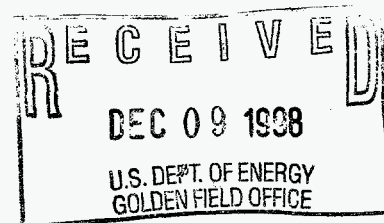


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DOE/GO/10145--T1

**DEVELOP IMPROVED METAL HYDRIDE TECHNOLOGY  
FOR THE STORAGE OF HYDROGEN**

**FINAL TECHNICAL REPORT**



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## Abstract

This report covers the work performed under a cost shared DOE program, contract #DE-FC36-96GO10145, by Energy Conversion Devices, Inc. (ECD) to "Develop Improved Metal Hydride Technology for the Storage of Hydrogen" utilizing ECD's extensive experience in metal hydride research, development and manufacturing. The overall objective was to develop commercially viable metal hydrides capable of reversibly storing at least 3 wt.% hydrogen for use with PEM fuel cells and hydrogen fueled internal combustion engine (HICE) applications. Such alloys are expected to result in system capacities of greater than 2 wt.%, making metal hydride storage systems (MHSS's) a practical means of supplying hydrogen for many consumer applications. ECD's past work on sputtered thin films of transition metal-based alloys led to the commercialization of it's nickel/metal hydride batteries, and similar work on thin film Mg-based alloys demonstrated potential to achieve very high gravimetric and volumetric energy densities approaching 2500 Wh/Kg and 2500 Wh/M<sup>3</sup> respectively. Under this 2-year cost shared project with the DOE, we have successfully demonstrated the feasibility of scaling up the Mg-based hydrides from thin film to bulk production without substantial loss of storage capacity. ECD made progress in alloy development by means of compositional and process modification. Processes used include Mechanical Alloying, Melt Spinning and novel Gas Phase Condensation. It was showed that the same composition when prepared by melt-spinning resulted in a more homogeneous material having a higher PCT plateau pressure as compared to mechanical alloying. It was also shown that mechanically alloyed Mg-Al-Zn results in much higher plateau pressures, which is an important step towards reducing the desorption temperature. While significant progress has been made during the past two years in alloy development and understanding the relationship between composition, structure, morphology, and processing parameters, additional R&D needs to be performed to achieve the goals of this work.

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## I. INTRODUCTION

### ***Why Metal Hydride Storage?***

Concerns about global warming, urban air quality, acid rain, and energy supply security are motivating increased interest in low-polluting alternative transportation fuels. PEM fuel cells represent a safe, quiet, high energy density, robust, and environmentally desirable means of powering transportation vehicles and portable electronics. In a hydrogen-powered fuel cell, hydrogen fuel combines with oxygen from air to form water, heat and electricity. One of the most difficult challenges remaining in reaching the performance and cost targets of fuel cells is the H-storage requirement. To alleviate the problems of onboard hydrogen storage for automotive applications, considerable effort is currently being directed at onboard reforming of liquid hydrocarbon fuels. However this method does not address the issue of moving away from hydrocarbon-fuel use and has associated problems, such as with transient response and start-up times. Onboard reforming is also not applicable for the very large market of two- and three-wheel vehicles used in much of the world or for portable electronics. Especially for these applications requiring rather low volumes of H<sub>2</sub> storage, compressed gas will result in neither a high energy density nor the degree of safety required. Liquid hydrogen requires special handling, and boil-off losses are a problem. The safest and most practical method for storing hydrogen is in the form of metal hydrides. With metal hydrides, the hydrogen is stored as a solid metal-hydrogen compound, therefore it is a low-pressure, highly compact storage method with very little free gaseous hydrogen.

Forms of solid hydrogen storage which have been proposed and are being investigated include:

Gas-Solid Adsorption: Low-temperature adsorption of hydrogen (at 150°K) on activated carbon has shown storage capacity of about 4 wt%. The storage capacity seems to be related to the porosity and surface properties of the carbon bed. While the potential for gravimetric energy density is high, the volumetric density is very low. Low adsorption temperatures dictate the use of insulated containers, and the boil-off calls for pressurized containers. These are significant drawbacks (1).

Carbon Nanotubes: Carbon nanotubes have been proposed for hydrogen storage as alternatives to carbon adsorption. In preliminary work, storage capacities between 5.2 and 6.8 wt% have been measured. This work is still at very early stages of development and the mechanism for the formation of nanotubes is not yet understood. Cryogenic storage (82 K) is still a problem. In addition, the rate of materials preparation is presently very slow (about 1mg/min) and estimates show that just the cost of electricity to produce these materials would be about \$1500/kg (2).

Carbon Nanofibers: Researchers at Northeastern University recently published results on carbon nanofibers as potential hydrogen storage materials (3). Carbon nanofibers differ from carbon nanotubes in that the fibers are composed of parallel graphite sheets and the

single-walled nanotubules are a new carbon allotrope with a structure similar to fullerenes. According to the claims made in the publication, the nanofibers were found to be able to absorb as much as ~70 wt.% hydrogen and desorb ~45 wt.%. The nanofibers, grown by the decomposition of hydrocarbon gases on small particles of crystalline metal catalyst, can be produced economically. While these claims could be significant, independent confirmation of the results and scale-up and manufacturing still need to be demonstrated for these materials.

**Fullerenes:** Another family of carbon materials which have generated substantial interest recently and which are similar in many respects to carbon nanotubes are the fullerenes, the  $C_{60}$  compounds.  $C_{60}$  materials have shown the ability to electrochemically charge and discharge hydrogen ( $C_{60}H_x$ ), indicating potential for use in hydride battery applications (4, 5). However, their superiority over metal hydride electrodes has not been demonstrated. Additionally, at present the cost is prohibitive.  $C_{60}H_{60}$  has potential for high theoretical capacity for hydrogen storage (7.7 wt%), which is similar to the theoretical capacity of magnesium metal hydride.

**Metal Hydrides:** Metal hydrides are solid alloys that are capable of reversibly storing large amounts of hydrogen at ambient temperatures and at much lower pressures than gaseous or liquid hydrogen. They can provide a safe, compact, energy efficient and environmentally sound means of storing hydrogen fuel for use with fuel cells and for H-ICE applications (6-16). An additional advantage of metal hydrides is their ability to deliver very pure hydrogen. This is especially advantageous for PEM fuel cells, which use catalysts that can be easily poisoned if any impurities (such as CO) are present in the hydrogen. Metal hydrides have negligible, if any, loss during storage, giving them extremely long shelf life. Being compact and solid-state also provides positional flexibility, which is a significant advantage for portable power and personal transportation vehicles. Large-scale manufacturing of certain types of metal hydrides has already been demonstrated by companies commercializing NiMH batteries, thus reducing the lead-time that will be required to progress from new alloy development to commercialization.

The safety, long life, and high volumetric energy density offered by metal hydrides is especially advantageous for small vehicles and for portable power. Detailed discussions with automobile and PEM fuel cell manufacturers suggest that H-Storage of >2 weight percent at the system level is sufficient to meet both gravimetric energy density and system cost targets. Therefore, the development and commercialization of high capacity, low cost metal hydride storage systems (MHSS's) will enable the broad-based commercialization of fuel cell technology and open many new markets for these storage systems.

## II. BACKGROUND

Hydride storage has been demonstrated in automobiles in the US and overseas by Mercedes-Benz, Mazda and Toyota (17) and on small two-wheeled scooters in India (18). In these demonstration vehicles the range has been limited because the low temperature alloys used have low gravimetric energy density ( $\leq 2$  wt.%). Current high capacity alloys, with gravimetric storage densities greater than 2 wt.%, are too stable for applications requiring operation below several hundred degrees Celsius. While several means of hydrogen supply are being investigated, including the production of hydrogen from reforming of gasoline and other liquid hydrocarbon fuels on board the vehicle, there are concerns about the complexity, safety, cost and environmental disadvantages of such methods. If metal hydride systems of improved gravimetric energy density were available, they would be the obvious choice for all mobile applications. Significant opportunities exist to advance the state-of-the-art by developing high capacity alloys that can release hydrogen at low-medium temperatures. With rapid progress occurring in the development of renewable energy (such as PV and wind), water electrolysis, and PEM fuel cell technology, the market for new improved metal hydrides can be enormous. While the primary goal is to develop metal hydrides for PEM fuel cell and H-ICE applications, the results of this work can be leveraged to provide many other markets, such as:

- Fuel storage for portable power
- Hydrogen storage/energy transportation medium
- Rechargeable batteries
- Non-CFC Heat pumps/air conditioners
- Catalysts
- Compressors
- H-gas separation medium

### ECD'S EXPERIENCE IN METAL HYDRIDE TECHNOLOGY

ECD has been involved in the research and development of metal hydrides for over 18 years and has developed and received patents on fundamental concepts in this field. ECD's research and development programs have led to many new families of metal hydrides, with hydrogen storage capacities ranging from 1.5 to more than 7 percent by weight. Many of the ECD hydrides were originally developed and tested as thin films. These thin film hydrides also had excellent resistance to poisoning. Based on its metal hydride technology, ECD has developed superior nickel-metal hydride batteries having two times the energy density of nickel-cadmium batteries for equal weight and volume. As a result, the company has achieved a world-wide leadership position in the metal hydride battery technology.



### III. TECHNICAL APPROACH

The primary objective of this project is to develop commercially viable metal hydrides that will result in a system storage capacity of >2 wt.%. For this we need to develop an alloy having at least 3 wt.% H-storage capacity, capable of delivering H<sub>2</sub> at the requirements for the PEM fuel cell, namely

- Above 1 at. pressure
- Below 150°C.

