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**AUTOMOTIVE STORAGE OF HYDROGEN USING
MODIFIED MAGNESIUM HYDRIDES**

Final Report, March 1976—March 1978

By
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MASTER

Work Performed Under Contract No. EY-76-C-03-1167

Solar Turbines International
San Diego, California

U. S. DEPARTMENT OF ENERGY

Division of Transportation Energy Conservation

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Final Report
Contract EY-76-C-1167

by

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RDR 1819-26

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FOREWORD

This Final Report covers the work performed under contract EY-76-C-1167 from March 1976 through March 1978. It is published for technical information only and does not necessarily represent recommendations, conclusions or approval of the Department of Energy (DOE), Division of Transportation Energy Conservation.

Contract EY-76-C-1167, with Solar Turbines International, an Operating Group of International Harvester Company, San Diego, California, is sponsored by DOE with Mr. Eugene Ecklund as the DOE Program Manager.

The program is being conducted at Solar Turbines International with Dr. David A. Rohy as the Principal Investigator. Contributing to the program are Messrs. J.F. Nachman, A. N. Hammer and T. E. Duffy.

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SUMMARY

Metal hydrides can store more hydrogen per unit volume than normal high pressure or cryogenic techniques. Little energy is required to store the hydrogen in the hydride, and high stability at room temperature ensures low losses over long storage periods. Safety features of metal hydride storage are favorable. Because of its low weight and high hydrogen storage densities, modified magnesium hydride offers the greatest potential for automotive storage of hydrogen. Experimental and analytical work in this program has been directed toward the optimization of this storage system. Due to the relative stability of MgH_2 , modifications of the $MgMH_x$ (M = metal ion) have been made to decrease the dissociation temperature while retaining high hydrogen capacity. This parameter is crucial since vehicle exhaust will supply the thermal energy to dissociate the hydride in an automobile. System studies indicate that hydride dissociation temperature (T_D) should be $200^\circ C$ to ensure uninterrupted fuel flow at all driving and idle conditions.

From experimental data developed in this four task study, we conclude that alloys comprised of Mg, Cu and Ni have come closest to meeting the dissociation temperature goal. Small additions of rare-earth elements to the basic alloy also contribute to a reduction of T_D . The best alloy developed in this program exhibits a $T_D = 223^\circ C$ and a hydrogen capacity near four weight percent compared to a theoretical 7.65 percent for MgH_2 . That alloy has been characterized for dissociation temperature, hydrogen capacity, kinetics, and P-C-T relationships.

Dissociation temperature, hydrogen capacity and material cost is reported for each alloy tested in this program.

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INTRODUCTION

2.1 BACKGROUND

Hydrogen is a candidate fuel for transportation in the long term (post 2000) period. While it is not a primary fuel, it offers several advantages. It is reasonably easy to produce. It can be consumed in heat engines or fuel cells without costly fuel preparation devices. If NO_x is controlled, hydrogen can be consumed with very low emissions. There are two major detractions for this fuel. Hydrogen is neither inexpensive to produce nor easy to store. The production problem is being approached by looking at thermochemical processes driven by the heat of a nuclear reactor. Four major methods have been advanced for hydrogen storage. They are shown in Table 1 with some advantages and disadvantages. E. E. Ecklund and F. L. Kester (Ref. 1) have analyzed these storage options and concluded that further research is warranted on lightweight metal hydrides.

2.1.1 Physical Description of Hydrides

Many metals (e.g., Ti, V, Nb, Pd, Sc, etc.) and alloys have the ability to absorb large amounts of hydrogen into interstitial crystal locations (see Fig. 1). The resulting material is a metal hydride. The hydrogen can be readily dissociated from some of these alloys by the application of thermal energy. The original alloy remains after the hydrogen has been removed. Hydrogen can be re-introduced into the metal and removed from it indefinitely with little change in the parent material.

The metal hydrides have several common features:

- Hydrogen is stored in interstitial sites in the metal lattice.

- Hydrogen density is equal to or greater than that in liquid hydrogen (0.07 g/cc).

- The heat of formation is relatively low ($\Delta H_f = -73.7 \times 10^3$ joules/mole).

- Hydriding and dehydriding can be performed indefinitely.

The amount of hydrogen absorbed into the lattice of the material varies with electronic and lattice structure of the material. Using these facts, one can select combinations of elements that are more likely to form hydrides with a

Table 1
Hydrogen Storage Concept

Concept	Advantages	Disadvantages
Metal Hydrides	High storage density Room temperature storage	High temperatures required to dissociate
Cryogenic	High storage density	Safety Energy required to liquify
Compressed Gas	Proven technology	Low storage density
Chemical	Good kinetics	High weight

Octahedral (O) and tetrahedral (T) sites in bct lattice. Metal ions show as the large open circles. In a bcc lattice, O_1 and O_2 sites are indistinguishable.

Figure 1. Interstitial Sites for Hydrogen in a bct Crystal Lattice.
C and A are Lattice Parameters of Tetragonal Cell.

high H/M (hydrogen/metal atom) ratio. Figure 2 shows the temperature pressure relationships for several metal hydrides. The hydrogen is absorbed into the metal through a multistep process. In the first step, the H_2 molecule must be adsorbed and then reduced to atomic hydrogen at the surface of the material. The hydrogen is then absorbed and diffused into the material. The hydrogen diffuses rapidly in the metal lattice occupying the interstitial locations.

The formation of the hydride in this manner is almost always exothermic once a threshold temperature or pressure has been obtained. The threshold level depends to a great extent on the condition of the metal surface. Oxide films inhibit the formation of the hydride, while small particle size is desirable for the rapid production of metal hydrides with a high H/M ratio. Since the lattice constants often expand by ten percent or more upon the introduction of hydrogen, many metals crumble, crack or become extremely brittle when hydrided. Cyclic absorption and desorption of hydrogen in a metal increases and cleans the surface area, resulting in the formation of the hydride at a lower threshold temperature. Maximum concentrations of one, two, or three hydrogens per metal atom are common with some ternary systems displaying higher H/M ratios under special conditions.

Figure 2. Dissociation Pressure-Temperature of Hydrides

2.1.2 Selection of Hydride Forming Alloys

Since so many alloys do form hydrides, criteria were developed to limit the scope of investigation to the most practical alloys. The criteria are:

- Inexpensive nonstrategic material
- Low weight density
- High hydrogen density
- Moderate dissociation temperature
- Good kinetics.

A comparison of the weight and volumetric densities with storage capacity is shown in Table 2 for several hydrides.

Table 2
Comparisons of Various Metal Hydrides With
Cryogenic Storage of Hydrogen

	Wt % Hydrogen	Relative* Weight Storage	Volumetric Storage of H ₂ g/ml	Relative** Volumetric Storage
LH ₂	100	1	0.07	1.0
MgH ₂	7.6	13	0.132	0.53
TiH ₂	4.0	25	0.187	0.37
VH ₂	3.8	26	0.234	0.30
FeTiH ₂	1.9	53	0.123	0.569
LaNi ₅ H _{6.7}	1.5	67	0.126	0.555

*Weight of metal hydride required to store one unit of hydrogen compared with LH₂. Container weight not included for hydrides or LH₂

**Volume required to store one unit of hydrogen compared with LH₂ storage

The two alloys that best satisfy the screening criteria are the magnesium based alloys and the iron-titanium alloys.

These two hydrides are compared in Table 3. FeTi is currently being used in experimental vehicles by Billings Energy Corporation of Provo, Utah and Daimler Benz. It has an advantage of a low dissociation temperature. The magnesium alloy hydrides offer considerably greater storage capacity per pound but suffer

Table 3
Hydride Comparison

	FeTi	Mg Alloys
Weight for 320 km (200 mi) range (kg)	577	191
Cost per Vehicle (\$)	1300	420
hydrogen Capacity (%)	2	7
Dissociation Temperature (°C)	0	220

from a high dissociation temperature. Due to the favorable storage density for magnesium, the current work is directed at reducing the dissociation temperature of the magnesium based alloys.

2.1.3 Description of a Hydrogen Storage System

A hydrogen storage system for automotive use might resemble that shown in Figure 3. That figure illustrates the general components of such a system but does not represent an actual system. The hydride bed shown in the lower right of Figure 3 would contain between 48 and 382 kg of metal hydride depending on the range of the vehicle and its energy requirements. This added weight penalty is small in comparison with battery systems. Figure 4 illustrates the difference in weight for fuel systems composed of magnesium hydride, iron-titanium hydride and NiCad batteries for the same vehicle range. While none can compare favorably with gasoline, magnesium hydrides are clearly superior to battery storage and the iron titanium alloys.

The cost of the alloy for a 191 kg magnesium alloy hydride bed is approximately \$475 in 1978 dollars. This is equivalent to \$2.49/kg (\$1.13/lb). The cost of tankage, heat exchangers, and systems components is not included in this estimate. Minimizing the hydrogen pressure and the mass of the hydride material will reduce the cost of the tankage and heat exchangers.

