction and transmission electron microscopy (TEM) [16,77,280-282,284,285]. After ball milling the Mg-based hydrogen storage alloys with Ni powders
Chapter Seven  Synthesis and Electrode Properties of Non-stoichiometric Amorphous Mg-based Alloys Made by Ball Milling

[16,278,281,282], the composition has the formula MgNi because the reaction during the ball milling process may be expressed by the equation: Mg$_2$Ni+Ni → 2MgNi.

There are many possibilities, for example, the Mg could be replaced by Al [17,278], Ti [283], Zr [283] or V [280] and Ni could be substituted by one or more elements, such as Co, Mn, Si, Cu, Ti, Zn, Fe, Zr and so on [14,17,277,279]. All the results so far have proved that the amorphous structure of Mg-based alloys is a key factor in achieving a large discharge capacity [14,16,17,77,277-285].

For the crystalline hydrogen storage alloys, it is well known that their stoichiometry is the most important factor in order to achieve high storage capacity. That is why the hydrogen storage alloys usually are classified into four types: AB$_5$ (eg, LaNi$_5$), AB$_2$ (eg, ZrMn$_2$), AB (eg, TiFe) and A$_2$B (eg, Mg$_2$Ni). The alloy components A and B can be substituted by many other elements.

In this chapter, nanocrystalline Mg$_2$Ni, amorphous MgNi, non-stoichiometric amorphous Mg-Ni and Mg-Ni-V alloys were fabricated by ball milling the crystalline Mg$_2$Ni alloy either with or without Ni and/or V powders. All the non-stoichiometric Mg-based alloys have amorphous structures, resulting in Mg-based alloy electrodes with very high discharge capacities by comparison with crystalline Mg$_2$Ni alloys. These results describe a novel method of achieving better Mg-based alloys electrodes with high discharge capacities and improved cycle life. The method enables a larger composition range to be achieved with a range of different elemental additions.
7.2 Nanocrystalline Mg$_2$Ni alloy

Ball milling was performed with a Fritsch (P5) planetary ball mill. The weight ratio of ball to sample was 30:1. The induction melted (IM) Mg$_2$Ni alloy was supplied by Santoku Metal Industry Co., Japan. To obtain more active alloy powders rapidly, a higher ball milling speed was applied. The IM Mg$_2$Ni alloy was mixed and ball-milled with Ni and V powders for a period of 70 hours at 200 rpm in an argon atmosphere. For the preparation of nanocrystalline Mg$_2$Ni, the IM Mg$_2$Ni alloy was ball-milled for a period of 70 hours at 200 rpm in an argon atmosphere. The alloy compositions are listed in Table 7.1.

Figure 7.1 shows the XRD patterns of the IM Mg$_2$Ni and ball milled Mg$_2$Ni alloys. The IM Mg$_2$Ni alloy is composed of a single Mg$_2$Ni phase. After mechanical milling for 70 hours, the structure of IM Mg$_2$Ni alloy became nanostructured with an average grain size of 13 nm. Its average grain size $d$ was estimated by using the Scherrer equation [257]:

$$d = \frac{0.89 \lambda}{\beta \cos \theta},$$

where $\lambda$ is the X-ray wavelength, $\beta$ is the peak width at half height and $\theta$ is the position of the selected Bragg angle.

The IM Mg$_2$Ni alloy was crushed into powder and mixed with Ni powder in the weight ratio of 1:1 to make electrodes. All the ball milled Mg-Ni based alloy powders used were also mixed with Ni powder in the weight ratio of 1:1 for electrode
preparation. The charge cycle was commenced using a current density of 100 mA per gram of hydrogen storage alloy for 10 hours. Then, after a one-minute rest, the discharge was continued using a current density of 50 mA/g until the voltage of the negative electrode against the mercury oxide electrode reached -0.6 V.