Additional requirements which will need to be addressed include:

- Cost and availability of raw materials
- Ease of large-scale manufacturing
- Cycle life
- Resistance to poisoning (depending on the source of hydrogen)

Since the total system performance and efficiency is important, in addition to the task of developing superior metal hydrides, it is important to examine the total metal hydride storage system from a fundamental and theoretical standpoint to maximize the system properties and efficiency.

#### Developing Improved Hydrides:

The real challenge in this program is to develop a metal hydride that has at least 3 wt.% reversible hydrogen storage capacity (HSC) with a 1 atmosphere desorption pressure below 150°C. High capacity alloys with reversible HSC greater than 3 wt.% are known, examples include MgH<sub>2</sub> and Mg<sub>2</sub>NiH<sub>4</sub>, 7.7 and 3.6 wt.% respectively. However these alloys have 1 atmosphere desorption temperatures of greater than 250°C. A number of intermetallic alloys are known which have atmospheric desorption temperatures below ambient, but these suffer from low reversible HSCs. Examples of these alloys include the well-known TiFeH<sub>-2</sub> and LaNi<sub>5</sub>H<sub>-6</sub>, which have reversible HSCs of approximately 1.7 and 1.4 wt.% respectively. Two approaches to developing hydride alloys to meet the program's primary objective are immediately apparent. The first is to try modifying high capacity Mg-based alloys to lower their desorption temperatures and the second is to modify the low capacity intermetallic alloys to increase their reversible HSCs. During this project the first approach was investigated. A proposal which focuses on the 2<sup>nd</sup> approach has been submitted to the DOE for the continuation of this work.

#### Approaches for Improved Hydride Development

ECD's overall approach to alloy design is to modify the near-neighbor environment / local chemistry / atomic configuration of the hydrogen bonding sites through compositional substitutions, introducing compositional disorder. This affects the bonding energies and thermodynamic properties of the absorbed hydrogen with the

host metal. Also by control of the processing techniques, the obtained structure and morphology can be optimized for hydrogen storage properties. Incorporation of selected elements from the middle part of the transition metal series is used to enhance catalytic activity, increasing the sorption kinetics. For Mg-based alloys, processing is important to be able to form novel alloys which will lower the required desorption temperatures.

### ***Mg-based Alloys***

The Mg-based alloys have reversible storage capacity greater than the target goal of 3 wt.%. However these alloys have 1 atmosphere desorption temperatures of more than 250°C. Therefore the challenge with these materials is to modify the hydrogen bonding environment to lower the enthalpy of hydride formation. For example  $\text{MgH}_2$  and  $\text{Mg}_2\text{NiH}_4$  have hydride formation enthalpies of about  $-75$  and  $-65 \text{ kJ}\cdot\text{mol}^{-1} \text{ H}_2$ . Hydrides with ambient temperature 1 atmosphere  $P_{\text{eq}}$  have enthalpies in the  $-20$ - $35 \text{ kJ}\cdot\text{mol}^{-1} \text{ H}_2$ . Conventional Mg-based materials also tend to suffer from poor sorption kinetics, low tolerance to impurities and short cycle lives due to disproportionation. To effect the thermodynamics of a Mg-based hydride, it is necessary to incorporate into the matrix other low weight elements that alloy with Mg. This has the potential to modify the near-neighbor environment / local chemistry / atomic configuration, thus affecting bond energies and the thermodynamic properties. Incorporation of selected elements from the middle part of the transition metal series is used to enhance catalytic activity. These elements include Mn, Fe, Ni, Mo, Cu. Since structural disorder is expected to increase the density of storage and catalytic sites, the addition of glass formers or novel synthesis methods to enhance disorder is utilized. Glass formers include B, Al, C, Si. Additionally, since small particles having a large number of grain boundaries enhance H-diffusion, special attention is paid to **processing techniques**. The challenge of this approach is made more difficult by the low miscibility of Mg with most transition metals and by its low melting temperature/high vapor pressure relative to most metals. Therefore novel alloy preparation methods are needed.

## **IV. RESULTS OF WORK PERFORMED**

**Processing Techniques**: During the past two years of this program, ECD explored the mechanical alloying method to prepare novel Mg-based alloys. Mechanical alloying allows the production of materials which cannot be prepared by traditional high temperature melting techniques. Other advantages of this method include the direct production of powders, including nanosized powders, independent control of bulk and surface morphologies-compositions and the ability to use various reactive or non-reactive gas environments. During this time, significant progress was made in understanding the effect of various processing parameters on the resultant alloys. Tremendous progress has been made on producing alloys which show dramatically improved sorption kinetics, tolerance to impurities and long cycle lives. However the

alloys produced to date still require at least 200°C for 1 atmosphere desorption. The results obtained to date will be discussed in the following.

While mechanical alloying has shown promise, it has also shown limitations in the type of materials which can be produced. Investigation of other novel methods of alloy synthesis have also been initiated for the Mg-based materials. These include melt-spinning, which is a rapid quench technique, and gas phase condensation (GPC). Melt-spinning allows the preparation of materials which have a very uniform composition throughout the bulk, but are structurally highly disordered. Alloys can be produced which have stoichiometries different from thermodynamically favorable compositions. The local bonding environment of hydrogen within these alloys can be expected to be very different from that of conventionally prepared alloys. With the GPC method, the metals are evaporated and condensed into fine (nanosized) particles. Again with this method new structures and stoichiometries are expected which cannot be produced by conventional methods, such as induction melting. Also powders of extremely small size are directly produced which will have high surface areas. Several studies have predicted that nanosized hydride powders will be advantageous. The preliminary work with these methods will be discussed in the following.

#### ***Process Optimization (Mechanical Alloying):***

**Processing Parameters:** During the last two years we have made significant progress in the processing and synthesis of Mg-based multi-component alloys by mechanical alloying. The effect of various processing parameters, such as grinding speed and the use of grinding aids, on the alloy's morphology, sorption properties and yield have been investigated.

**Speed:** We have demonstrated that the grinding speed during mechanical alloying can be used to control the degree and nature of alloying. We have also shown that in order for the Mg and the TM elements to be in close proximity and enhance the probability of alloying, high grinding speeds are desirable. Alloying was done at speeds varying from 150 - 1000 rpm. The scanning electron micrographs (SEMs) in Figure 1 show the effect of increasing the grinding speed from 150 to 600 rpm with a 3 hour grinding duration. At lower grinding speeds, the surface of the Mg particles are coated with transition metal particles, with a more uniform coating at 300 rpm than at 150 rpm. However, there is very little incorporation of the transition metals into the bulk of the Mg. When the grinding speed is increased to 600 rpm, more fragmentation and deformation of the Mg particles is observed resulting in a laminated particle with transition metal particles dispersed throughout the bulk of the Mg. At 1000 rpm and longer grinding duration, very fine particles are obtained with the transition metals uniformly dispersed. X-ray diffraction data of the powders obtained after 6 hours of grinding at 1000 rpm show the diffraction lines for the Mg<sub>2</sub>Ni binary intermetallic compound.

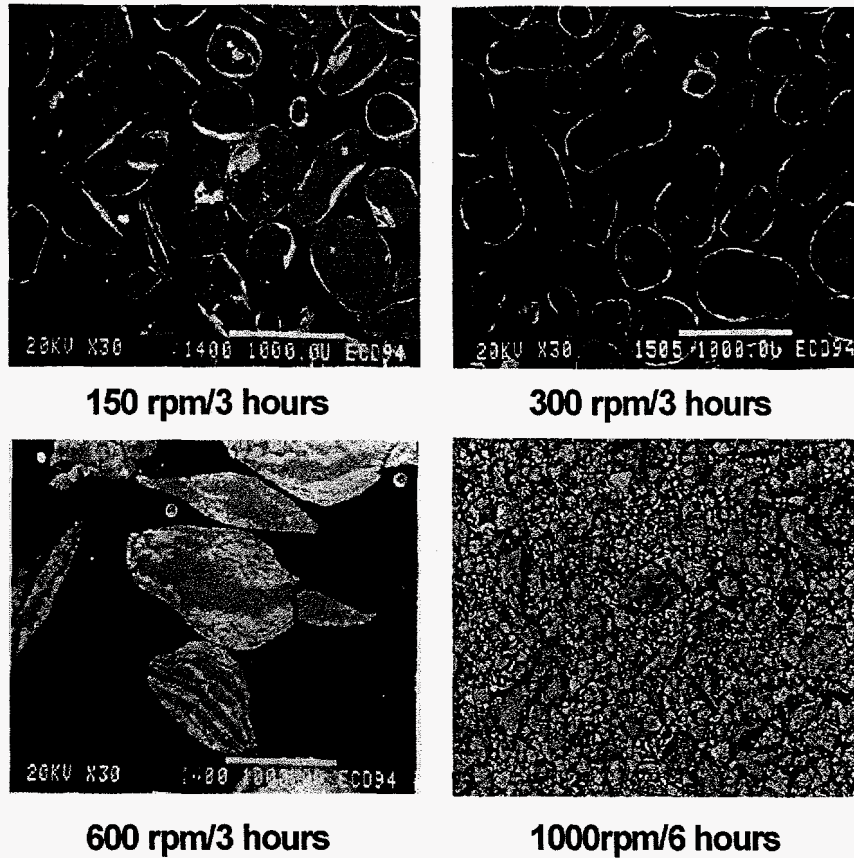


Figure 1: Effect of grinding speed on alloy morphology.