2.2 PROGRAM GOALS

On-board fuel storage is a basic limitation to the use of hydrogen as an automotive fuel. Metal hydrides can store hydrogen at the same volumetric density as cryogenic methods, but generally incur serious weight penalties. Among the relatively common materials, magnesium-base alloys offer the best

Figure 3. Automotive Hydrogen Storage System

Figure 4. Energy Storage Weight for 200 Mile Range

(lowest) weight density. The objective of this program is to develop a magnesium-base alloy to store hydrogen that meets the operating constraints of a conventional automobile with a spark ignition engine. Specific constraints include:

- Dissociation Temperature - The dissociation temperature of the magnesium hydride must be 200°C or less. The hydride bed must provide hydrogen at one atmosphere pressure when heated to that temperature.
- Weight - It must store 9 to 23 kg (20 to 50 pounds) of hydrogen with total weight of hydride metal plus containment tank and heat exchanger system sufficiently low to not seriously impair vehicle performance.
- Waste Heat Utilization - The heat of dissociation and temperature pressure relationship must be in a range that allows waste heat of the engine to be utilized for hydrogen generation.
- Rate of Dissociation - The hydride must dissociate at a rate to supply a continuous flow of hydrogen for steady state 0.62 g/sec to 1.25 g/sec (5 to 10 pph) and transient 3.15 to 6.3 g/sec (25 to 50 pph) fuel flow rates. The system must be designed to handle virtually instantaneous flow transients from idle to maximum flow.
- Cost - The cost of the basic hydride must be compatible with automotive requirements of approximately \$2.20/kg (\$1.00/lb) (1976 dollars).
- Startup - A startup system to supply hydrogen immediately from cold start must be provided.
- Storage Density - The volume/pound of hydrogen must be sufficiently low to allow installation in a vehicle and, thus, must be close to the density of liquid hydrogen 0.07 g/cm³ (4.4 lbs/ft³).

2.3 DISSOCIATION TEMPERATURE GOALS

The dissociation temperature goals have been recalculated. The original goal was 200°C (reported in TEC-75/002) (Ref. 2). This goal was based on a minimum exhaust gas temperature of 866°K derived from gasoline fueled internal combustion engine. The calculations presented here are based on the data from King and Mogens (Ref. 3) as presented in TEC-75/003 (Ref. 4) as Figure 5.1. Two operating points were chosen: Equivalence Ratio = 0.5 and Equivalence Ratio = 1.0. The temperatures measured 7.6 cm from the exhaust valve were recorded as 640°K and 825°K (see Fig. 5). Using the equation on page 46 of Reference 2, we find for the higher temperature, 825°K:

Figure 5. Exhaust Gas Temperature for CFR Engine Fueled With Hydrogen (Ref. 4). Two Operating Points are Shown With Dots.

$$59.9 \text{ J/kg} \times \frac{(825^\circ\text{K} - z)}{(825^\circ\text{K} - 293^\circ\text{K})} = 27.4 \times 10^6 \text{ J/kg}$$

$$z = 493^\circ\text{K} (220^\circ\text{C})$$

and for the lower temperature, 640°K:

$$59.5 \text{ J/kg} \times \frac{(640^\circ\text{K} - z)}{(640^\circ\text{K} - 293^\circ\text{K})} = 37.4 \times 10^6 \text{ J/kg}$$

$$z = 423^\circ\text{K} (150^\circ\text{C})$$

To minimize the size and cost of heat exchangers it is common to utilize a 28°C (50°F) temperature difference between fluids in the heat exchanger. Thus the maximum temperature of the hydride will be

$$T_{\text{hydride}} = 220 - 28 = 192^\circ\text{C} \\ \text{for Equivalence Ratio} = 1.0$$

$$T_{\text{hydride}} = 150 - 28 = 122^\circ\text{C} \\ \text{for Equivalence Ratio} = 0.6$$

The first number is essentially the same as our past goal of 200°C. The second number is significantly lower. Recent communications (Ref. 5) from Professor Adt and his coworkers at the University of Miami indicate that new data for exhaust temperatures are higher. If this is confirmed the temperature goals will be shifted upward accordingly.

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RATIONALE FOR SELECTION OF ALLOYING ADDITIONS

Many metals and alloys form reversible hydrides. Because of the constraints discussed in Section 2 only the magnesium based hydrides have been selected for further work. Magnesium hydride properties can be tailored significantly by alloying it with additional elements. Without a system or reasonable basis for choosing the additional elements, one could spend significant effort "looking" for an alloy with the proper characteristics. The rationale for alloy selection in this program is presented in this section. In all cases the investigations have been goal oriented. Thus when an alloy was not significantly better than previous alloys (based on program goals), it was dropped from further study. This section is organized by elements.

3.1 Mg-Zn-Ni AND Mg-Cu-Ni SYSTEMS

The Mg-Zn-Ni and Mg-Cu-Ni alloy systems emerged from a previous study (Ref. 2) as the most promising for further investigation. A low dissociation temperature, T_D^* , of 260°C was observed in the prior research, and was attained with the addition of a minimal amount of the more expensive and strategic element, nickel.

A combination of these two alloy systems formed the basis for the study of a series of quaternary alloys containing varying amounts of Mg-Ni-Cu-Zn; however, no significant reductions in T_D nor increases in the H/M ratios were achieved with this series.

Multiple Linear regression analyses of these quaternary alloys containing both copper and zinc also indicated that this particular combination would not be likely to decrease the dissociation temperatures (T_D) below 254°C. Hydriding experiments conducted on Mg-Cu-Ni alloys resulted in a T_D of 254°C for $Mg_{0.85}Cu_{0.05}Ni_{0.1}$, along with a favorable H/M (hydrogen stored per metal ion) ratio of 1.21. Quaternary additions made to this basic system eventually led to the development of Alloy 149, which was later selected for complete characterization. These studies are covered more completely under Section 3.4, Alloy Optimization and Experimental Procedure sections.

* T_D , for the purposes of this program, is defined as the temperature at which the dissociation pressure of a fully hydrided alloy equals one atmosphere under equilibrium conditions.

3.2 TIN, GALLIUM, VANADIUM, AND SILICON ADDITIONS

As it was apparent that the lower limit of T_D had been achieved within the Mg-Ni-Cu-Zn systems, a new series was initiated to include tin, gallium, vanadium, and silicon alloying additions. The results of the previous program indicated beneficial effects upon the dissociation pressure of the Mg-Ni_{0.1} basic alloy with minor additions of tin and gallium.

Brookhaven National Laboratories (BNL) (Ref. 6) reported a spontaneous decomposition of $VH_{1.2}$ at room temperature to form the monohydride. Even though vanadium undergoes a monotectic reaction with magnesium, and therefore has a very limited solubility in liquid magnesium, it was felt that perhaps a dispersion of fine droplets of vanadium in the magnesium alloy matrix might be achieved, particularly with the vigorous stirring action of the Tocco induction melting unit operating at 10,000 Hertz.

Further increases in dissociation pressure of $VH_{1.2}$ were observed by BNL in the presence of certain impurities. Silicon appeared to have the greatest effect in this respect, with an increase in dissociation pressure of 41 times that of the hydride made from pure zone-refined vanadium. This fact was the basis for the addition of a small amount of silicon in a ratio of four atomic percent of the vanadium content. This pronounced effect of silicon upon the dissociation pressure of $VH_{1.2}$ can be attributed to the "rule of reversed stability", which states that the stability of the intermetallic hydride is inversely proportional to the stability of the intermetallic compound. V_5Si_3 is an extremely stable compound with a melting point of $\sim 2150^\circ\text{C}$, so that its hydride would be expected to be rather unstable.

Vanadium additions provided a significant decrease in T_D (249°C) in Alloy 107.43. With additions of both vanadium and silicon to the basic Mg-Ni-Cu system, a T_D of 238°C was obtained (Alloy 130). This T_D compares very favorably with the T_D of the Mg_2Ni baseline alloy, but has the following additional advantages of (1) less than 10 percent nickel versus more than 25 percent for Mg-Mg₂Ni, (2) improved hydriding-dehydriding kinetics, and (3) lower density than the baseline Mg-Mg₂Ni alloy.

The addition of tin did not result in any improvement in T_D .

The lowest dissociation temperature (235°C) of this entire series was obtained with an alloy containing two atomic percent gallium, the balance consisting of 80.75 Mg, 5 Ni, 7.5 Cu, and 4.5 Zn. Because of the extremely high cost of gallium, this addition was not deemed practical for automotive use and was therefore eliminated from future consideration.

3.3 BORON, ALUMINUM, AND INDIUM

Because the high cost of gallium precludes its use in automotive hydrides, investigations were continued with other less costly Group IIIA elements such

as boron, aluminum, and indium, which by virtue of their periodic grouping might be expected to exhibit behavior similar to gallium.

Because of the formation of the NiAl refractory phase and the inability to produce a homogeneous melt, aluminum was alloyed without nickel in the form of the quaternary, $\text{Mg}_{0.8}\text{Cu}_{0.1}\text{Al}_{0.05}\text{Sn}_{0.05}$ (Alloy 132). The resulting T_D was unimpressive and the H/M ratio was a very low 0.23. No further experiments were carried out with aluminum.

In their investigations of the hydriding behavior of various intermetallic compounds of magnesium and aluminum, BNL observed a hydrogen capacity of 3.31 percent in a hydrided $\text{Mg}_{17}\text{Al}_{12}$ intermetallic phase (Ref. 10). Investigations of the Mg-10 w/o Al system by Douglass indicated a hydrogen capacity of seven percent and a resistance to comminution during the hydriding and dehydriding cycle (Ref. 11). In the light of these observations, the investigation of alloys based upon the Mg-Al system should be reopened again. Additional studies of this system are planned in future work.

An alloy of $\text{Mg-Ni}_{0.05}\text{Cu}_{0.075}\text{B}_{0.02}\text{Zn}_{0.045}$ (Alloy 134) yielded a T_D of 238°C, which was not significantly better than that obtained with the alloys of Mg-Ni-Cu-Zn, without the boron additions.

Substitution of indium for gallium (Alloy 133) produced a hydride with a T_D 30°C higher than that obtained with an equal atomic percentage of gallium. This alloying element was also dropped from further consideration.

3.4 RARE-EARTH AND RELATED ELEMENTS

It is our opinion that the rare earths occur in the Mg-Ni-Cu alloys as the RNi_5 intermetallic compounds, as the RNi_5 compounds exhibit very high thermodynamic stabilities. The stability of the RNi_5 intermetallic compounds and their relationship to the "rule of reversed stability" with respect to the ternary hydrides are well illustrated in Table 4. The RNi_5 compounds are listed in ascending stability, and the ternary hydrides in descending order of stability. The rule of "reversed stability" was originally proposed in the work of van Mal and his associates (Ref. 7).