Table 7.1  The compositions of ball milled alloys

<table>
<thead>
<tr>
<th>Mg$_2$Ni, Ni and V ratio (molar)</th>
<th>Alloy formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$_2$Ni</td>
<td>Mg$_2$Ni</td>
</tr>
<tr>
<td>Mg$_2$Ni + Ni</td>
<td>MgNi (Mg$<em>{0.5}$Ni$</em>{0.5}$)</td>
</tr>
<tr>
<td>Mg$_2$Ni + 1.28 Ni</td>
<td>MgNi$<em>{1.14}$ (Mg$</em>{0.467}$Ni$_{0.533}$)</td>
</tr>
<tr>
<td>Mg$_2$Ni + Ni + 0.1V</td>
<td>MgNiV$<em>{0.1}$ (Mg$</em>{0.476}$Ni$<em>{0.476}$V$</em>{0.048}$)</td>
</tr>
<tr>
<td>Mg$_2$Ni + Ni + 0.2V</td>
<td>MgNiV$<em>{0.2}$ (Mg$</em>{0.455}$Ni$<em>{0.455}$V$</em>{0.09}$)</td>
</tr>
<tr>
<td>Mg$_2$Ni + Ni + 0.4V</td>
<td>MgNiV$<em>{0.4}$ (Mg$</em>{0.417}$Ni$<em>{0.417}$V$</em>{0.166}$)</td>
</tr>
<tr>
<td>Mg$_2$Ni + 1.28 Ni + 0.1V</td>
<td>MgNi$<em>{1.14}$V$</em>{0.1}$ (Mg$<em>{0.446}$Ni$</em>{0.509}$V$_{0.045}$)</td>
</tr>
</tbody>
</table>
Chapter Seven  Synthesis and Electrode Properties of Non-stoichiometric Amorphous Mg-based Alloys Made by Ball Milling

Figure 7.1  X-ray diffraction patterns of IM crystalline Mg\textsubscript{2}Ni and nanocrystalline Mg\textsubscript{2}Ni alloys.
Discharge capacities of induction melted crystalline Mg$_2$Ni and nanocrystalline Mg$_2$Ni alloys as a function of cycle number at a discharge current density of 50 mA/g at 25 °C are shown in Figure 7.2. The IM crystalline Mg$_2$Ni alloy has an extremely low discharge capacity of only 18 mAh/g, which is much less than the capacity obtained by converting the capacity in the gas-phase reaction into electrochemical units. This indicates that IM crystalline Mg$_2$Ni alloy has very poor electrochemical hydriding/dehydriding behaviour in the alkaline solution, so that the amount of the electrochemically absorbed hydrogen is much less than that in the gas-phase.

The initial discharge capacity of the nanocrystalline Mg$_2$Ni alloy is about 111 mAh/g, which is much higher than that of the IM crystalline Mg$_2$Ni alloy, but is only around 10% of the calculated theoretical electrochemical capacity of Mg$_2$Ni alloy (999 mAh/g). Because the average grain size of the nanocrystalline Mg$_2$Ni alloy is around 13 nm, the atoms in its grain boundaries could be estimated [141] (also see Chapter 2, Figure 2.8) and should be about 16%. Due to the good catalytic activity [109,110] and electrocatalytic activity [263-265] of nanocrystalline materials, it could also be inferred that only the atoms in the grain boundaries of the nanocrystalline Mg$_2$Ni alloy were electrochemically reacted with hydrogen to form the hydride.

Woo et al. [298,299] reported that BM nanocrystalline Mg$_2$Ni alloy (the average grain size was less than 20 nm) has a discharge capacity of 175 mAh/g at a small discharge current density of 10 mA/g at 30 °C. Inoue and co-workers obtained a BM
nanocrystalline Mg$_2$Ni alloy with an average grain size of about 10 nm and an initial discharge capacity of about 200 mAh/g at 30 °C [300]. They also reported that ball milled nanocrystalline Mg$_2$Ni alloys had initial discharge capacities of only 130 mAh/g [301] and 260 mAh/g [281].

In summary, all the reported BM nanocrystalline Mg$_2$Ni alloys have improved discharge capacities although they are not identical. This is because the ball milling process is very complicated, allowing the effects of many preparation parameters. Also the electrode properties of hydrogen storage alloy electrodes are affected by many different sample preparation factors.

As show in Figure 7.2, the discharge capacity of the nanocrystalline Mg$_2$Ni alloy decreases rapidly after several cycles. This result is very similar to the reported results [281,298-301]. The main cause of the degradation of the nanocrystalline Mg$_2$Ni alloy electrodes is the formation of a passive Mg(OH)$_2$ layer. These layers nucleate at the electrode surface to block the absorbing hydrogen at the surface and decrease the discharge capacity [299].