**Grinding Aids:** Two types of grinding aids have been used. Graphitic carbon was used as a solid grinding aid and heptane as a liquid grinding aid. Addition of heptane improves the alloy yield substantially and C, in addition to acting as a lubricant, has a significant effect on the enhancement of sorption kinetics for Mg-based materials. Figures 2 - 6 show the experimental results investigating the addition of grinding aids. Experiments were carried out investigating the time, frequency and amount of grinding aid addition.

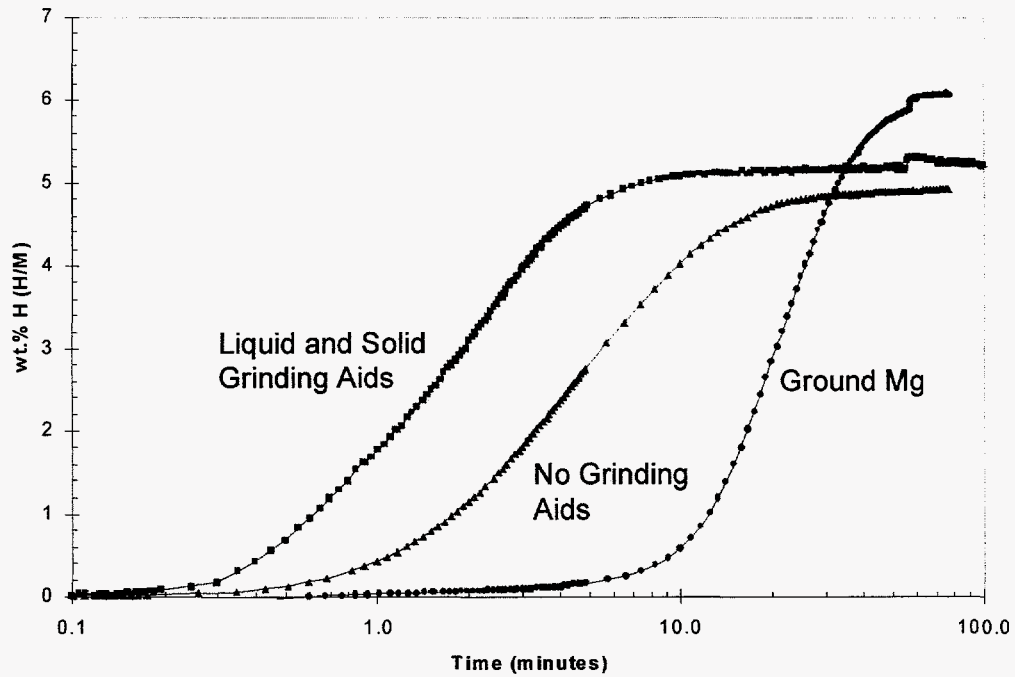


Figure 2: Effect of Grinding Aid Addition on 300°C Desorption Kinetics

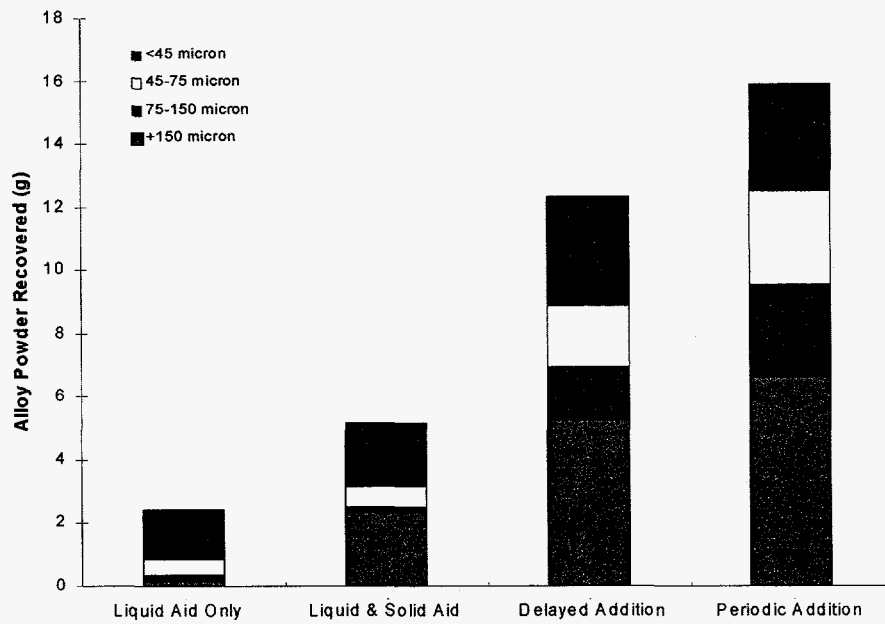


Figure 3: Effect of Grinding Aid Addition on Yield and Particle Size

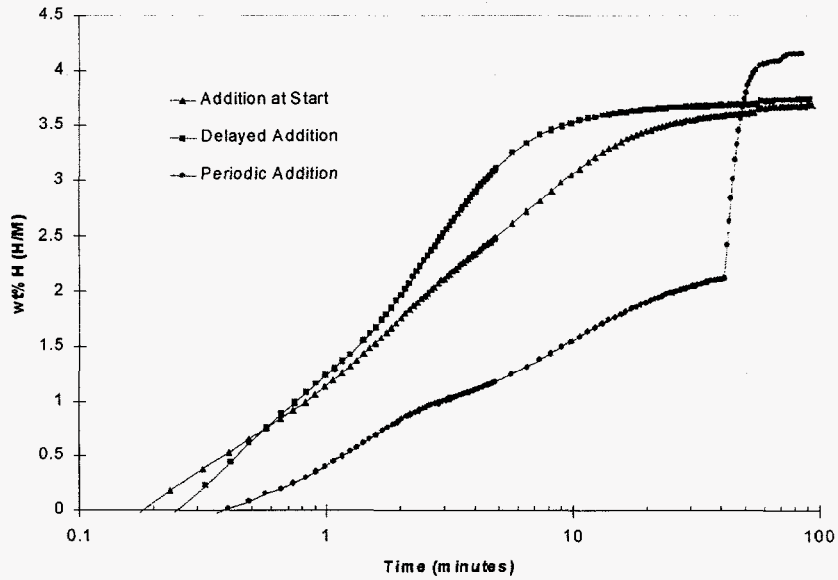


Figure 4: Effect of Grinding Aid Addition on 300°C Desorption Kinetics

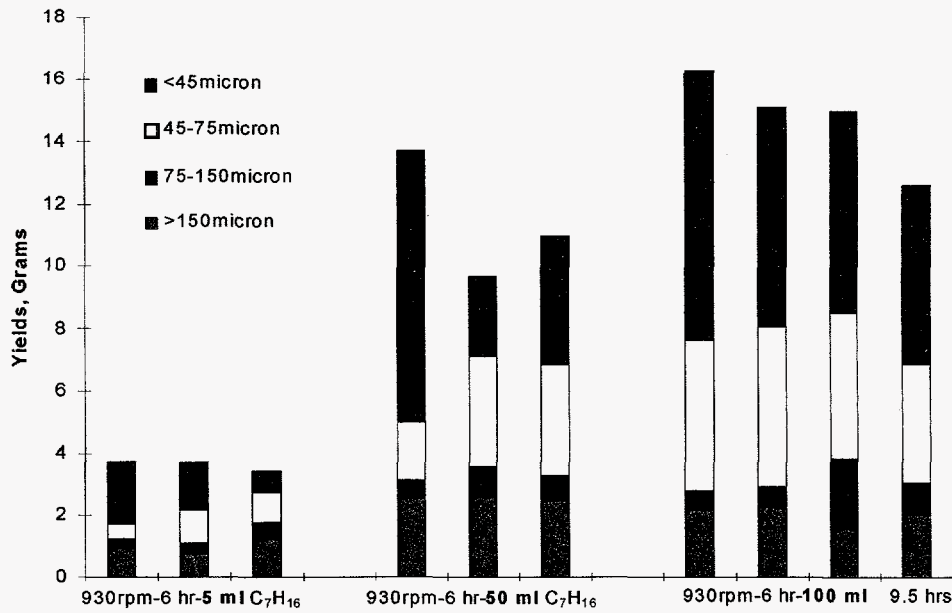


Figure 5: Effect of Liquid Aid Quantity on Yield and Particle Size



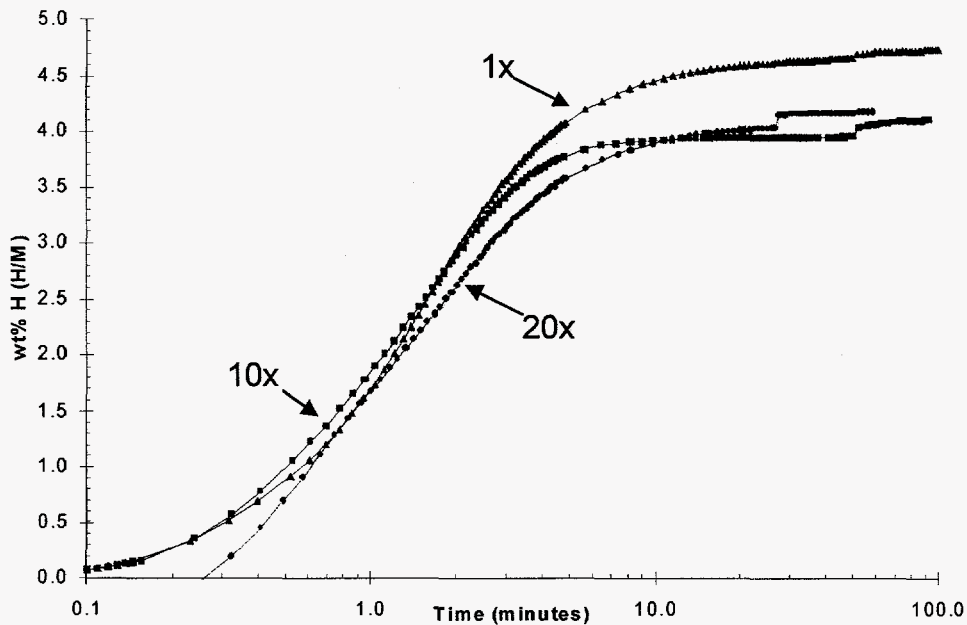


Figure 6: Effect of Liquid Aid Quantity on 300°C Desorption Kinetics

The summary of process optimization for the laboratory-scale mechanical alloying technique is as follows:

- Alloy yield has been substantially increased.
- Increasing the grinding speed improves diffusion of TM into the Mg particles, enhances break-up into smaller particle sizes, resulting in improved kinetics.
- Addition of graphitic carbon and heptane drastically improves the alloy yield and also its kinetics.
- There is a trade-off between increase in yield and time needed for alloying.