Two alloys with cerium additions of 0.5 and 1 atomic percent to the basic $\text{Mg-Ni}_{0.05}\text{Cu}_{0.1}$ system gave the lowest T_D values of all alloys studied to date. Both exhibited T_D equilibrium temperatures of 227 and 232°C on duplicate determinations. These results also support the "rule of reversed stability".

The success achieved with cerium additions led to the investigation of other rare-earths, such as mischmetal (MM), a natural mixture of light rare earths (see Table 5 for typical composition) and yttrium, a related Group IIIB metal that behaves as a rare earth. These were studied as 0.5 to 1.0 atomic percent additions to the basic $\text{Mg-Ni}_{0.05}\text{Cu}_{0.1}$ alloy.

Table 4
Characteristics of Selected RNi_5^* Compounds and Their Hydrides (Ref. 8)

Compound	M.P. (°C)	Plateau Pressure, atm	Temperature (°C)	ΔH calc. kcal/mole
$LaNi_5$	1329	2.5	20	-13 ± 5
$CeNi_5$	1320	-	-	--
YNi_5	1490	12	23	--
$PrNi_5$	1365	12	20	-8 ± 5
$NdNi_5$	--	20	20	-7 ± 5
$^{**}MMNi_5$	--	20	RT	--
$SMNi_5$	--	60	20	-6 ± 5
$GdNi_5$	~ 1500	120	20	-5 ± 5
*R = ,rare earth **MM = mischmetal				

Table 5
Typical Composition of Mischmetal in Weight Percent

Ce	La	Pr	Nd	Other Rare Earths (ORE)
48-56	22-27	4-6	14-18	1-3

Mischmetal additions of one atomic percent to the basic $Mg-Ni_{0.05}Cu_{0.1}$ system (Alloy 131M) produced a low hydride dissociation temperature of $229^\circ C$, which compares very favorably with that obtained with the cerium additions ($227-232^\circ C$). The low cost of mischmetal would make it the preferred addition.

Substitution of yttrium for cerium in the $Mg-Ni_{0.05}Cu_{0.1}$ alloy resulted in one of the lowest hydride dissociation temperatures of $223^\circ C$, with the exception of Alloy 163, which has too high a density because of its heavy metal content. This very promising result indicated more work was needed in

this area. The use of the lower cost yttrium-"mischmetal" (a mixture of the heavy rare earths) as an alloying addition is described in more detail in Section 6.2.

The dissociation temperature data obtained with rare-earth additions appear to follow in a rough manner what might be expected with the "rule of reversed stability" as illustrated in Table 6. In appraising the data generated throughout the alloying study, it is also apparent that the rare-earth elements are among the most effective in decreasing the hydride dissociation temperatures, while at the same time maintaining high ratios of H/M and good hydriding kinetics. Homogeneity of these alloys is also very good with no evidence of gross segregation by X-ray examination. This latter factor is a very important consideration for large scale melting of alloys with uniform properties.

Table 6
Melting Points of Lanthanum Intermetallic Compounds

Compound	Melting Point, °C
LaB ₆	>2500
La ₂ Sn	1423

The Multiple Linear Regression (MLR) computer analysis described in Section 5.1 also indicates that the most effective addition elements for reducing T_D based on these data are the rare-earths and silicon.

Using the rationale of the "rule of reversed stability", other rare-earth intermetallics were given a cursory examination. These included minor additions of tin and boron to the rare-earth-containing alloys. Table 6 lists the possible compounds and their melting points, which are an approximate measure of their relative stabilities. Although data could only be found for the lanthanum compounds, they can be considered indicative of the stabilities of the rare-earth compounds in general.

Boron additions were abandoned because it became apparent that it would not be possible to put the refractory rare-earth borides into solution without resorting to excessively high temperatures, with the attendant danger of vaporizing magnesium and other more volatile elements.

The data obtained with the combination tin and rare-earth additions indicated that there was substantially no improvement in T_D over the ternary Mg_{0.85}Ni_{0.05}Cu_{0.1} system (Alloy 107R). There were therefore no further plans to use tin additions in future alloys.

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ALLOY OPTIMIZATION

Based upon the results of Task I and II alloy studies, plus the MLR computer program predictions, one alloy system was chosen for further investigation under the Alloy Optimization Task (Task III). The desirable characteristics of the chosen alloy systems include low decomposition temperatures and favorable H/M ratios, without the attendant problems of inhomogeneity due to formation of highly insoluble phases in the magnesium matrix. In addition, this combination of alloying elements achieves low density, maintains strategic nickel content to a minimum, and keeps the cost at a reasonable level.

The system and its variants investigated under Task III consisted of Mg-Ni-Cu-Si-RE, where the allowed range of each constituent in atomic fraction was:

$$0.77 \leq \text{Mg} \leq 0.96$$

$$0.04 \leq \text{Ni} \leq 0.10$$

$$0 \leq \text{Cu} \leq 0.10$$

$$0 \leq \text{Si} \leq 0.01$$

$$0 \leq \text{RE} \leq 0.2 \times \text{Ni}$$

$$\text{RE} = \text{Mischmetal, Y, Y-mischmetal}$$

The final series of alloys studied were derived from the basic Mg-Ni_{0.05}Cu_{0.10} system with rare-earth and related element additions. From 0.5 to 1.0 atomic percent additions of cerium, mischmetal (MM), neodymium, yttrium, and yttrium-mischmetal, along with minor amounts of silicon were made to the Mg-Ni-Cu alloy system. Best results were obtained with the Mg-Ni_{0.05}Cu_{0.10}Y_{0.005} Alloy No. 149, which exhibited the lowest hydride dissociation temperature of 223°C, with the exception of Alloy No. 163 which has a higher weight density because of its heavy metal content. The lower H/M ratio of 0.72 is another disadvantage of that alloy.

Within the limits of this study it appeared that the lower limit of T_D at 223°C had been attained with Alloy No. 149. Thus it was selected for full characterization in Task IV.

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5

DATA ANALYSIS METHODS

Data generated by the various tests have undergone a continuing analysis for correlation of dissociation temperature, T_D , and hydrogen capacity, H/M with composition of the alloys. Three calculator programs facilitate the following analyses.

5.1 MULTIPLE LINEAR REGRESSION

The first program is Hewlett-Packard 9830A Stat Pac, Volume 2, Multiple Linear Regression (MLR). This program determines the least squares regression of a dependent variable, T_D or H/M , on a set of up to 12 independent variables, the composition of the alloys by element. The results are given as an equation in the form:

$$y = b_0 + b_1x_1 + \dots + b_kx_k ,$$

where y is the dependent variable, x the independent variables, and b the coefficients assigned to them. The program also computes coefficient of multiple correlation, R^2 , a measure of the "goodness" of fit of the derived equation to the data; t -values for each of the coefficients, an indication of their statistical significance; and residuals, the difference between the calculated and actual value of each dependent data point. The Hewlett-Packard program was slightly modified to permit storage of all data on one cassette tape, eliminating the need to type in data repetitively. A listing of the program used to access the auxiliary data storage is in Table 7. The MLR program has the capability of performing various transformations, such as adding, multiplying, taking to a power, taking logarithms, etc., on the input data to investigate synergistic effects of the alloying additions or to improve the correlation coefficient of the derived equation.

Data from the first 25 candidate alloys screened for equilibrium condition T_D was subjected to MLR analysis with the following results:

<u>Element</u>	<u>T</u> <u>D</u>		<u>H/M</u>	
	<u>Coefficient</u>	<u>Power</u>	<u>Coefficient</u>	<u>Power</u>
b ₀	1147.55		-3.983	
Mg	-9.038	1	0.054	0.333
Ni	-31.267	0.5	0.419	0.333
Cu	-21.685	0.5	-0.1476	1
Si	-14.875	1	0.095	1
V	-4.894	1	-0.079	1
R.E.	-16.182	1	0.280	1
n	-0.272	1	-0.137	1
R ²	0.78		0.93	

Table 7
Multiple Linear Regression Program Listing

```

1000 COM B[14]
1010 FIND 13
1040 DISP "HOW MANY OLD DATA LINES, N";
1050 INPUT N
1070 DISP "HOW MANY NEW DATA LINES, NI";
1080 INPUT NI
1090 P=N+NI
1100 Q=1+N
1120 DISP "HOW MANY IND. VAR./LINE";
1130 INPUT K
1140 FOR I=0 TO P
1150 DISP "LOAD DATA BY ELEMENT, DEP. VAR. 131";
1160 INPUT B[K+2]
1170 FOR J=1 TO K
1180 INPUT A[J+1]
1190 NEXT J
1200 STORE DATA 12+I,B
1210 NEXT I
1220 REWIND
1230 DISP "SCRATCHA. INSERT STATPAC. LOADKEY1"
1240 WAIT 10000
1250 END

```

These coefficients were programmed into the Hydride Composition Prediction equation (see Section 5.2) and scanned for a metallurgically reasonable range of alloying with the results seen in Table 8. Zinc, tin, cobalt, and aluminum were eliminated from consideration as having been shown in previous analyses to be ineffective. The significant difference between the predicted compositions minimizing T_D and maximizing H/M is the lack of copper in the latter. Both rely on maximum additions of silicon and rare earths (R.E.) to achieve the desired effect. There is, in fact, an apparent limit to the benefits of rare-earth additions as seen in test results of alloy 150. The predicted T_D and H/M values are therefore better than what can be reasonably expected. The value of this technique is as a method for screening the results to establish relative benefits of the varying alloying elements.