Above all, most of ball milled nanocrystalline Mg$_2$Ni alloy electrodes have lower discharge capacities in comparison with amorphous Mg-based alloys described in this chapter (about 400 mAh/g, at a discharge current density of 50 mA/g) and in other papers [14,16,277-282].
Figure 7.2  Discharge capacities of induction melted crystalline Mg$_2$Ni and nanocrystalline Mg$_2$Ni alloys as a function of cycle number at a discharge current density of 50 mA/g at 25 °C.
7.3 Amorphous and non-stoichiometric amorphous Mg-Ni alloys

Figure 7.3 shows the XRD patterns of the IM Mg$_2$Ni alloy ball-milled with Ni powders in different ratios, indicating that homogenous amorphous MgNi and MgNi$_{1.14}$ were formed:

\[
\text{Mg}_2\text{Ni} + \text{Ni} \rightarrow 2\text{MgNi} \text{ (Mg}_{0.5}\text{Ni}_{0.5}) \quad (7.1)
\]

\[
\text{Mg}_2\text{Ni} + 1.28 \text{Ni} \rightarrow 2\text{MgNi}_{1.14} \text{ (Mg}_{0.467}\text{Ni}_{0.533}) \quad (7.2)
\]

Orimo et al [226,302] reported that the high resolution TEM image and its diffraction pattern of compound Mg$_2$Ni ball milled with Ni powder (molar ratio: 1:1, e.g., Mg-50 at.% Ni, or MgNi) shows that an amorphous structure was obtained. The ball milled alloys of the composition of Mg-33 at.% Ni, Mg-38 at.% Ni and Mg-43 at.% Ni only have a nanostructure or a mixture of partial nanostructure and partial amorphous structure [226,302]. This means that decreasing the Mg content may cause more difficulty in obtaining an amorphous structure for Mg-Ni alloys. My result indicates that an amorphous structure can be obtained even if the nickel content is increased.

The hydrogen storage alloy Mg$_2$Ni reacts with H$_2$ readily at 325 °C and 300 Pa, and the reaction in the plateau region can be expressed by the equation: Mg$_2$Ni + H$_2$
Mg$_2$NiH$_4$ [3]. The theoretical electrochemical capacity of hydride Mg$_2$NiH$_4$ is 999 mAh/g. However, the maximum hydrogen content of the amorphous MgNi region, is 2.2 wt. %, corresponds to a formula of MgNiH$_{1.9}$ [226] and a calculated electrochemical capacity of 613 mAh/g.

The decrease in the discharge capacities of the amorphous MgNi and MgNi$_{1.14}$ alloys after repeated charge-discharge cycles at a discharge current density of 50 mA/g is shown in Figure 7.4. The crystalline IM Mg$_2$Ni alloy has a very low discharge capacity of only about 18 mAh/g (because of its poor hydriding kinetics at 25°C) while amorphous MgNi and MgNi$_{1.14}$ alloys have much higher capacities. The initial discharge capacities of amorphous MgNi and MgNi$_{1.14}$ alloys are approximately the same: 336 mAh/g, much higher than that of crystalline IM Mg$_2$Ni compound. After several charge-discharge cycles, the discharge capacities of both amorphous MgNi and MgNi$_{1.14}$ alloys decrease rapidly. But non-stoichiometric amorphous MgNi$_{1.14}$ alloy has a slightly better cycle life than that of amorphous MgNi. This result encourages me to add other elements in a different way from traditional substitution, making non-stoichiometric Mg-based alloy electrodes.
Figure 7.3  X-ray diffraction patterns of the IM Mg$_2$Ni alloy ball-milled with Ni powders in different ratios, namely, homogenous amorphous MgNi and non-stoichiometric amorphous MgNi$_{1.14}$ (Mg$_{0.467}$Ni$_{0.533}$) alloys.
Figure 7.4 Discharge capacities of the amorphous MgNi and MgNi\textsubscript{1.14} (Mg\textsubscript{0.467}Ni\textsubscript{0.533}) alloys after repeated charge-discharge cycles at a discharge current density of 50 mA/g at 25°C.
7.4 Non-stoichiometric amorphous Mg-Ni-V alloys

7.4.1 Structure and stability

Recently, solid state amorphisation by MA and MM has become the most effective method to obtain amorphous alloys [35-46]. The amorphous composition range achievable by MA is normally larger than that of other techniques. Lee et al. [92] have reported that the MA Ni-Nb alloy system has a wider amorphous composition range than that of melt quenching. Therefore, it seems likely that it would be possible to synthesise non-stoichiometric amorphous MgNi alloy by adding other elements to MgNi alloy using the MA or MM method.