### ***Alloy Optimization:***

**Compositional Modification:** Figure 7 shows the affect of modifying Mg with selected transition metal elements on the 300°C desorption kinetics of Mg metal. This figure shows that the dehydrating kinetics of the novel mechanical alloys have been significantly improved over Mg. Figure 8 shows the 300°C desorption P-C Isotherms for three of the compositions. The increase in the higher plateau pressure phase indicates a lowering of the desorption enthalpies of this phase. Figure 9 shows the desorption kinetics for one of the modified alloys at 250, 280 and 300°C.

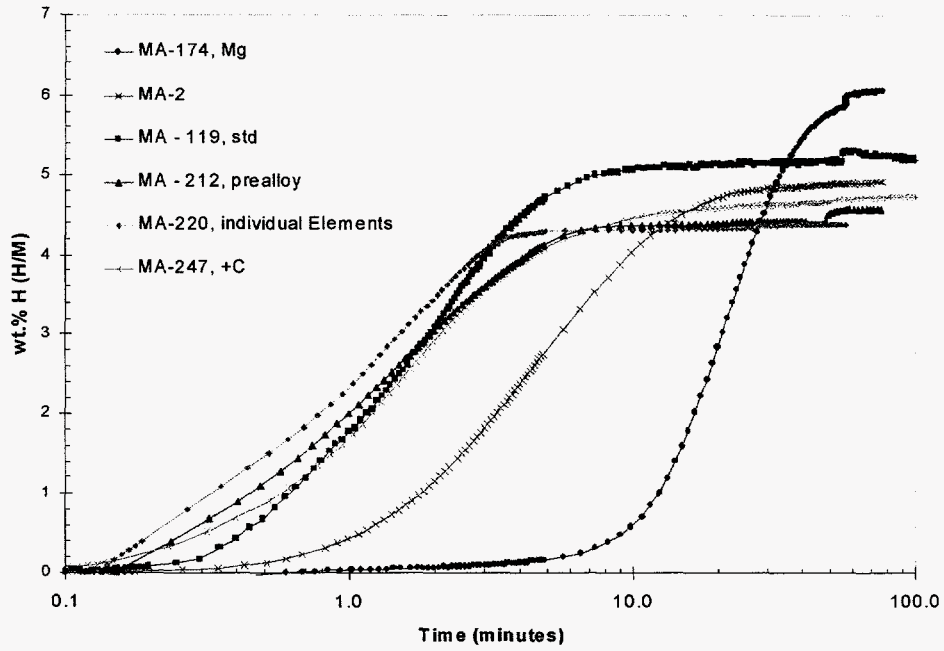


Figure 7: 300°C Desorption Kinetics of mechanically ground Mg and several alloys.

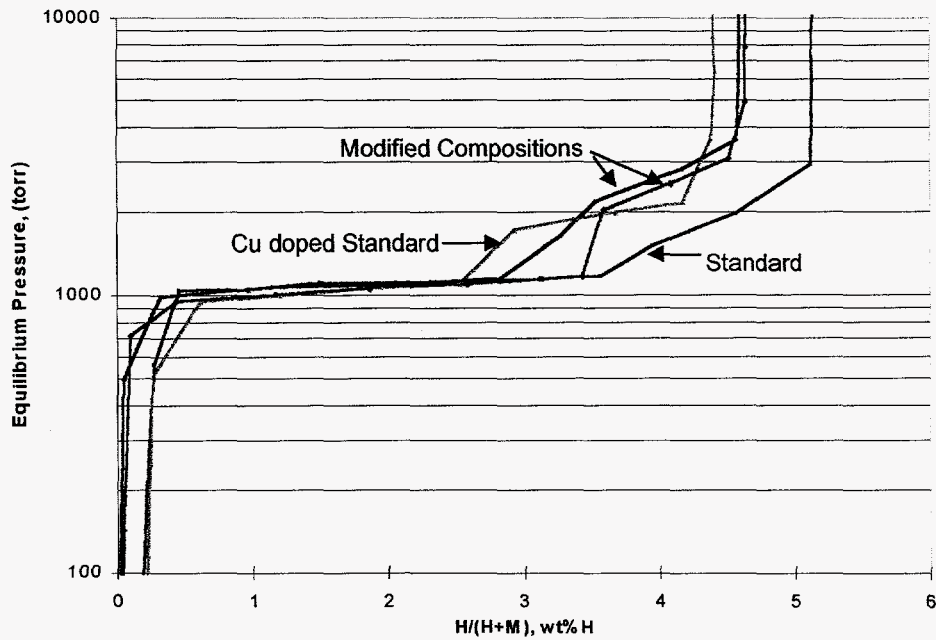


Figure 8: 300°C Desorption P-C-T Curves for several Mg-Ni based Alloys



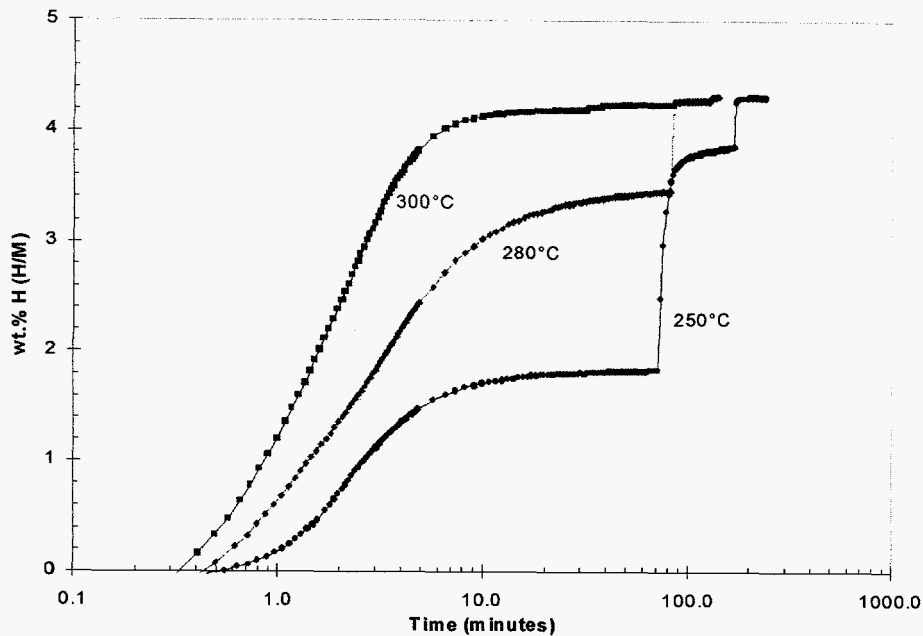


Figure 9: Desorption Kinetics for a Mg-Ni based Alloy

**Surface Modification:** Kinetics and thermodynamics can sometimes be independently controlled. The purpose of surface modification is to improve H-sorption kinetics. Several experiments were done to study the effect of surface modifiers on the kinetics of clean, mechanically ground Mg.

Previously we had found that using the laboratory attritor for mechanical alloying, best yields and particle size distribution were achieved by grinding at 930 rpm for 6 h, in the presence of grinding agents such as graphitic C and heptane. For the surface modification experiments, catalytic materials were added during the last 30 minutes of grinding (except in the case of Ni where three different durations were tried).

Surface modifiers used included: Ni, NiMo and Mg<sub>2</sub>Ni. **Figure 10** shows the effect of surface modification on the desorption kinetics. While a surface coating of Mg<sub>2</sub>Ni had the most significant effect, 30 minutes of NiMo has the same effect as 90 minutes of Ni grinding.