5.2 HYDRIDE COMPOSITION PREDICTION

The second program used in these analyses is one developed at Solar, which, scans all possible combinations of the alloying elements, within fixed limits, applying the previously derived MLR coefficients to each, and computes the optimum composition for either the lowest T_D or highest H/M. The program can be used to print all possible combinations which will produce results either above or below a specified limit; or to print only those combinations which are an improvement over previous values calculated by the program, i.e., to select the optimum composition. The listing of this program, Hydride Composition Prediction, is seen in Table 9. Typical output is shown in Table 8.

The Multiple Linear Regression Analysis program, and the Alloy Scanning Program have been used for the prediction of promising trends in alloying, both for lowering the dissociation temperature, and for increasing the hydrogen content. Figure 6 was generated by this program and indicates the effects of the compositions of the three major alloying elements on the dissociation temperature and hydrogen capacity. While some improvement is possible by inclusion of quaternary or quinary alloying, it is obvious that a compromise is necessary between compositions which favor the highest possible capacity or the lowest dissociation temperature.

5.3 HYDRIDE DATA ANALYSIS

A third program is used to calculate weight percentages and weights for preparation of the candidate alloys in specified sample sizes. Up to eight elements can be included in the alloy from a bank of 32, mostly metals. The program converts either from atomic to weight percent and weight of the elements, or the reverse, at the user's option, and is titled, Composition Calculations. A listing is seen in Table 10. The program calculates the H/M ratio based upon weight gain in hydriding, or the weight loss in dehydriding. This program has been modified slightly during the course of the research. The revised program includes:

(Text continued on page 37)

Table 8

Typical Output of Hydride Composition Prediction Computer Program
 The Table Shown in A is for T_D Prediction While
 B is the Output for H/M Predictions

A	ATOMIC PERCENT							TD, C > 250
	MG	NI	CU	B	SI	SN	V	R.E. PRED.
	96.0000	4.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000 217
	95.0000	4.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000 210
	94.0000	4.0000	0.0000	0.0000	0.0000	0.0000	0.0000	2.0000 203
	93.0000	4.0000	0.0000	0.0000	0.0000	0.0000	0.0000	3.0000 196
	92.7500	4.0000	0.0000	0.0000	0.2500	0.0000	0.0000	3.0000 194
	92.5000	4.0000	0.0000	0.0000	0.5000	0.0000	0.0000	3.0000 193
	88.0000	4.0000	5.0000	0.0000	0.0000	0.0000	0.0000	3.0000 193
	87.7500	4.0000	5.0000	0.0000	0.2500	0.0000	0.0000	3.0000 191
	87.5000	4.0000	5.0000	0.0000	0.5000	0.0000	0.0000	3.0000 190

THE EQUATION IS:

VALUE= 1147.5500 +-9.0380 *MG† 1.0000 +-31.2670 *NI† 0.5000 +
 -21.6850 *CU† 0.5000 +-0.2720 *B† 1.0000 +-14.8750 *SI† 1.0000
 + 0.0000 *SN† 1.0000 +-4.8940 *V† 1.0000 +-16.1820 *R.E.† 1.0000

LIMITS:	MIN.	MAX.	STEPS
NI	4.0000	10.0000	2.0000
CU	0.0000	10.0000	5.0000
B	0.0000	0.1000	0.0500
SI	0.0000	0.5000	0.2500
SN	0.0000	0.0000	1.0000
V	0.0000	2.0000	1.0000
R.E.	0.0000	3.0000	1.0000

B	ATOMIC PERCENT							H/M > 1.20
	MG	NI	CU	B	SI	SN	V	R.E. PRED.
	96.0000	4.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000 1.87
	95.0000	4.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000 2.09
	94.0000	4.0000	0.0000	0.0000	0.0000	0.0000	0.0000	2.0000 2.32
	93.0000	4.0000	0.0000	0.0000	0.0000	0.0000	0.0000	3.0000 2.54
	92.7500	4.0000	0.0000	0.0000	0.2500	0.0000	0.0000	3.0000 2.55
	92.5000	4.0000	0.0000	0.0000	0.5000	0.0000	0.0000	3.0000 2.56

THE EQUATION IS:

VALUE=-3.9830 + 0.0540 *MG† 1.0000 + 0.4190 *NI† 0.3333 +-0.1476
 *CU† 0.3333 +-0.1370 *B† 1.0000 + 0.0950 *SI† 1.0000 + 0.0000 *SN†
 1.0000 +-0.0790 *V† 1.0000 + 0.2800 *R.E.† 1.0000

LIMITS:	MIN.	MAX.	STEPS
NI	4.0000	10.0000	2.0000
CU	0.0000	10.0000	5.0000
B	0.0000	0.1000	0.0500
SI	0.0000	0.5000	0.2500
SN	0.0000	0.0000	1.0000
V	0.0000	2.0000	1.0000
R.E.	0.0000	3.0000	1.0000

Table 9
Hydride Composition Program Listing

```

1000 FORMAT 8F8.4,F5.0
1010 FORMAT 8F8.4,F5.2
1020 X=0
1030 DISP "0 FOR T(D); 1 FOR H/M";
1040 INPUT Y
1041 DISP "DO YOU WANT BEEPING";
1042 INPUT X9
1050 IF Y=1 THEN 1210
1060 PRINT
1070 PRINT
1080 PRINT
1090 DISP "WHAT UPPER LIMIT FOR TD,C";
1100 INPUT S9
1110 W=S9
1120 DISP "RESULTS IN DESCENDING ORDER";
1130 INPUT S7
1140 PRINT "TO CHANGE LIMITS HIT STOP AND CONT. 2230"
1150 PRINT
1160 PRINT
1170 PRINT
1180 FIXED 0
1190 PRINT TAB15;"ATOMIC PERCENT ";TAB63;"TD,C";S9
1200 GOTO 1360
1210 DISP " WHAT LOWER LIMIT FOR H/M";
1220 INPUT S8
1225 W=S8
1230 DISP "RESULTS IN ASCENDING ORDER";
1240 INPUT S7
1250 PRINT
1260 PRINT
1270 PRINT
1280 PRINT
1290 PRINT
1300 PRINT "TO CHANGE LIMITS HIT STOP AND CONT. 2230"
1310 PRINT
1320 PRINT
1330 PRINT
1340 FIXED 2
1350 PRINT TAB15;"ATOMIC PERCENT ";TAB63;"H/M>";S8
1360 PRINT "-----"
1370 PRINT TAB67;"-----"
1380 PRINT TAB4"MG      NI      CU      B ";
1390 PRINT TAB36"SI      SN      V      R.E.  PRED."
1400 IF X=1 THEN 1670
1410 DISP "B(0)";
1420 INPUT B
1430 IF X=1 THEN 2330
1440 DISP "MG-B,POWER";
1450 INPUT B1,P1
1460 IF X=1 THEN 2360
1470 DISP "NI-MIN,MAX,STEP,B,PWR";

```

Table 9 (Continued)

```

1480 INPUT N1,N2,N3,B2,P2
1490 IF X=1 THEN 2390
1500 DISP "CU-MIN,MAX,STEPS,B,PWR";
1510 INPUT C1,C2,C3,B3,P3
1520 IF X=1 THEN 2420
1530 DISP "B -MIN,MAX,STEPS,B,POWER";
1540 INPUT G1,G2,G3,B4,P4
1550 IF X=1 THEN 2450
1560 DISP "SI-MIN,MAX,STEPS,B,POWER";
1570 INPUT I1,I2,I3,B5,P5
1580 IF X=1 THEN 2480
1590 DISP "SH-MIN,MAX,STEPS,B,POWER";
1600 INPUT S1,S2,S3,B6,P6
1610 IF X=1 THEN 2510
1620 DISP "V-MIN,MAX,STEPS,B,POWER";
1630 INPUT V1,V2,V3,B7,P7
1640 IF X=1 THEN 2540
1650 DISP "R.E.-MIN,MAX,STEPS,B,POWER";
1660 INPUT Z1,Z2,Z3,B8,P8
1670 FOR N=N1 TO N2 STEP N3
1680 FOR C=C1 TO C2 STEP C3
1690 FOR G=G1 TO G2 STEP G3
1700 FOR I=I1 TO I2 STEP I3
1710 FOR S=S1 TO S2 STEP S3
1720 FOR V=V1 TO V2 STEP V3
1730 FOR Z=Z1 TO Z2 STEP Z3
1740 M=100-N-C-G-I-S-V-Z
1750 IF M/5=INT(M/5) THEN 1770
1760 GOTO 1800
1770 IF X9=1 THEN 1772
1771 GOTO 1780
1772 BEEP
1780 DISP M
1790 WHILE 3000
1800 T=B+B1*M+P1+B2*N+P2+B3*C+P3+B4*G+P4+B5*I+P5+B6*S+P6+B7*V+P7+B8*Z+P8
1805 IF S7=0 THEN 1870
1810 IF Y=1 THEN 1850
1820 IF T>W THEN 1950
1830 W=T
1840 GOTO 1070
1850 IF T<W THEN 1950
1860 W=T
1870 IF Y=1 THEN 1900
1880 IF T>89 THEN 1950
1890 GOTO 1910
1900 IF T<88 THEN 1950
1910 IF Y=0 THEN 1940
1920 WRITE (15,1010)M,N,C,G,I,S,V,Z,T
1930 GOTO 1950
1940 WRITE (15,1000)M,N,C,G,I,S,V,Z,T
1950 NEXT Z