The XRD patterns of non-stoichiometric MgNiV0.1, MgNiV0.2, MgNiV0.4 and MgNi1.14V0.1 alloys are shown in Figure 7.5. The patterns indicate that the alloys MgNiV0.1, MgNiV0.2, MgNiV0.4 and MgNi1.14V0.1 are amorphous alloys. This conclusion was also confirmed by the results of differential thermal analysis (see next paragraph). These solid reactions correspond to the following reaction:

\[
\text{Mg}_2\text{Ni} + x \text{Ni} + y \text{V} \rightarrow 2\text{MgNi}_{(x+1)/2}y_{y/2}
\]  

(7.3)

where \(x\) and \(y\) are molar fractions of Ni and V respectively. Thus, different amounts of vanadium can be added to the amorphous Mg-Ni alloy to make a range of non-
stoichiometric Mg-based alloys without changing their basic amorphous structure.

The DTA traces of the ball milled MgNi, MgNiV\textsubscript{0.1}, MgNiV\textsubscript{0.2} and MgNiV\textsubscript{0.4} alloys at a heating rate of 10 °C/min are shown in Figure 7.6. The TG traces of the four alloys show straight lines that indicate that there are no chemical reactions during the heating process. However, all the DTA traces of the ball milled non-stoichiometric Mg-Ni-V alloys show obvious exothermic crystallisation peaks which confirm that their structure was amorphous. The DTA trace of the MgNi alloy has two obvious exothermic crystallisation peaks around 360 °C and 440 °C. These peaks correspond to the crystallising reaction to Mg\textsubscript{2}Ni and MgNi\textsubscript{2} phase, respectively [226,296]. The exothermic crystallisation peak values of MgNiV\textsubscript{0.1} alloy are around 373 °C for Mg\textsubscript{2}Ni-type phase and 450 °C for MgNi\textsubscript{2}-type phase, respectively. They are about 10 °C higher than that of the MgNi alloy. When vanadium is increased to 0.2, exothermic crystallisation peak values of MgNiV\textsubscript{0.2} alloy are around 364 °C for Mg\textsubscript{2}Ni-type phase and 452 °C for MgNi\textsubscript{2}-type phase, which are almost the same as for the MgNiV\textsubscript{0.1} alloy. But when vanadium is increased to 0.4, the MgNiV\textsubscript{0.2} alloy has a large exothermic crystallisation peak with a peak value of 391 °C and a very small crystalline peak. Orimo and co-workers [303] mechanically alloyed the mixture of Mg\textsubscript{2}Ni, Ni and V using a planetary ball mill (Fritsch P7) at a high speed of 400 rpm for 80 hours at ambient temperature. However, they could not obtain an amorphous single phase at a stoichiometric composition of MgNi\textsubscript{0.6}V\textsubscript{0.4}. My experimental results indicate that for the amorphous Mg-Ni-V alloys, a larger
composition range of vanadium can be achieved by the non-stoichiometric addition of vanadium in Mg-Ni alloys through a ball milling method. A small amount of non-stoichiometric addition of vanadium in Mg-Ni alloys has no significant effects on the thermal stability of amorphous MgNi alloy.

7.4.2 SEM morphologies and X-ray mapping analysis

Figure 7.7 (a) shows the SEM micrograph of amorphous MgNiV_{0.1} alloy powders while Figure 7.7 (b) is the micrograph of a bigger particle of the MgNiV_{0.1} alloy. Figures 7.7 (c) and (d) are X-ray maps in the same field of V and Ni, respectively. The particle sizes of the MgNiV_{0.1} alloy powders are around 5-12 μm. The powder surface of the MgNiV_{0.1} alloy (Figure 7.7 (b)) looks concave-convex which should be a more activated amorphous surface with a high catalytic activity. The V and Ni concentrations in the MgNiV_{0.1} alloy are fairly evenly distributed, showing that the alloy has a homogenous amorphous MgNiV_{0.1} component and indicating that the MA non-stoichiometric Mg-based alloy can achieve a uniform amorphous structure.
Figure 7.5  X-ray diffraction patterns of non-stoichiometric MgNiV$_{0.1}$, MgNiV$_{0.2}$, MgNiV$_{0.4}$ and MgNi$_{1.14}$V$_{0.1}$ alloys.
Figure 7.6  DTA traces of the ball milled MgNi, MgNiV$_{0.1}$, MgNiV$_{0.2}$ and MgNiV$_{0.4}$ alloys at a heating rate of 10 °C/min under the protection of a pure argon atmosphere.
Figure 7.7  SEM micrograph of (a) the MgNiV_{0.1} alloy powders. (b) The micrograph of a larger particle of MgNiV_{0.1} alloy, X-ray mapping of (c) V and (d) Ni of MgNiV_{0.1} alloy in the same field, respectively.
Figure 7.7 (continued)
7.4.3 Discharge capacities of non-stoichiometric Mg-Ni-V alloys