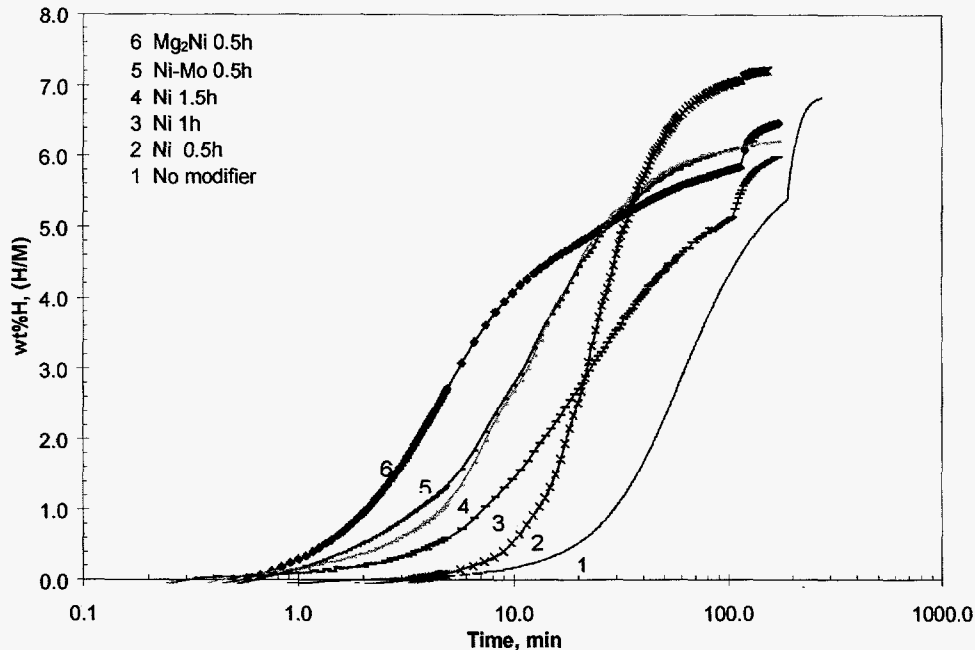


Figure 10: 300°C Desorption Kinetics of Surface Modified Samples.

**Mechanical Alloying vs. Melt Spinning:** The same multi-component material was prepared using melt spinning (MS) and mechanical alloying (MA) processes. While the overall composition was the same, three significant differences were observed:

The kinetics of the as-prepared MS sample was poorer than that of the MA sample, but this drawback was overcome by using the results from surface modification experiments, discussed above. The MS ribbon was coated with a thin layer of Mg<sub>2</sub>Ni by grinding in the attritor for 30 minutes. Figure 11 shows the desorption kinetics of two MA samples (curves 2, 2a), and the MS sample without (curve 1) and with surface modification (curves 3).

Figure 12 shows the PCT profiles of several samples. Curve labeled \* shows the improvements obtained over pure Mg by compositional modification. Curves 1, 2, and 3 are for samples of identical composition, except that 2 and 3 are for MS samples and curve 1 is for the MA sample.

Thus, preliminary results indicate that alloys made by melt spinning (rapid quenching) allow for more interactions and result in materials that are more homogeneous, and result in a higher plateau pressure. The experimentally measured values of  $\Delta H$ , showing a systematic improvement, decrease in the value of the heat of formation from 75.5 kJ/mole for pure Mg to 51.3 kJ/mole for the modified Mg-alloy made by melt spinning.

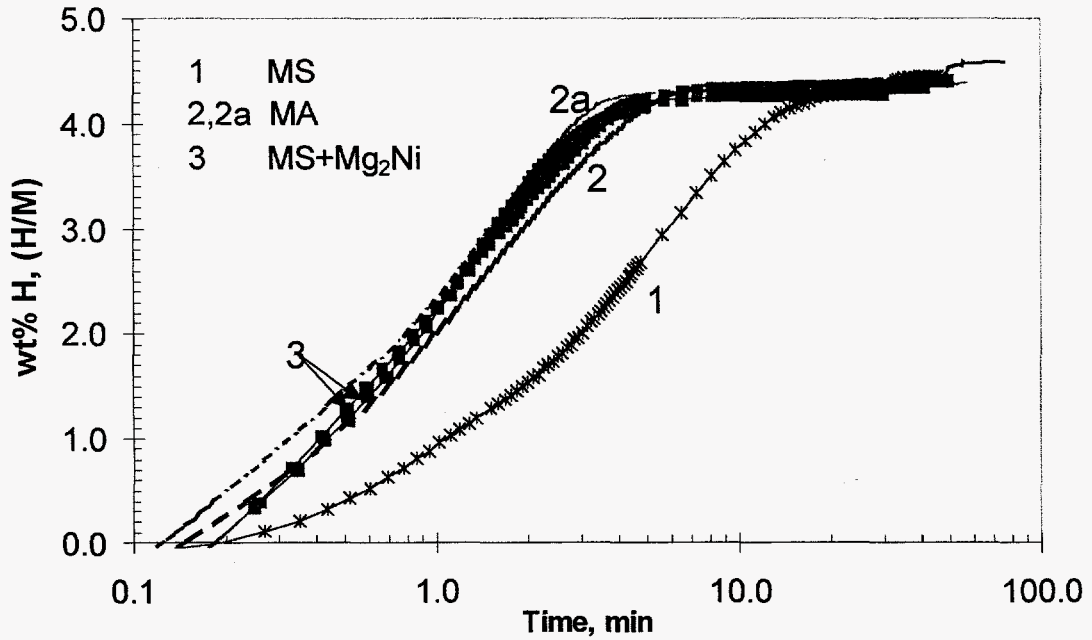


Figure 11: Comparison of 300°C Desorption Kinetics for Melt-Spun samples (as-cast and surface modified) with Mechanically Alloyed Samples.

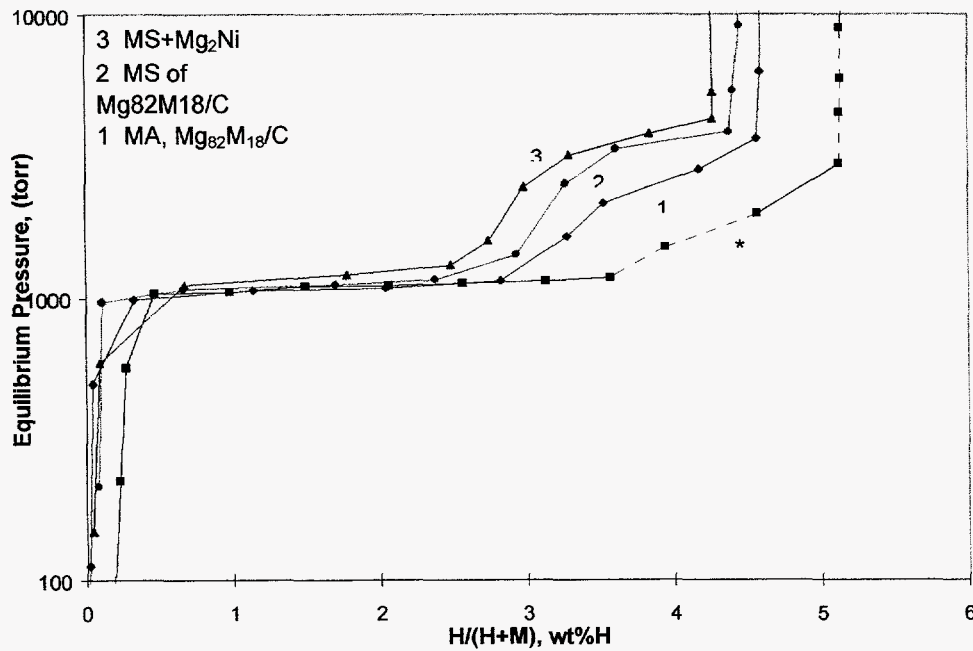


Figure 12: 300°C Desorption P-C Isotherms Comparing Melt-Spun and Mechanically Alloyed Samples.

**Modification of Mg with Al and Zn:** This is part of our approach to use using light-weight elements as modifiers. **Figure 13** shows desorption P-C isotherms of  $Mg_{50}Al_{45}Zn_5$  prepared by MA. Due to the lower percentage of Mg in the alloy (50% as compared to about 82% in all previous samples), the H-Storage capacity is lower as expected. However, the equilibrium pressure is much higher than the plateau pressure due to pure  $MgH_2$ , which is almost non-existent in the PCT data. X-ray diffraction data, **Figure 14** showing diffraction patterns for both mechanically alloyed and induction melted samples, confirm that very little elemental Mg remains in the sample. The absence of pure  $MgH_2$  is an indication of Mg modification. While the desorption temperature is still high, the increase in plateau pressure is substantially higher as compared with the Mg-transition metal alloy, shown as dotted line. **Figure 15** shows the comparison in desorption kinetics between Mg-Al-Zn prepared with and without C as a grinding aid. For comparison the desorption kinetics of a Mg-transition metal alloy is also shown. All samples were prepared by mechanical alloying.