```

Table 9 (Continued)

```

1960 NEXT V
1970 NEXT S
1980 NEXT I
1990 NEXT G
2000 NEXT C
2010 NEXT N
2020 PRINT
2030 PRINT "THE EQUATION IS:"
2040 PRINT
2050 FIXED 4
2060 PRINT "VALUE=";B;"+";B1;"*MG+";P1;"+";B2;"*NI+";P2;"+";B3;"*CU+";P3;"+";
2070 PRINT B4;"*B+";P4;"+";B5;"*SI+";P5;"+";B6;"*SN+";P6;"+";B7;"*V+";P7;
2080 PRINT "+";B8;"*R.E.+";P8
2090 PRINT
2100 PRINT
2110 PRINT "LIMITS:           MIN.           MAX.           STEPS"
2120 PRINT " NI           ";N1;TAB35;N2;TAB56;N3
2130 PRINT " CU           ";C1;TAB35;C2;TAB56;C3
2140 PRINT " B           ";G1;TAB35;G2;TAB56;G3
2150 PRINT " SI           ";I1;TAB35;I2;TAB56;I3
2160 PRINT " SN           ";S1;TAB35;S2;TAB56;S3
2170 PRINT " V           ";V1;TAB35;V2;TAB56;V3
2180 PRINT " R.E.         ";Z1;TAB35;Z2;TAB56;Z3
2190 PRINT
2200 PRINT " -----"
2210 PRINT
2220 FIXED 8
2230 DISP "CHANGE LIMITS? 1 FOR YES";
2240 INPUT X
2250 IF X=1 THEN 2300
2260 PRINT
2270 DISP "          END OF PROGRAM"
2280 REWIND
2290 END
2300 DISP "B(0)";
2310 INPUT X1
2320 IF X1=1 THEN 1410
2330 DISP "MG";
2340 INPUT X2
2350 IF X2=1 THEN 1440
2360 DISP "NI";
2370 INPUT X3
2380 IF X3=1 THEN 1470
2390 DISP "CU";
2400 INPUT X4
2410 IF X4=1 THEN 1500
2420 DISP "B";
2430 INPUT X5
2440 IF X5=1 THEN 1530
2450 DISP "SI";

```

Table 9 (Continued)

```

2460 INPUT X6
2470 IF X6=1 THEN 1560
2480 DISP "SN";
2490 INPUT X7
2500 IF X7=1 THEN 1590
2510 DISP "V";
2520 INPUT X8
2530 IF X8=1 THEN 1620
2540 DISP "R.E.";
2550 INPUT X9
2560 IF X9=1 THEN 1650
2570 GOTO 1050

```

Figure 6. Sensitivity of H/M Ratio and Dissociation Temperature to Alloy Composition

Table 10
Listing of Hydride Data Analysis Program

```

1000 DISP "WHAT DATE";
1010 INPUT D$
1020 DISP "SCROLL";
1030 INPUT B4
1040 PRINT TAB(30);"DATE: ";D$
1050 DISP "SAMPLE/H2 WEIGHT CALCULATION";
1060 INPUT U6
1070 IF U6=0 THEN 1390
1080 DISP "  0 FOR LOSS    1 FOR GAIN";
1090 INPUT U7
1100 FIXED 4
1110 DISP "SAMPLE IDENTIFICATION";
1120 INPUT C$
1130 PRINT "ALLOY:          "C$
1140 DISP "CONTAINER WEIGHT";
1150 INPUT C
1160 DISP "INITIAL TOTAL WEIGHT";
1170 INPUT W1
1180 DISP "FINAL WEIGHT";
1190 INPUT W2
1200 PRINT
1210 PRINT "CONTAINER WEIGHT:          "C
1220 PRINT "INITIAL TOTAL WEIGHT:      "W1
1230 PRINT "FINAL TOTAL WEIGHT:         "W2
1240 PRINT
1250 A=W1-C
1260 A2=W2-C
1270 H=W2-W1
1280 IF U7=0 THEN 1340
1290 PRINT "ALLOY WEIGHT:          ",A
1300 PRINT "ALLOY HYDRIDE WEIGHT: ",A2
1310 PRINT "HYDROGEN WEIGHT:          ",H
1320 PRINT
1330 GOTO 1050
1340 PRINT "ALLOY WEIGHT:          ",A2
1350 PRINT "ALLOY HYDRIDE WEIGHT: ",A
1360 PRINT "HYDROGEN WEIGHT:          ",-H
1370 PRINT
1380 GOTO 1050
1390 DISP "CONVERSION OF W/O TO A/O: 1=YES";
1400 INPUT L
1410 DISP "WHAT ALLOY NO.";
1420 INPUT C$
1430 REM*****MM=MISCHMETAL
1440 REM *****YM=YTTRIUM MISCHMETAL
1450 REM*****XX= INERT ELEMENT, $0.00 COST, 10+10 ATOMIC WEIGHT,
1460 REM ***** TO BE USED WITH W/O CALCULATIONS
1470 W=S=0
1480 DISP "HOW MANY ELEMENTS (8 MAX.)";
1490 INPUT A
1500 IF A>4 THEN 1530
1510 FIXED 4
1520 GOTO 1570
1530 IF A>7 THEN 1560
1540 FIXED 3
1550 GOTO 1570
1560 FIXED 2
1570 DIM A$(10),B$(80),C$(40),D$(10)
1580 DIM C(80),F(80),M(80),X(80)

```


Table 10 (Continued)

```

1590 B#="MNZHNINGCUSISNGAALTIZRBEV CRFECOCBMOAGTAC H W LACEINMMNDPRB Y GDYMX"
1600 B#[69,78]="PTPDCABALI"
1610 E[1]=E[2]=E[3]=E[4]=E[5]=E[6]=E[7]=E[8]=E[9]=0
1620 W[1]=W[2]=W[3]=W[4]=W[5]=W[6]=W[7]=W[8]=0
1630 X[1]=X[2]=X[3]=X[4]=X[5]=X[6]=X[7]=X[8]=1E-90
1640 D[1]=D[2]=D[3]=D[4]=D[5]=D[6]=D[7]=D[8]=0
1650 Y[1]=Y[2]=Y[3]=Y[4]=Y[5]=Y[6]=Y[7]=Y[8]=0
1660 T[1]=T[2]=T[3]=T[4]=T[5]=T[6]=T[7]=T[8]=0
1670 FOR B=1 TO A
1680 DISP "WHAT ELEMENT";
1690 INPUT A#
1700 IF A#"MN" THEN 1770
1710 C[B]=1
1720 F[B]=2
1730 X[B]=54.938
1740 M[B]=0.6
1750 Y[B]=7.6
1760 Z[B]=89.6
1770 IF A#"ZN" THEN 1840
1780 C[B]=3
1790 F[B]=4
1800 X[B]=65.37
1810 M[B]=0.4
1820 Y[B]=9.16
1830 Z[B]=58.4
1840 IF A#"LI" THEN 1910
1850 C[B]=77
1860 F[B]=78
1870 X[B]=6.939
1880 M[B]=10
1890 Y[B]=13.02
1900 Z[B]=54
1910 IF A#"NI" THEN 1980
1920 C[B]=5
1930 X[B]=58.71
1940 F[B]=6
1950 M[B]=2.2
1960 Y[B]=6.59
1970 Z[B]=123.8
1980 IF A#"MG" THEN 2050
1990 C[B]=7
2000 X[B]=24.312
2010 F[B]=8
2020 M[B]=0.52
2030 Y[B]=14
2040 Z[B]=50.6
2050 IF A#"CU" THEN 2120
2060 C[B]=9
2070 X[B]=63.54
2080 F[B]=10
2090 M[B]=0.74
2100 Y[B]=7.11
2110 Z[B]=106.7
2120 IF A#"SI" THEN 2190
2130 C[B]=11
2140 F[B]=12
2150 X[B]=28.086
2160 M[B]=0.05
2170 Y[B]=12.07

```

Table 10 (Continued)

2180	Z[B]=93.3	2770	C[B]=27
2190	IF A##"SN" THEN 2260	2780	F[B]=28
2200	C[B]=13	2790	M[B]=2.44
2210	F[B]=14	2800	Y[B]=8.72
2220	X[B]=118.69	2810	Z[B]=103.8
2230	M[B]=3.65	2820	IF A##"FE" THEN 2890
2240	Y[B]=16.3	2830	X[B]=55.847
2250	Z[B]=66.5	2840	C[B]=29
2260	IF A##"GA" THEN 2330	2850	F[B]=30
2270	C[B]=15	2860	M[B]=0.1
2280	F[B]=16	2870	Y[B]=7.09
2290	X[B]=69.72	2880	Z[B]=118.2
2300	M[B]=293	2890	IF A##"PD" THEN 2960
2310	Y[B]=11.81	2900	X[B]=106.4
2320	Z[B]=74.8	2910	C[B]=71
2330	IF A##"AL" THEN 2400	2920	F[B]=72
2340	C[B]=17	2930	M[B]=875
2350	F[B]=18	2940	Y[B]=8.87
2360	X[B]=26.982	2950	Z[B]=98.3
2370	M[B]=0.3	2960	IF A##"CO" THEN 3030
2380	Y[B]=10	2970	X[B]=58.9332
2390	Z[B]=86.6	2980	C[B]=31
2400	IF A##"TI" THEN 2470	2990	F[B]=32
2410	X[B]=47.9	3000	M[B]=4.4
2420	C[B]=19	3010	Y[B]=6.69
2430	F[B]=20	3020	Z[B]=123.5
2440	M[B]=2.7	3030	IF A##"CB" THEN 3100
2450	Y[B]=12.01	3040	X[B]=92.906
2460	Z[B]=96.8	3050	C[B]=33
2470	IF A##"ZR" THEN 2540	3060	F[B]=34
2480	X[B]=91.22	3070	M[B]=35
2490	C[B]=21	3080	Y[B]=10.83
2500	F[B]=22	3090	Z[B]=130.7
2510	M[B]=15	3100	IF A##"MO" THEN 3170
2520	Y[B]=14.02	3110	X[B]=95.94
2530	Z[B]=100.6	3120	C[B]=35
2540	IF A##"BE" THEN 2610	3130	F[B]=36
2550	X[B]=9.0122	3140	M[B]=3
2560	C[B]=23	3150	Y[B]=9.38
2570	F[B]=24	3160	Z[B]=128.8
2580	M[B]=61	3170	IF A##"AG" THEN 3240
2590	Y[B]=4.88	3180	X[B]=107.87
2600	Z[B]=125.6	3190	C[B]=37
2610	IF A##"V" THEN 2680	3200	F[B]=38
2620	X[B]=50.942	3210	M[B]=61.67
2630	C[B]=25	3220	Y[B]=10.27
2640	F[B]=26	3230	Z[B]=81.4
2650	M[B]=3.54	3240	IF A##"TA" THEN 3310
2660	Y[B]=8.36	3250	X[B]=180.948
2670	Z[B]=120.8	3260	C[B]=39
2680	IF A##"PT" THEN 2750	3270	F[B]=40
2690	X[B]=195.09	3280	M[B]=45
2700	C[B]=69	3290	Y[B]=10.8
2710	F[B]=70	3300	Z[B]=130.9
2720	M[B]=2508.33	3310	IF A##"C" THEN 3380
2730	Y[B]=9.1	3320	X[B]=12.011
2740	Z[B]=115.8	3330	C[B]=41
2750	IF A##"CR" THEN 2820	3340	F[B]=42
2760	X[B]=51.996	3350	M[B]=0.05