The discharge capacities of the amorphous alloys MgNi (Mg_{0.5}Ni_{0.5}), MgNiV_{0.1} (Mg_{0.476}Ni_{0.476}V_{0.048}), MgNiV_{0.2} (Mg_{0.455}Ni_{0.455}V_{0.09}), MgNiV_{0.4} (Mg_{0.417}Ni_{0.417}V_{0.166}) and MgNi_{1.14}V_{0.1}(Mg_{0.446}Ni_{0.509}V_{0.045}) after repeated charge-discharge cycles at a discharge current density of 50 mA/g are shown in Figure 7.8. The discharge capacities were calculated based on the total weight of the alloys. Compared with the discharge capacity of the amorphous stoichiometric MgNi alloy (336 mAh/g), the non-stoichiometric alloys MgNiV_{0.1}, MgNiV_{0.2}, MgNiV_{0.4} and MgNi_{1.14}V_{0.1} have higher discharge capacities and better cycle characteristics. The initial discharge capacities of alloys MgNiV_{0.1}, MgNiV_{0.2}, MgNiV_{0.4} and MgNi_{1.14}V_{0.1} are 414, 357, 361 and 363 mAh/g, respectively. The non-stoichiometric alloys MgNiV_{0.2}, MgNiV_{0.4} and MgNi_{1.14}V_{0.1} have almost the same discharge capacity and cycle life, while MgNiV_{0.1} alloy has the highest discharge capacity and best cycle life. This shows that non-stoichiometric additions of vanadium can increase both the discharge capacity and cycle life of amorphous MgNi alloy electrodes, and that the amorphous MgNi alloy containing 0.1 molar addition of vanadium has the best electrode properties. These initial discharge capacities are higher than those of AB_5-type and AB_2-type hydride electrodes. Increasing the V content did not alter the electrode properties of the amorphous MgNi alloys. If the discharge capacities of the alloys are calculated based on Mg_2Ni content [16,278-282], the capacity of MgNiV_{0.1} alloy will
be 658 mAh/g at a discharge current density of 79 mA/g. The non-stoichiometric addition of vanadium and nickel in MgNi alloy cannot further increase its discharge capacity (MgNi<sub>1.14</sub>V<sub>0.1</sub> alloy) although it is still high (363 mAh/g). Because amorphous alloys have excellent electrocatalytic activity [11,273], all the non-stoichiometric amorphous Mg-based alloys have good hydriding/dehydriding kinetics at 25 °C and high electrochemical hydrogen storage abilities.

In many previous papers, authors have tried to improve the discharge capacity and cycle life of amorphous MgNi alloy by conventional stoichiometric elemental substitution. For examples, Lei et al. [14] reported that the partial substitution of cobalt, aluminium or silicon for nickel in amorphous MgNi alloy results in a reduction in discharge capacity. Liu and co-workers [279,304] investigated more than ten different amorphous Mg-based alloys, in which nickel had been partially stoichiometric replaced by other elements (Mg<sub>0.5</sub>Ni<sub>0.45</sub>M<sub>0.05</sub>, M = Ti, Zn, Mn, Fe, Co, Zr, W, Cr, Se and Sb). Their results show that the stoichiometric substitution of Fe, W, Cu, Mn, Cr, or Al for Ni decreases both the deterioration rate and discharge capacity, and the substitution of Se, Sb, Co, or Si decreases both the discharge capacity and cycle life. But my results show that it is possible to achieve better Mg-based alloy electrodes with high discharge capacities and improved cycle life by the method of making non-stoichiometric amorphous Mg-based alloys. This is because that the amorphous structure of Mg-based alloys is the key factor in achieving a high

Department of Materials Engineering, University of Wollongong, NSW 2522, Australia
discharge capacity, and the amorphous alloys can be obtained in a range of alloy composition.

The discharge capacity degradation of all the non-stoichiometric Mg-based alloys is still fast due to the oxidation of Mg in the KOH solution [14,280,305]. However, it is possible for amorphous Mg-based alloys to have longer cycle lives. Some previous results have shown that amorphous Mg-based alloys have good corrosion resistance [306,307].