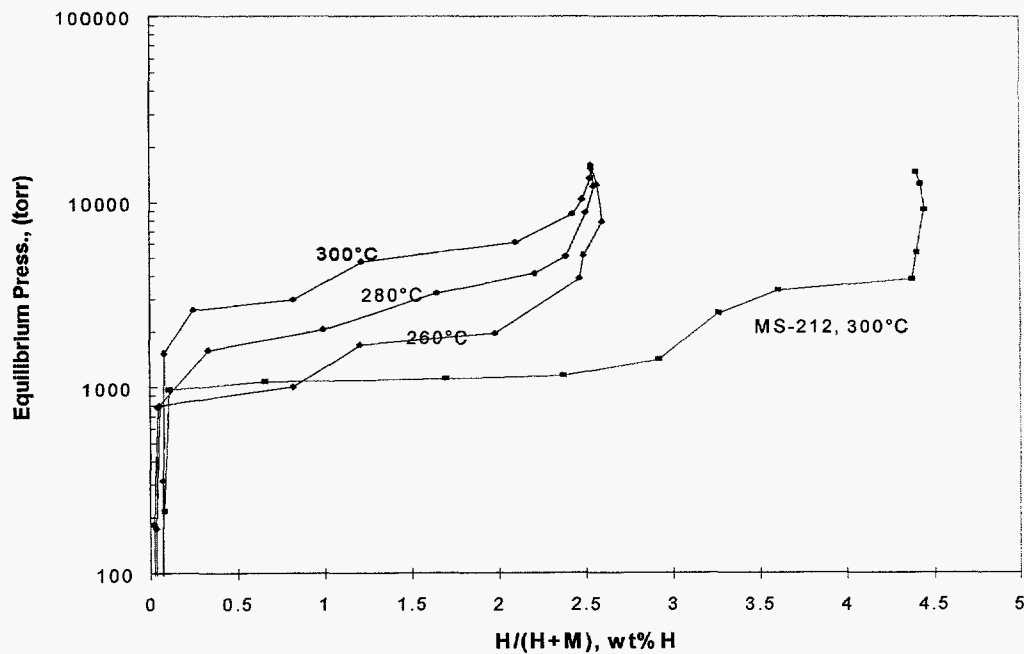


Figure 13: 300°C Desorption P-C Isotherms of a Mechanically Alloyed Mg-Al-Zn/C alloy with a Melt-Spun Mg-M sample.

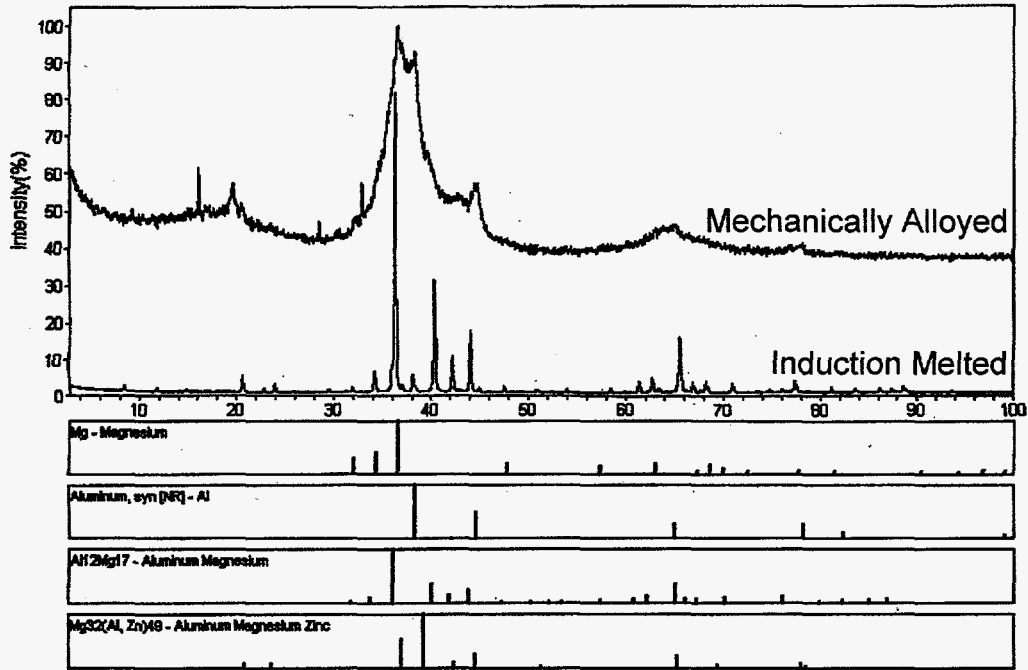


Figure 14: XRD Data Comparing Mechanically Alloyed and Induction Melted samples of a Mg-Al-Zn alloy.

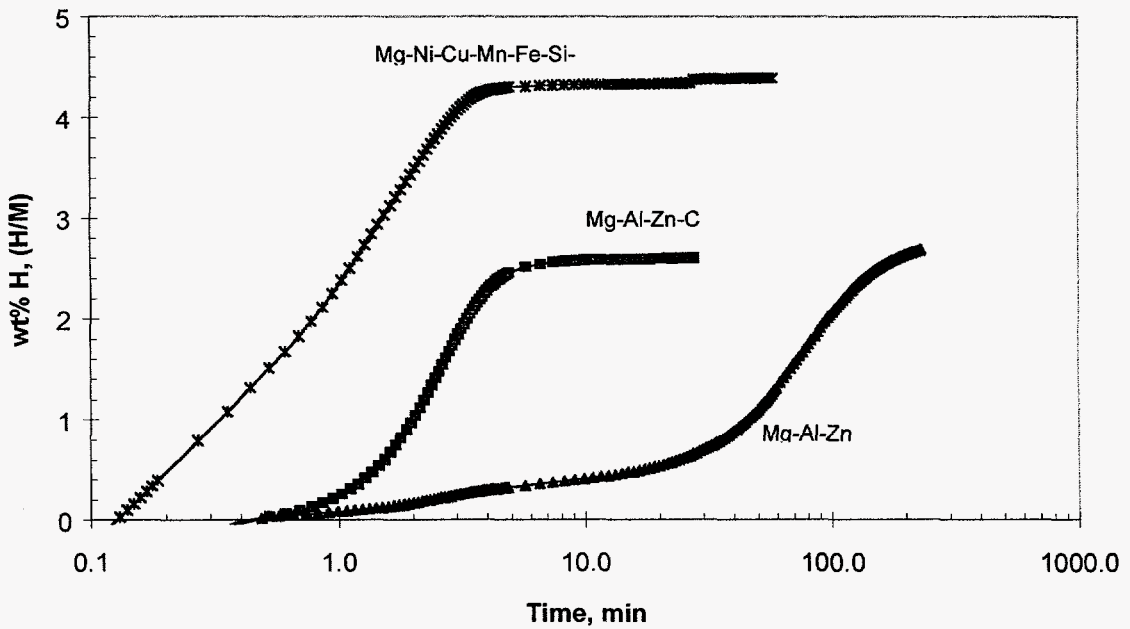


Figure 15: 300°C Desorption Kinetic Data for Mechanically Alloyed Mg-Al-based alloys.

**Cycling Data:** Several samples were subjected to over 500 absorption/desorption cycles. Figures 16 and 17 show two typical results. Figure 16 is for Mg-Ni-Cu-Mo-Si-Fe-C prepared by mechanical alloying and Figure 17 for Mg-Ni-Cu-Mo-Si-Fe prepared by melt spinning. Results show that

- There is some degradation in desorption kinetics after 500 cycles, but
- Negligible loss of H-Storage capacity on cycling

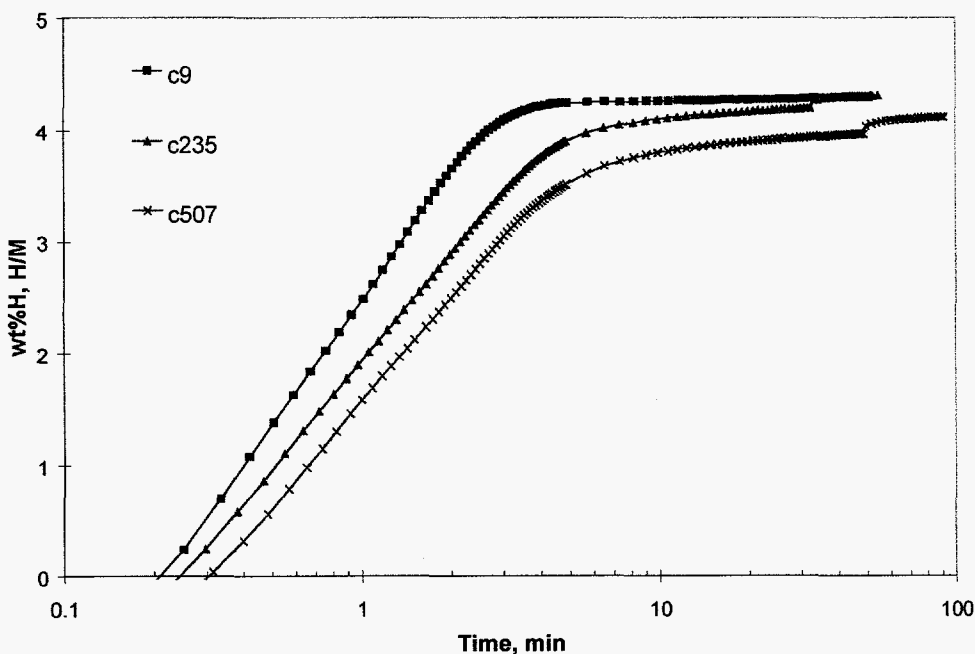


Figure 16: Cycling Data for a Mechanically Alloyed Mg-M alloy (300°C Desorption Kinetics).