Table 10 (Continued)

```

3360 Y[B]=3.42
3370 Z[B]=223.5
3380 IF A##"H" THEN 3450
3390 X[B]=1.008
3400 C[B]=43
3410 F[B]=44
3420 M[B]=0
3430 Y[B]=1.62
3440 Z[B]=179.3
3450 IF A##"W" THEN 3520
3460 X[B]=183.85
3470 C[B]=45
3480 F[B]=46
3490 M[B]=30
3500 Y[B]=9.55
3510 Z[B]=145.4
3520 IF A##"LA" THEN 3590
3530 X[B]=100.91
3540 C[B]=47
3550 F[B]=48
3560 M[B]=24
3570 Y[B]=22.54
3580 Z[B]=66.4
3590 IF A##"CE" THEN 3660
3600 X[B]=140.12
3610 C[B]=49
3620 F[B]=50
3630 M[B]=15
3640 Y[B]=20.7
3650 Z[B]=68.7
3660 IF A##"IN" THEN 3730
3670 X[B]=114.82
3680 C[B]=51
3690 F[B]=52
3700 M[B]=148.02
3710 Y[B]=15.73
3720 Z[B]=61.3
3730 IF A##"MM" THEN 3800
3740 X[B]=141.0332
3750 C[B]=53
3760 F[B]=54
3770 M[B]=3.5
3780 Y[B]=20
3790 Z[B]=70
3800 IF A##"NI" THEN 3870
3810 X[B]=144.24
3820 C[B]=55
3830 F[B]=56
3840 M[B]=60
3850 Y[B]=20.59
3860 Z[B]=60.6
3870 IF A##"XX" THEN 3940
3880 X[B]=1000000000000000
3890 C[B]=67
3900 F[B]=60
3910 M[B]=0
3920 Y[B]=1
3930 Z[B]=1
3940 IF A##"PR" THEN 4010
3950 X[B]=140.907
3960 C[B]=57
3970 F[B]=58
3980 M[B]=100
3990 Y[B]=20.82
4000 Z[B]=63.8
4010 IF A##"BA" THEN 4080
4020 X[B]=137.34
4030 C[B]=75
4040 F[B]=76
4050 M[B]=1
4060 Y[B]=38.08
4070 Z[B]=33.2
4080 IF A##"B" THEN 4150
4090 X[B]=10.811
4100 C[B]=59
4110 F[B]=60
4120 M[B]=0.05
4130 Y[B]=3.25
4140 Z[B]=208.3
4150 IF A##"Y" THEN 4220
4160 X[B]=88.905
4170 C[B]=61
4180 F[B]=62
4190 M[B]=40
4200 Y[B]=19.88
4210 Z[B]=64.5
4220 IF A##"CA" THEN 4290
4230 X[B]=40.08
4240 C[B]=73
4250 F[B]=74
4260 M[B]=0.2
4270 Y[B]=26.19
4280 Z[B]=41.9
4290 IF A##"YM" THEN 4360
4300 X[B]=114.9952
4310 C[B]=65
4320 F[B]=66
4330 M[B]=12
4340 Y[B]=20
4350 Z[B]=70
4360 IF A##"GD" THEN 4430
4370 X[B]=157.25
4380 C[B]=63
4390 F[B]=64
4400 M[B]=40
4410 Y[B]=19.94
4420 Z[B]=63.7
4430 IF L=1 THEN 4480
4440 DISP "HOW MANY ATOMS";
4450 INPUT NCB]
4460 S=S+NCB]
4470 GOTO 4500
4480 DISP "WHAT W/O OR WEIGHT";
4490 INPUT WCB]
4500 NEXT B
4510 O=A
4520 IF A>7 THEN 4700
4530 IF A>6 THEN 4680

```

Table 10 (Continued)

```

4540 IF A>5 THEN 4660
4550 IF A>4 THEN 4640
4560 IF A>3 THEN 4620
4570 IF A>2 THEN 4600
4580 D[Q]=D[Q-1]=0
4590 GOTO 4710
4600 D[Q]=D[Q-1]=D[Q-2]=0
4610 GOTO 4710
4620 D[Q]=D[Q-1]=D[Q-2]=D[Q-3]=0
4630 GOTO 4710
4640 D[Q]=D[Q-1]=D[Q-2]=D[Q-3]=D[Q-4]=0
4650 GOTO 4710
4660 D[Q]=D[Q-1]=D[Q-2]=D[Q-3]=D[Q-4]=D[Q-5]=0
4670 GOTO 4710
4680 D[Q]=D[Q-1]=D[Q-2]=D[Q-3]=D[Q-4]=D[Q-5]=D[Q-6]=0
4690 GOTO 4710
4700 D[Q]=D[Q-1]=D[Q-2]=D[Q-3]=D[Q-4]=D[Q-5]=D[Q-6]=D[Q-7]=0
4710 IF A<8 THEN 4730
4720 D[Q-7]=0
4730 FOR B=1 TO A
4740 IF L=1 THEN 4760
4750 GOTO 4820
4760 Y7=(W[1]/X[1]+W[2]/X[2]+W[3]/X[3]+W[4]/X[4]+W[5]/X[5])
4770 Y8=(W[6]/X[6]+W[7]/X[7]+W[8]/X[8])
4780 D[B]=W[B]/X[B]/(Y7+Y8)
4790 Z7=D[1]*Y[1]+D[2]*Y[2]+D[3]*Y[3]+D[4]*Y[4]+D[5]*Y[5]
4800 Z8=(Z7+D[6]*Y[6]+D[7]*Y[7]+D[8]*Y[8])/100
4810 GOTO 4830
4820 D[B]=(D[B]*100)/S
4830 E[B]=X[B]*D[B]/100
4840 Z7=D[1]*Y[1]+D[2]*Y[2]+D[3]*Y[3]+D[4]*Y[4]+D[5]*Y[5]
4850 Z8=(Z7+D[6]*Y[6]+D[7]*Y[7]+D[8]*Y[8])/100
4860 IF L=1 THEN 4880
4870 W=W+D[B]
4880 NEXT B
4890 FOR K=1 TO A
4900 R[K]=(Y[K]+D[K])/((100+Z8)
4910 T[K]=R[K]*Z[K]
4920 NEXT K
4930 G=E[1]+E[2]+E[3]+E[4]+E[5]+E[6]+E[7]+E[8]+E[9]
4940 PRINT
4950 PRINT
4960 PRINT
4970 PRINT "ALLOY ";C#
4980 FOR H=1 TO A-1
4990 PRINT TAB4;B#[C[H],F[H]];" ";
5000 NEXT H
5010 PRINT " ";B#[C[A],F[A]]
5020 PRINT "ATS";
5030 FOR Q=1 TO A-1
5040 IF L=0 THEN 5080
5050 N[Q]=D[Q]
5060 PRINT D[Q];"";
5070 GOTO 5090
5080 PRINT N[Q];"";
5090 NEXT Q
5100 IF L=0 THEN 5140
5110 PRINT D[A]
5120 N[A]=D[A]

```

Table 10 (Continued)

```

5130 GOTO 5150
5140 PRINT NCAJ
5150 PRINT "A/O";
5160 FOR I=1 TO A-1
5170 IF L=0 THEN 5200
5180 PRINT D(I)*100;
5190 GOTO 5210
5200 PRINT D(I);
5210 NEXT I
5220 IF L=0 THEN 5250
5230 PRINT D(A)*100
5240 GOTO 5260
5250 PRINT D(A)
5260 PRINT "W/O";
5270 FOR J=1 TO A-1
5280 W(J)=E(J)/G*100
5290 PRINT W(J);
5300 NEXT J
5310 PRINT E(A)/G*100
5320 DISP "WHAT WEIGHT BUTTON";
5330 INPUT M
5340 PRINT "GMS";
5350 FOR K=1 TO A-1
5360 PRINT M/100*E(K)/G*100;
5370 NEXT K
5380 PRINT M/100*E(A)/G*100
5390 PRINT "TOTAL";M;"GRAMS"
5400 PRINT
5410 H7=T(1)+T(2)+T(3)+T(4)+T(5)+T(6)+T(7)+T(8)
5420 IF B4=0 THEN 5490
5430 DISP "0=RERUN 1=H/M 2=$/KG 3=GAS VOLUME 4=ELEMENT LIST 5=SAMPLE WT. 6=H.S-P
5440 WAIT 2000
5450 FOR I=1 TO 40
5460 SCROLL 200
5470 NEXT I
5480 WAIT 1000
5490 DISP "ORN 1H/M 2$ 3V 4LST. 5SAMP 6HSP";
5500 INPUT Q1
5510 IF Q1=1 THEN 5830
5520 IF Q1=2 THEN 5640
5530 IF Q1=3 THEN 5620
5540 IF Q1=4 THEN 5660
5550 IF Q1=5 THEN 1080
5560 IF Q1=6 THEN 5580
5570 GOTO 5630
5580 FIXED 4
5590 PRINT "HILDEBRAND SOLUBILITY PARAMETER:      ",H7
5600 PRINT
5610 GOTO 5490
5620 GOTO 6460
5630 GOTO 1390
5640 FIXED 2
5650 GOTO 5760
5660 PRINT
5670 PRINT "ELEMENT","ATOM. WT.,""$ /KG.,""AT. VOL.,""SOL. PAR."
5680 FOR B=1 TO A
5690 FIXED 3
5700 PRINT B*(C(B),F(B)),X(B);
5710 FIXED 2