The galvanostatic discharge curves of the MgNi (Mg$_{0.5}$Ni$_{0.5}$), MgNiV$_{0.1}$ (Mg$_{0.476}$Ni$_{0.476}$V$_{0.048}$), MgNiV$_{0.2}$ (Mg$_{0.455}$Ni$_{0.455}$V$_{0.09}$), MgNiV$_{0.4}$ (Mg$_{0.417}$Ni$_{0.417}$V$_{0.166}$) and MgNi$_{1.14}$V$_{0.1}$(Mg$_{0.446}$Ni$_{0.509}$V$_{0.045}$) electrodes at the first charge-discharge cycle are shown in Figure 7.9. The discharge curves of all the non-stoichiometric Mg-Ni-V alloys have almost same plateau regions at about -0.78 V vs. Hg/HgO electrode which is as same as that of the amorphous stoichiometric MgNi alloy. This indicates that the non-stoichiometric addition of vanadium in amorphous MgNi alloy does not alter its plateau voltage, but increases the discharge capacity of amorphous MgNi alloy.

In summary, the non-stoichiometric amorphous Mg-based alloys can be achieved by the mechanical alloying method for a range of V additions. The non-stoichiometric Mg-based alloy electrodes studied have shown improved initial discharge capacities.
These results describe a novel method of achieving better Mg-based alloy electrodes with high discharge capacities and improved cycle life. The method enables a larger composition range to be achieved with a range of different elemental additions.

**Figure 7.8** Discharge capacities of the amorphous alloys MgNi, MgNiV0.2, MgNiV0.4 and MgNi1.14V0.1 after repeated charge-discharge cycles at a discharge current density of 50 mA/g.
Figure 7.9  Galvanostatic discharge curves of the amorphous MgNi (Mg0.5Ni0.5), MgNiV0.1 (Mg0.476Ni0.476V0.048), MgNiV0.2 (Mg0.455Ni0.455V0.09), MgNiV0.4 (Mg0.417Ni0.417V0.166) and MgNi1.14V0.1 (Mg0.446Ni0.509V0.045) alloy electrodes at first charge-discharge cycle.
7.5 Conclusions

In this chapter, nanocrystalline Mg$_2$Ni, amorphous MgNi, non-stoichiometric amorphous Mg-Ni and Mg-Ni-V alloys were fabricated by ball milling the crystalline Mg$_2$Ni alloy either with or without Ni and/or V powders. The electrode properties of all the Mg-based alloys were investigated as rechargeable anode electrodes in the Ni-MH battery. The conclusions are:

- Nanocrystalline Mg$_2$Ni alloy with an average grain size of about 13 nm can be fabricated by mechanical milling of induction melted crystalline Mg$_2$Ni alloy. The initial discharge capacity of the nanocrystalline Mg$_2$Ni alloy is about 111 mAh/g, which is much higher than that of the IM crystalline Mg$_2$Ni alloy (only 18 mAh/g), but is only around 10 % of the calculated theoretical electrochemical capacity of Mg$_2$Ni alloy (999 mAh/g).

- Up to the present time, most of the research work on the Mg-based hydrogen storage alloy electrodes has been focused on the stoichiometric compositions of Mg$_2$Ni-type and MgNi-type alloys. My research results indicate that non-stoichiometric amorphous Mg-Ni alloy can be achieved by increasing the nickel content. The non-stoichiometric amorphous MgNi$_{1.14}$ (Mg$_{0.467}$Ni$_{0.533}$)
alloy has the same initial discharge capacity and a better cycle life in comparison with the stoichiometric amorphous MgNi alloy.

- The non-stoichiometric uniform amorphous MgNi\(_x\)V\(_y\) alloys (\(x = 1, 1.28; \ y = 0.1, 0.2, 0.4\)) have been synthesised by mechanical alloying induction melting Mg\(_2\)Ni alloy, Ni and V powders based on a stoichiometric amorphous MgNi alloy component. The results indicate that non-stoichiometric amorphous Mg-based alloys can be obtained by either increasing the Ni content or adding a range of vanadium or both through the mechanical alloying method.

- The non-stoichiometric Mg-based alloy electrodes studied have shown improved initial discharge capacities compared with the stoichiometric amorphous MgNi alloy. These results describe a novel method of achieving better Mg-based alloy electrodes with high discharge capacities. The method enables a larger composition range to be achieved with a range of vanadium additions.
CHAPTER 8 SUMMARY

The formation of amorphous and nanocrystalline FeTi alloys were investigated, and the feasibility of utilising the special structural nanocrystalline and amorphous FeTi hydrogen storage alloys as a low cost and high performance negative electrode material for the Ni-MH rechargeable battery was exploited for the first time in this study. The electrode performance of FeTi alloys was greatly improved by making a nanocrystalline or amorphous structure. An amorphous FeTi alloy electrode with an initial discharge capacity of 220 mAh/g at a discharge current density of 50 mA/g has been obtained, which is almost comparable with the capacities of rare-earth system negative electrode materials used in commercial Ni-MH batteries.