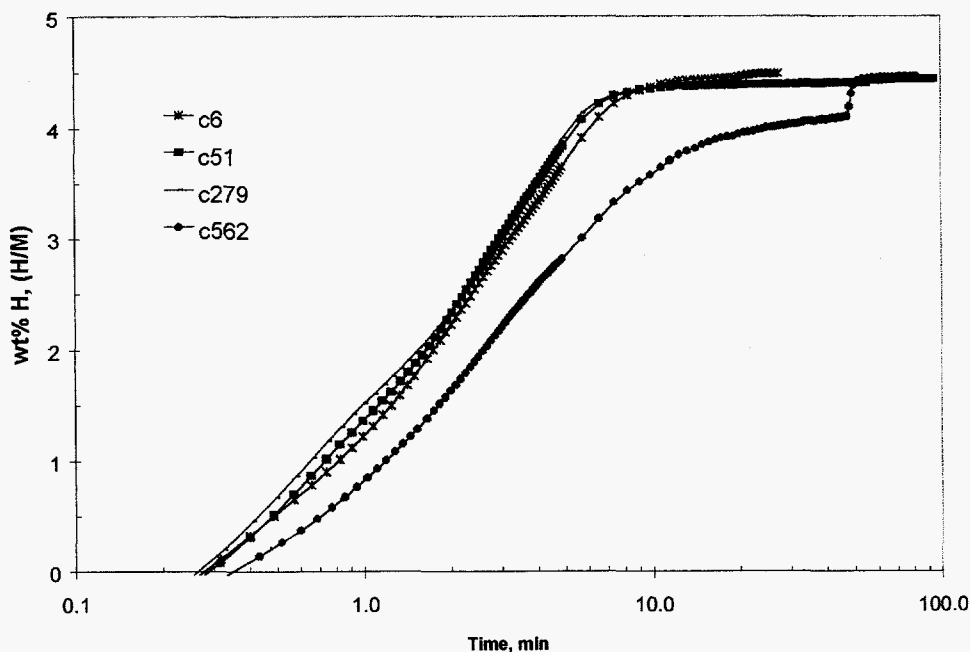


Figure 17: Cycling Data for a Melt-Spun Mg-M alloy (300°C Desorption Kinetics).

### Novel Alloy Process:     *Gas Phase Condensation (GPC) Process*

As discussed previously, we have shown that for the same alloy composition, the synthesis process and related processing parameters can substantially affect the alloy structure, morphology, degree of alloying and hence its H-storage properties. The GPC process was originally invented at Argonne National Laboratory and is in the early stages of being evaluated for its application to H-storage materials. During 1996-1997, we carried out several preliminary experiments in collaboration with Dr. Jeff Eastman of ANL. In 1997-1998, a simple system using the GPC concept was designed and constructed in our laboratory. **Figure 18** shows the schematic of this ECD system which is as yet un-optimized. The principle of operation is as follows:

Source materials evaporate under a controlled pressure of inert (Ar) or reactive ( $H_2$ ) gas resulting in the condensation of nanometer size particles which are collected on to a liquid nitrogen cooled finger. Important deposition parameters include source temperature, gas pressure, gas species, source-cold finger distance, and the nature of the source material.

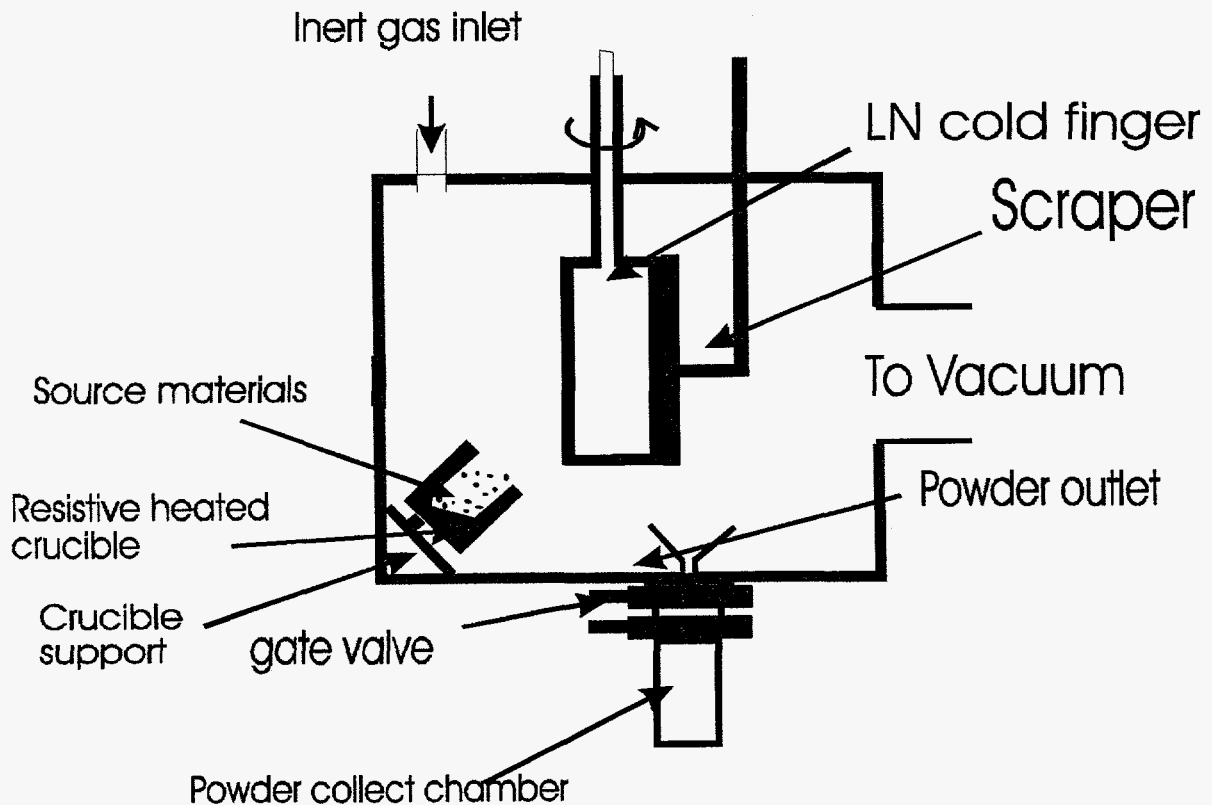


Figure 18:     Schematic of ECD's GPC Apparatus

While the system is not optimized, three samples were prepared using ECD's GPC system:

- Mg in Argon
- Mg in Hydrogen
- Mg + trace amounts of Cu (in Argon)

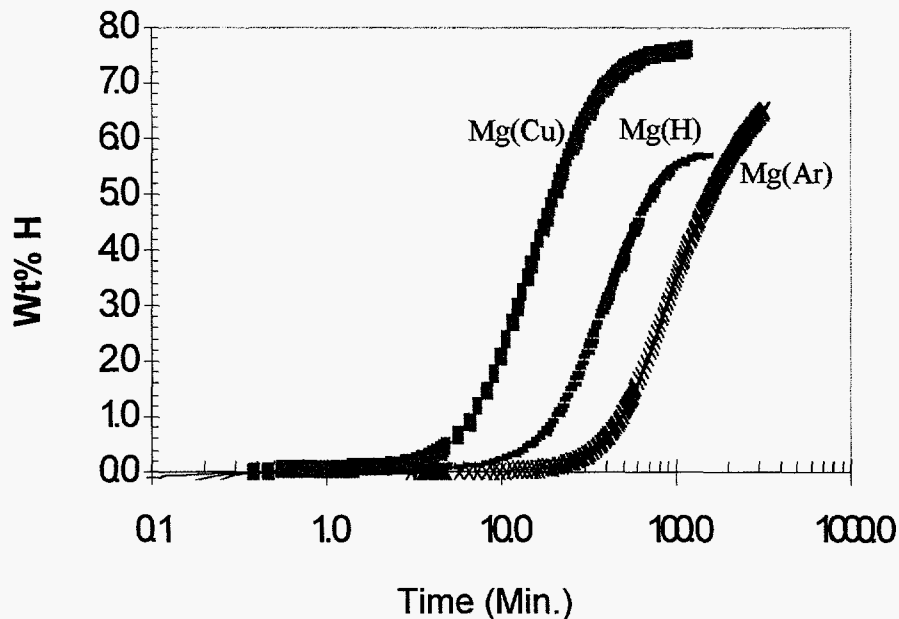


Figure 19: 350°C Desorption Kinetics of Ultrafine Powders prepared by GPC.

The samples were charged with hydrogen and subjected to the normal activation procedure. **Figure 19** shows the H-desorption kinetics of these samples.

SEM's in **Figure 20** show the pronounced effect of gas pressure on particle size. Lower chamber pressure results in smaller particle size of the resultant material. The particle sizes are relatively independent of temperature but higher temperatures promote higher yield. **Figure 21** shows that the particle morphology is relatively independent of the source temperature.

Higher deposition pressure results in longer residence time and more collisions, leading to well-defined crystalline structures and crystal sizes of about 2 microns. Lower pressures allow for fewer collisions before the particles are drifted to, and collected on to the cold finger, resulting in particle sizes of a few hundred nm. The samples were very clean (oxygen-free) as determined by Auger analysis.

The present ECD system does not easily allow for the evaporation of transition metal elements. If funding permits, future planned modifications to the system include the addition of a sputtering target to allow for incorporation of multiple transition metal elements to improve the kinetics.