```

Table 10 (Continued)

```

5720 PRINT TAB30;2.205*MC B];TAB45;Y[B];TAB60;Z[B]
5730 NEXT B
5740 PRINT
5750 GOTO 5490
5760 IF A>7 THEN 6270
5770 IF A>6 THEN 6200
5780 IF A>5 THEN 6140
5790 IF A>4 THEN 6080
5800 IF A>3 THEN 6020
5810 IF A>2 THEN 5960
5820 GOTO 5910
5830 IF A>7 THEN 6250
5840 IF A>6 THEN 6180
5850 IF A>5 THEN 6120
5860 IF A>4 THEN 6060
5870 IF A>3 THEN 6000
5880 IF A>2 THEN 5940
5890 PRINT "(M)H";DC Q]/(DC Q-1))
5900 GOTO 6320
5910 PRINT "PRICE/KG.=#";((100-WC Q-1))*MC Q]+WC Q-1))*MC Q-1))*2.205/100
5920 PRINT
5930 GOTO 6240
5940 PRINT "(M)H";DC Q]/(DC Q-1)+DC Q-2))
5950 GOTO 6320
5960 P8=(100-WC Q-2)-WC Q-1))*MC Q]
5970 P8=P8+WC Q-2))*MC Q-2))+WC Q-1))*MC Q-1]
5980 PRINT "PRICE/KG.=#";P8*2.205/100
5990 GOTO 6240
6000 PRINT "(M)H";DC Q]/(DC Q-1)+DC Q-2)+DC Q-3))
6010 GOTO 6320
6020 P8=(100-WC Q-3)-WC Q-2)-WC Q-1))*MC Q]
6030 P8=P8+WC Q-3))*MC Q-3))+WC Q-2))*MC Q-2))+WC Q-1))*MC Q-1]
6040 PRINT "PRICE/KG.=#";P8*2.205/100
6050 GOTO 6240
6060 PRINT "(M)H";DC Q]/(DC Q-1)+DC Q-2)+DC Q-3)+DC Q-4))
6070 GOTO 6320
6080 P8=(100-WC Q-4)-WC Q-3)-WC Q-2)-WC Q-1))*MC Q]
6090 P8=P8+WC Q-4))*MC Q-4))+WC Q-3))*MC Q-3))+WC Q-2))*MC Q-2))+WC Q-1))*MC Q-1]
6100 PRINT "PRICE/KG.=#";P8*2.205/100
6110 GOTO 6240
6120 PRINT "(M)H";DC Q]/(DC Q-1)+DC Q-2)+DC Q-3)+DC Q-4)+DC Q-5))
6130 GOTO 6320
6140 P8=(100-WC Q-5)-WC Q-4)-WC Q-3)-WC Q-2)-WC Q-1))*MC Q]
6150 P8=P8+WC Q-5))*MC Q-5))+WC Q-4))*MC Q-4))+WC Q-3))*MC Q-3))+WC Q-2))*MC Q-2))+WC Q-1))*MC Q-1]
6160 PRINT "PRICE/KG.=#";P8*2.205/100
6170 GOTO 6240
6180 PRINT "(M)H";DC Q]/(DC Q-1)+DC Q-2)+DC Q-3)+DC Q-4)+DC Q-5)+DC Q-6))
6190 GOTO 6320
6200 P8=(100-WC Q-6)-WC Q-5)-WC Q-4)-WC Q-3)-WC Q-2)-WC Q-1))*MC Q]
6210 P8=P8+WC Q-6))*MC Q-6))+WC Q-5))*MC Q-5))+WC Q-4))*MC Q-4))+WC Q-3))*MC Q-3))+WC Q-2))*MC Q-2))+WC Q-1))*MC Q-1]
6220 P8=P8+WC Q-3))*MC Q-3))+WC Q-2))*MC Q-2))+WC Q-1))*MC Q-1]
6230 PRINT "PRICE/KG.=#";P8*2.205/100
6240 GOTO 5490
6250 PRINT "(M)H";DC Q]/(DC Q-1)+DC Q-2)+DC Q-3)+DC Q-4)+DC Q-5)+DC Q-6)+DC Q-7))
6260 GOTO 6320
6270 P8=(100-WC Q-7)-WC Q-6)-WC Q-5)-WC Q-4)-WC Q-3)-WC Q-2)-WC Q-1))*MC Q]
6280 P8=P8+WC Q-7))*MC Q-7))+WC Q-6))*MC Q-6))+WC Q-5))*MC Q-5))+WC Q-4))*MC Q-4))+WC Q-3))*MC Q-3))+WC Q-2))*MC Q-2))+WC Q-1))*MC Q-1]
6290 P8=P8+WC Q-3))*MC Q-3))+WC Q-2))*MC Q-2))+WC Q-1))*MC Q-1]
6300 PRINT "PRICE/KG.=#";P8*2.205/100

```

Table 10 (Continued)

```

6310 GOTO 5490
6320 DISP "1 FOR GAIN; 0 FOR LOSS";
6330 INPUT Z6
6340 IF Z6=0 THEN 6400
6350 PRINT "CALCULATED FROM WEIGHT GAIN"
6360 PRINT
6370 GOTO 5490
6380 PRINT
6390 GOTO 1390
6400 PRINT "CALCULATED FROM WEIGHT LOSS"
6410 PRINT
6420 GOTO 5490
6430 PRINT
6440 PRINT
6450 GOTO 1390
6460 DISP "WHAT WT. H2, GMS";
6470 INPUT W
6480 FIXED 4
6490 PRINT W;"GRAMS OF H2 IS A VOLUME OF:"
6500 PRINT "-----"
6510 PRINT
6520 PRINT " "W/0.08988;"LITERS AT STP. ("W/0.08988/28.3"CU.FT.)".
6530 PRINT
6540 PRINT " "W/0.0899/3000*14.7;"LITERS AS A GAS AT 3000 PSI."
6550 PRINT
6560 PRINT " "W/70;"LITERS AS A LIQUID BELOW -252 C. (-422 F.)"
6570 DISP "RESULT AS A HYDRIDE";
6580 INPUT W
6590 IF W=0 THEN 6610
6600 GOTO 6650
6610 DISP " " "END";
6620 INPUT M1
6630 IF M1=1 THEN 6750
6640 GOTO 5490
6650 DISP "WEIGHT AND DENSITY OF ALLOY ";
6660 INPUT W1,D
6670 PRINT
6680 PRINT " "W1/D/1000;"LITERS AS";W1;"GRAMS OF HYDRIDE AT STP., ASSUMING"
6690 PRINT " " "A DENSITY OF";D
6700 PRINT
6710 DISP " " "END";
6720 INPUT Z1
6730 IF Z1=1 THEN 6750
6740 GOTO 5490
6750 DISP " " "PROGRAM COMPLETED"
6760 REWIND
6770 END

```

- a) Addition of more metallic elements.
- b) Calculation of absorbed or evolved hydrogen from sample weights.
- c) Calculation of alloy costs.
- d) Listing of element properties, atomic weight, atomic volume, solubility parameter, and cost.
- e) Calculation of hydrogen capacity as an H/M ratio.
- f) Calculation of the volume of an equivalent weight of hydrogen as a gas at standard temperature and pressure, as a compressed gas, as a liquid, and as a hydride.

Sample calculations of these several values are seen in Table 11. In the example, a 15.7025 gram sample gained 0.554 grams in hydriding, corresponding to a H/M ratio of 1.06.

Table 11
Sample Calculations

ALLOY: 149Y DATE: 10/20/77

CONTAINER WEIGHT: 30.0000
 INITIAL TOTAL WEIGHT: 45.0000
 FINAL TOTAL WEIGHT: 45.5000

ALLOY WEIGHT: 15.0000
 ALLOY HYDRIDE WEIGHT: 15.5000
 HYDROGEN WEIGHT: 0.5000

ALLOY 149Y

MG	NI	CU	Y
ATS 0.8450	0.0500	0.1000	0.0050
A/O 84.5000	5.0000	10.0000	0.5000
W/O 67.8500	9.6953	20.9858	1.4682
GMS 10.1776	1.4543	3.1479	0.2202
TOTAL 15.0000	GRAMS		

PRICE/KG.=\$ 3.48

ELEMENT	ATOM. WT.	\$/KG.	AT. VOL.	SOL. PAR.
MG	24.312	2.03	14.00	50.60
NI	58.710	4.85	6.59	123.80
CU	63.540	1.63	7.11	106.70
Y	88.905	88.20	19.88	64.50

HILDEBRAND SOLUBILITY PARAMETER: 55.6415

ALLOY 149Y-H

MG	NI	CU	Y	H
ATS 0.422	0.025	0.050	0.002	0.500
A/O 42.224	2.498	4.997	0.250	50.031
W/O 65.662	9.383	20.309	1.421	3.226
GMS 10.178	1.454	3.148	0.220	0.500
TOTAL 15.500	GRAMS			

(M)H 1.001
 CALCULATED FROM WEIGHT GAIN

0.5000 GRAMS OF H2 IS A VOLUME OF:

5.5630 LITERS AT STP. (0.1966 CU.FT.)

0.0273 LITERS AS A GAS AT 3000 PSI.

0.0071 LITERS AS A LIQUID BELOW -252 C. (-422 F.)

0.0060 LITERS AS 15.5000 GRAMS OF HYDRIDE AT STP., ASSUMING
 A DENSITY OF 2.6000

6

ALLOY OPTIMIZATION

6.1 EXPERIMENTAL PROCEDURES

Experimental alloy preparation was conducted with a 30 kW Tocco motor generator, which because of its low induction current frequency, 10,000 Hz, produces a vigorous stirring in the melt. Except for the rare earths, high-purity elemental metals of better than 99.9 percent were used in the alloy preparation. The rare-earth metal additions were of 99+ percent purity. Certain elements were prepared as master alloys by non-consumable arc melting in partial pressure of gettered, static argon, prior to addition to the induction melt. These are listed in Table 12.