The preparation and electrode properties of amorphous and nanocrystalline magnesium-based hydrogen storage alloys were also investigated in this study. Like the amorphous and nanocrystalline FeTi alloys, the electrode performance of magnesium-based alloys can be greatly improved by making an amorphous or nanocrystalline structure. Most of the amorphous magnesium-based alloy electrodes have very high initial discharge capacities, which are higher than that of rare-earth system and zirconium-based Laves phase alloys in commercial batteries. A novel method of achieving better Mg-based alloy electrodes with high discharge capacities
and improved cycle life has been developed by making non-stoichiometric amorphous Mg-based alloys. The method enables a larger composition range to be achieved with a range of different elemental additions.

The following general conclusions can be summarised from this study:

1. Nanocrystalline and amorphous FeTi alloys can be obtained by ball milling using a planetary ball mill under the protection of an argon atmosphere. Electric arc melted crystalline FeTi alloy after mechanical milling 40 hours became nanostructured powders with an average grain size of about 8 nm, a particle size of about 13 \( \mu m \) and a specific surface area of 1.18 m\(^2\)/g. Fe and Ti powders after mechanical alloying 40 hours became amorphous powders with a particle size of about 10 \( \mu m \) and a specific surface area of 2.49 m\(^2\)/g. Small amounts of oxygen present during the mechanical alloying process have a significant effect on the formation of the FeTi alloy.

2. Crystalline FeTi alloy has an extremely low discharge capacity of only 3 mAh/g at a discharge current density of 50 mA/g, which is negligibly small compared with its theoretical discharge capacity. This is probably because the crystalline FeTi alloy has very poor electrochemical hydriding/dehydriding behaviour in an alkaline solution. Therefore, crystalline FeTi alloy is not suitable for use as a rechargeable anode material in an alkaline solution at room temperature. The nanocrystalline FeTi
alloy has an improved discharge capacity of 54 mAh/g at the first discharge, which is much higher than that of crystalline FeTi alloy, but is only around 10% of the calculated theoretical electrochemical capacity of FeTi alloy. Due to its good discharge capacity during the first twenty cycles, it may be possible to improve the electrochemical discharge capacity of FeTi-type alloy with good cycle life by achieving a nanocrystalline structure.

3. Unlike commercial AB₅-type hydrogen storage alloy electrodes, the amorphous FeTi alloy can achieve its highest discharge capacity of 220 mAh/g at the first charge-discharge cycle at a discharge current density of 50 mA/g. This is probably because the amorphous alloys have no long range ordering, their surfaces are much richer in low-coordination sites and defects which play important roles in the catalytic activity of materials. This discharge capacity is almost comparable with the capacities of commercial alloys used in Ni-MH batteries. Although the discharge capacity of the amorphous FeTi alloy decreases rapidly with prolonged the charge-discharge cycles, it still has a discharge capacity of 78 mAh/g at the twentieth cycle. Thus, ball milling is an effective method for the FeTi-type alloy to achieve high discharge capacity as an anode material in the Ni-MH battery.

4. At a discharge current density of 50 mA/g, crystalline Mg₂Ni alloys prepared by sintering Mg and Ni powders have extremely low discharge capacities of only 15 or 18 mAh/g, induction melted crystalline Mg₂Ni alloy has also an extremely low
discharge capacity of 18 mAh/g. The discharge capacity of sintered crystalline Mg$_2$Ni$_{0.6}$Co$_{0.4}$ alloy is still very poor (about 20 mAh/g), demonstrating that cobalt addition does not alter the discharge capacity of crystalline Mg-Ni alloys. All the discharge capacities are negligibly small in comparison with their theoretical discharge capacity. These results could be attributed to their very poor electrochemical hydriding/dehydriding behaviours in alkaline solution, resulting from the incompleted hydriding reaction and oxidation of Mg-based alloys. Thus, common crystalline Mg$_2$Ni-type alloy is not suitable for use as a rechargeable anode material in an alkaline solution at room temperature.

5. Although conventional metallurgical techniques can be used to manufacture Mg-based alloy electrodes, ball milling improves the discharge capacities of the electrodes significantly. For sintered Mg-based alloys followed by ball milling with Ni powders, it is better to select a lower sintering temperature to achieve high discharge capacities of the Mg-Ni alloys. In the ball milling process using a planetary ball mill, the ball milling parameters have significant effects on the discharge capacities of the Mg-based alloy electrodes. Increasing the ball milling time and the ratio of ball to sample weight are effective methods to further improve the discharge capacity for Mg-based alloy electrodes.