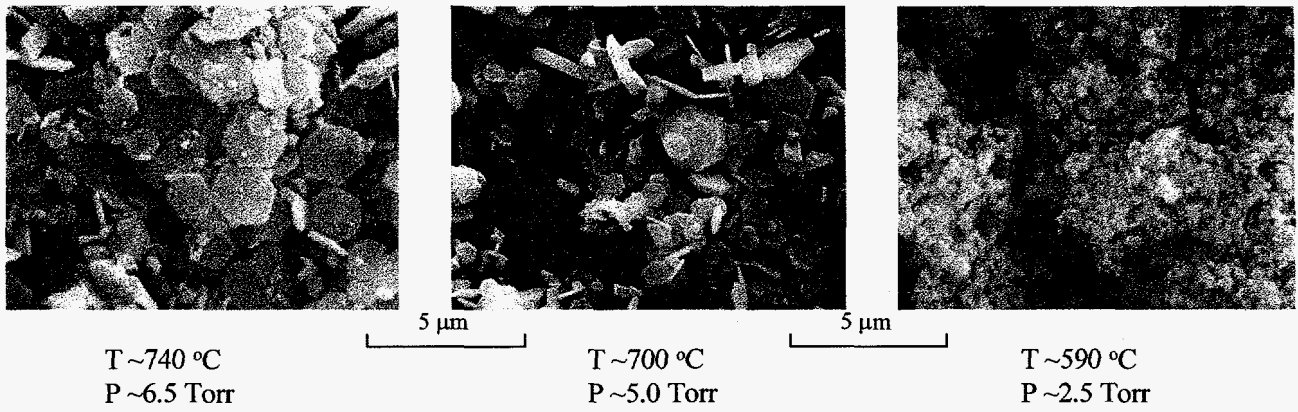


Figure 20: SEM's showing effect of background gas pressure on particle size for GPC Method.

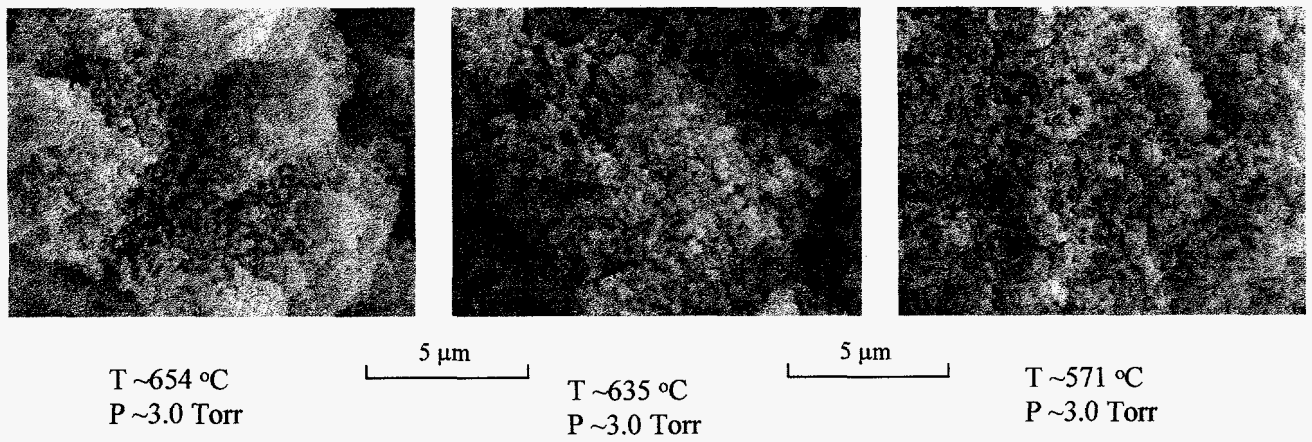


Figure 21: SEM's showing minimal effect of source temperature on particle size for GPC Method.

## V. PUBLICATIONS, PATENTS AND PRESENTATIONS

1. "Investigation of the effect on the equilibrium plateau pressure by the partial substitution of Ni by various metals in Mg-based hydrides," 28th ACS Central Regional Meeting: Metal Hydrogen Systems Symposium, 9-12 June, 1996, Dayton, OH.
2. "The kinetics of some specially tailored Mg-based alloys," 11th World Hydrogen Energy Conference, 23-28 June, 1996, Stuttgart, Germany.
3. "An investigation on the hydrogen equilibrium plateau pressures and sorption kinetics of disordered, multiphase Mg-based hydrides," International Symposium on Metal-Hydrogen Systems- Fundamentals and Applications, 25-30 August, 1996, Les Diablerets, Switzerland.
4. "Overview of the USDOE Hydrogen Program," UNDP workshop on hydrogen, Banaras Hindu University, India, December, 1996.
5. "Development of Improved Metal Hydride Technology," UNDP workshop on hydrogen, Banaras Hindu University, India, December, 1996.
6. ARO/CIA sponsored Workshop on Hydrogen Storage and Generation Technologies for Medium-Power and -Energy Applications, Orlando, FL, April 1997.
7. "Development of a Small Scale Hydrogen Production-Storage System for Hydrogen Applications". Proceedings of the 32<sup>nd</sup> IECEC Conference, Volume 3, p. 1947, July 27-August 1, 1997.
8. "An Integrated PV-Electrolysis Metal Hydride Hydrogen Generation & Storage System", Poster paper presented at the 9<sup>th</sup> Annual US hydrogen Meeting, 3-5 March 1998.
9. "Disordered Mg-Based Alloys for Hydrogen Storage", Poster paper presented at the 9<sup>th</sup> Annual US hydrogen Meeting, 3-5 March 1998.
10. "Development of a Self-Heating, High Temperature Mg-Based Hydride Hydrogen Storage System", Poster paper presented at the 9<sup>th</sup> Annual US hydrogen Meeting, 3-5 March 1998.
11. "An Integrated Hydrogen Production/Storage System Based on PV/Electrolysis/Metal Hydrides for Near Term Applications", to be presented at the 12<sup>th</sup> World Hydrogen Energy Conference at Buenos Aires, Argentina, June 1998.

12. "Effect of Processing Parameters on Mg-Based Hydrogen Materials prepared by Mechanical Alloying", to be presented at the 12<sup>th</sup> World Hydrogen Energy Conference at Buenos Aires, Argentina, June 1998.
13. Two U.S. patents issued: #5,697,221 (Dec. 16, 1997) "Robust Metal Hydride Hydrogen Storage System" and #5,778,972 (Jul. 14, 1998) "Robust Metal Hydride Hydrogen Storage System with Metal Hydride Support Structure."
14. Two patent applications filed/pending (a) "Metal Hydride Hydrogen Storage Container with Valved Ports", filed 1/20/1998, and (b) "Self-Heating Metal Hydride Hydrogen Storage System", filed 2/13/1998.

## VI. ACADEMIC CONTACTS

- Pennsylvania State University, Department of Materials Science (discussions on possible collaboration on novel synthesis technique developed at PSU)
- Argonne National Laboratory (on-going discussions on Gas Phase Condensation method developed at ANL, and presently being evaluated at ECD)
- Visit and detailed discussions with Naval Research Laboratory, Materials Science & Technology Division on modified GPC technique.
- Swarthmore College, PA. Department of Engineering. Telephonic interaction and literature compilation for ECD's PV-Electrolysis-HM storage technology for student project.

## VII. INDUSTRY CONTACTS

Automotive Companies, Fuel Cell Manufacturers, and Electrolyzer Manufacturers.

- Detailed informal discussions with Ford Motor Company on the requirements of H-Storage for FCEV, and advantages of MH on-board storage if certain weight/volume requirements are met.
- Detailed informal discussions with Ballard Power Systems and H-Power to identify markets for MH-storage Systems. Identification of system performance and cost goals. Letters of interest received from both.
- Stuart Energy Systems (Division of Electrolyzer Corporation), and Proton Energy Systems. Discussions on the availability and cost of electrolyzers for "Integrated Hydrogen Systems."

- DCH Technology. Discussions on their need for metal hydride storage systems and renewable hydrogen generation systems.
- H-Power Corporation. Discussions on their need for metal hydride storage systems.

### VIII. PLANS FOR FUTURE WORK

Future plans for the development of improved Mg-based alloys include:

- Continue to optimize alloy composition for improvement in the thermodynamic properties of Mg-based materials.
- Reproduce samples made by melt spinning. The problem is lack of laboratory size melt spinner within the group. Ovonic Battery production system is too large and often not available. Additional funds of about \$100,000-150,000 will allow building of a small system to be dedicated to this work.
- Cycling and poisoning studies

While the lowering of the desorption temperature of Mg-based alloys holds promise for hydrogen storage hydrides with over 3 wt.% storage capacity, the investigation of transition metal hydrides is also planned. While the goal is still to develop a material with greater than 3 wt.% hydrogen storage capacity, the challenge is to increase the reversible storage capacity from 1-2 wt.% without increasing the desorption temperature of the current conventional alloys. An advantage of this approach over the Mg-based alloys is that these alloys are applicable in niche applications for hydrogen storage today and any improvement will open up new markets and applications.

A proposal for the continuation of this work which emphasizes investigation of transition metal intermetallics has been submitted to the DOE for evaluation.

### IX. SUMMARY

The following conclusions summarizes the findings of this work:

- The challenge to substantially alter the thermodynamic properties and thus significantly reduce the desorption temperature remains.
- For mechanically alloyed materials, grinding aids and modifiers result in improved kinetics and higher yields.
- Surface modification improves kinetics of Mg.
- Melt spinning leads to homogeneous materials and better alloying possibilities as

compared to mechanical alloying.

- Novel GPC process results in direct formation of nanosize Mg powders.
- Bulk alloy modification results in improvement in thermodynamic properties of Mg.
- After 500 absorption/desorption cycles, minimum loss of storage capacity.
- Preliminary market analysis indicates many niche markets for metal hydrides exist. Improved alloys will substantially enlarge these markets. Markets range from the U.S. military to transportation and other used in developing nations.

It has also been concluded that a two-fold approach of simultaneously investigating the low weight percent but ambient temperature operating intermetallic hydrides with the high weight percent but high temperature operating hydrides would be best. The transition metal hydrides are practical for niche applications today and any improvement would open up new applications for their use. While the high temperature hydrides have a greater potential for high gravimetric hydrogen storage, they are more limited in their potential for current use.

## X. REFERENCES

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