6. Nanocrystalline Mg$_2$Ni alloy with an average grain size of about 13 nm can be fabricated by mechanical milling induction melted crystalline Mg$_2$Ni alloy. The
initial discharge capacity of the nanocrystalline Mg$_2$Ni alloy is about 111 mAh/g, which is much higher than that of the IM crystalline Mg$_2$Ni alloy (only 18 mAh/g). Like the nanocrystalline FeTi alloy, the discharge capacity of nanocrystalline Mg$_2$Ni alloy is only 10% of the calculated theoretical electrochemical capacity of Mg$_2$Ni alloy. The percentage of atoms in the grain boundaries of the nanocrystalline FeTi and Mg$_2$Ni alloys can be estimated to be about 20% and 16%, respectively.

7. All the ball milled sintered Mg-Ni and Mg-Ni-Co alloy electrodes studied have completely or mainly amorphous structures, showing very high initial discharge capacities (around 300 mAh/g) compared with their crystalline counterparts. The addition of a small amount of Co to amorphous Mg-Ni alloys can increase their initial discharge capacities and increase their cycle lives. Increasing the Co addition in the amorphous Mg-Ni alloy results in a lower initial discharge capacity but a slightly better cycle life. All the results indicate that the amorphous structure is a key factor in order to obtain high initial discharge capacities for Mg-based alloy electrodes. The results have shown that the initial discharge capacity of amorphous Mg-based alloy electrodes is higher than that of rare-earth system and zirconium-based Laves phase alloys in commercial batteries. Thus, Mg-based hydrogen storage alloys are very promising negative materials for the Ni-MH battery.

8. Up to the present, the most research work on the Mg-based hydrogen storage alloy electrodes is focused on the stoichiometric compositions of Mg$_2$Ni-type and
MgNi-type alloys. My research results in this study indicate that non-stoichiometric amorphous Mg-Ni alloy can be achieved by increasing the nickel content, and the non-stoichiometric amorphous MgNi$_{1.14}$ (Mg$_{0.467}$Ni$_{0.533}$) alloy has the same initial discharge capacity and a better cycle life in comparison to the stoichiometric amorphous MgNi alloy.

9. The non-stoichiometric uniform amorphous MgNi$_x$V$_y$ alloys ($x = 1, 1.28; y = 0, 0.1, 0.2, 0.4$) have been successfully synthesised by mechanical alloying induction melting Mg$_2$Ni alloy, Ni and V powders based on a stoichiometric amorphous MgNi alloy component. The results indicate that non-stoichiometric amorphous Mg-based alloys can be obtained by either increasing the Ni content or adding a range of vanadium or both through the mechanical alloying method. The non-stoichiometric Mg-based alloy electrodes studied have shown improved initial discharge capacities (more than 400 mAh/g) compared with the stoichiometric amorphous MgNi alloy (about 330 mAh/g). These results describe a novel method of achieving better Mg-based alloy electrodes with high discharge capacities. The method enables a larger composition range to be achieved with a range of vanadium additions.
REFERENCES


References


Department of Materials Engineering, University of Wollongong, NSW 2522, Australia
References

References


References


References


References


References


241. C. Iwakura, T. Asaoka, H. Yoneyama, T. Sakai, K. Oguro and H. Ishikawa, 


References


Department of Materials Engineering, University of Wollongong, NSW 2522, Australia


PUBLICATIONS DURING PHD STUDY

I. **Refereed International Journal Papers:**


   One of SEM micrographs in this paper was selected for the cover of the *Journal of Materials Science Letters.*

3. **L. Sun, H.K. Liu, D.H. Bradhurst and S.X. Dou,** “Electrode properties of Mg\textsubscript{1.9}Al\textsubscript{0.1}Ni\textsubscript{0.8}Co\textsubscript{0.1}Mn\textsubscript{0.1} alloy by mechanical grinding with Ni powders”, *Electrochemical & Solid-State Letters*, 2 (1999) 164-166.


13 G.X. Wang, L. Sun, J. Horvat, S. Zhong, D.H. Bradhurst, H.K. Liu and S.X. Dou, “Kinetic characterisation of LiNi$_{0.8}$Co$_{1.8}$ electrodes in lithium ion cells”, *Journal of Applied Electrochemistry*, in press.


**II. Patent**

III. Conference papers


Extended Abstracts of 24th annual condensed matter meeting of the Australian and New Zealand Institutes of Physics, February 1-4, 2000. Wagga Wagga, Australia.