Induction melting was conducted in argon in a low carbon steel crucible which also serves as a susceptor. The melt was allowed to solidify and cool within the crucible before removal to air. The ingots were radiographically examined and those which showed undissolved elements, evidenced by less dense areas of the radiograph were remelted. Figures 7 and 8 are reproductions of radiographs of sample alloy ingots before and after remelting. The sample was subsequently reduced to powder within a tool steel mortar and pestle and sized to -12 mesh.

The sample, about 15 grams, was placed in an Inconel 600 reactor, evacuated and backfilled at least three times with ultra high purity hydrogen to purge the system, and finally pressurized to 300 psig. The reactor was heated, under pressure to 400°C, and then alternately evacuated and pressurized, about five minutes per cycle, for five cycles. The sample was held at temperature and pressure for one to two hours, and then cooled under pressure to room temperature. The reactor with a volume of 71 cc was evacuated, sealed, and reheated to 400°C. The pressure and temperature were monitored and plotted on an X-Y recorder. A photograph and schematic diagram of the apparatus is seen in Figure 9. The point at which the pressure increases to one atmosphere is defined as the temperature of dissociation, T_p . These data are recorded in Table 13 for each "run" of the alloy. A much slower heating rate, approaching equilibrium conditions results in lower dissociation temperatures, as indicated by asterisks (*) in Table 13. A gradual improvement in temperature can be noted for almost all alloys as they progress through the series of repetitive runs, indicative of the fact that the alloy becomes "conditioned" or breaks into finer powder size through the influence of hydrogen absorption and desorption.

After the final cool-down under pressure, the hydride sample was removed from the retort and reweighed. Weight gain is attributable to hydrogen pickup,

Table 12
Master Alloys Used in Magnesium Alloy Preparation

	CO	V
ATS	0.6630	0.3370
A/O	66.3000	33.7000
W/O	69.4747	30.5253

	CO	V
ATS	0.6630	0.3370
A/O	66.3000	33.7000
W/O	69.4747	30.5253

	CO	SI
ATS	0.9500	0.0500
A/O	95.0000	5.0000
W/O	97.5531	2.4469

	CO	SI
ATS	0.9500	0.0500
A/O	95.0000	5.0000
W/O	97.5531	2.4469

	MG	CE
ATS	3.0000	1.0000
A/O	75.0000	25.0000
W/O	34.2333	65.7667

	MG	CE
ATS	3.0000	1.0000
A/O	75.0000	25.0000
W/O	34.2333	65.7667

	MG	MM
ATS	3.0000	1.0000
A/O	75.0000	25.0000
W/O	34.0871	65.9129

	MG	MM
ATS	3.0000	1.0000
A/O	75.0000	25.0000
W/O	34.0871	65.9129

	MG	GD
ATS	3.0000	1.0000
A/O	75.0000	25.0000
W/O	31.6857	68.3143

	MG	GD
ATS	3.0000	1.0000
A/O	75.0000	25.0000
W/O	31.6857	68.3143

	MG	Y
ATS	17.0000	3.0000
A/O	85.0000	15.0000
W/O	60.7783	39.2217

	MG	Y
ATS	17.0000	3.0000
A/O	85.0000	15.0000
W/O	60.7783	39.2217

	NI	V	SI
ATS	1.0000	1.0000	1.0000
A/O	33.3333	33.3333	33.3333
W/O	42.6244	36.9847	20.3909

	NI	V	SI
ATS	1.0000	1.0000	1.0000
A/O	33.3333	33.3333	33.3333
W/O	42.6244	36.9847	20.3909

	NI	V
ATS	1.0000	1.0000
A/O	50.0000	50.0000
W/O	53.5421	46.4579

	NI	V
ATS	1.0000	1.0000
A/O	50.0000	50.0000
W/O	53.5421	46.4579

	NI	SI
ATS	1.0000	1.0000
A/O	50.0000	50.0000
W/O	67.6414	32.3586

	NI	SI
ATS	1.0000	1.0000
A/O	50.0000	50.0000
W/O	67.6414	32.3586

	CU	SI
ATS	5.0000	1.0000
A/O	83.3333	16.6667
W/O	91.8776	8.1224

	CU	SI
ATS	5.0000	1.0000
A/O	83.3333	16.6667
W/O	91.8776	8.1224

	NI	B
ATS	1.0000	1.0000
A/O	50.0000	50.0000
W/O	84.4493	15.5507

	NI	B
ATS	1.0000	1.0000
A/O	50.0000	50.0000
W/O	84.4493	15.5507

Figure 7.

Radiographic Positive of 40 Gram Ingot Showing Heterogeneity

Figure 8.

Radiographic Positive of 40 Gram Ingot Showing Solution of All Elements and Homogeneity

from which the hydrogen atom to metal atom ratio, H/M, can be calculated (see section on Data Analysis). The hydrided sample was then placed inside a cold wall, high-vacuum furnace for dehydriding and the consequent weight loss used in a cross-check calculation of H/M ratio.

6.2 ADVANCED ALLOY STUDIES

Twenty alloys (Alloys No. 152 through 171) were prepared in Task III and tested for T_D and H/M ratio within the Mg-Ni-Cu-Si-RE alloy family selected for optimization. These alloys are included on the master chart (Table 13).

This series included the use of low-cost yttrium-mischmetal as a substitute for yttrium and other heavy rare earths (Alloys 149YM, 149YM-1, 149YM-2). See Table 14 for a typical analysis of yttrium-mischmetal. Other alloys contained neodymium and mixtures of rare-earth additions such as gadolinium and yttrium (Alloy No. 154). The best dissociation temperature of 228°C (av. T_D) was achieved with Alloy No. 155 for this group of alloys. Alloy No. 159

Figure 9. Photograph and Schematic of Hydriding Test Apparatus

Table 13
Experimental Alloy Dissociation Data

Alloy	T _D (°C) Run										H/M	ΔT, C°	\$/kg	w/o H ₂
	1	2	3	4	5	6	7	8	9	10				
Mg ₂ Ni	249	249									0.32	28	3.57	0.90
102	Mg _{0.8} Zn _{0.1} Ni _{0.1}										0.037	6	2.31	0.12
	304	291	291	279	279	279								
103	Mg _{0.85} Zn _{0.05} Ni _{0.1}										0.39	11	2.47	1.31
	315	315	274	265	263	263								
104	Mg _{0.85} Zn _{0.1} Ni _{0.1}										0.28	61	2.05	0.93
	N-R	274	279	270	N-R	N-R	268*							
104.1	Mg _{0.8} Zn _{0.15} Ni _{0.05}										0.70	42	1.94	2.13
	304	302	296											
104.2	Mg _{0.75} Zn _{0.2} Ni _{0.05}										0.73	11	1.83	2.09
	357	338	343											
104.3	Mg _{0.8} Zn _{0.2}										0.62	14	1.57	1.89
	388	366												
105	Mg _{0.8} Cu _{0.1} Ni _{0.1}										0.93	69	2.47	2.88
	313	282	268	266	260*									
106	Mg _{0.85} Cu _{0.05} Ni _{0.1}										1.21	111	2.54	3.93
	274	266	266	266	254*									
107	Mg _{0.85} Cu _{0.1} Ni _{0.1}										1.42	83	2.23	4.55
	282	274	274											
107.1	Mg _{0.75} Ni _{0.05} Cu _{0.10} Zn _{0.10}										0.86	61	1.98	2.48
	279	285	274											
107.2	Mg _{0.85} Ni _{0.05} Cu _{0.10} Zn _{0.10}										1.34	97	2.14	4.31
	282	277	279	279										
107.3	Mg _{0.70} Ni _{0.1} Cu _{0.1} Zn _{0.1}										1.20	100	2.20	3.27
	299	274	276	271										
107.4	Mg _{0.8275} Ni _{0.05} Cu _{0.0775} Zn _{0.045}										1.18	8	2.11	3.69
	274	277	265	265										
107.5	Mg _{0.7775} Ni _{0.1} Cu _{0.0775} Zn _{0.045}										0.84	83	2.38	2.54
	268	265	265	265										
107.6	Mg _{0.7275} Ni _{0.15} Cu _{0.0775} Zn _{0.045}										0.44	61	2.60	1.27
	282	271	282	279										
107.8	Mg _{0.7525} Ni _{0.1} Cu _{0.08} Zn _{0.0675}										0.77	61	2.31	2.26
	274	277	277	277										
107.7	Mg _{0.8025} Ni _{0.05} Cu _{0.08} Zn _{0.0675}										1.10	72	2.07	3.35
	282	271	282	279										
107.9	Mg _{0.7025} Ni _{0.15} Cu _{0.08} Zn _{0.0675}										0.63	83	2.53	1.76
	277	268	271	268										
107.91	Mg _{0.65} Ni _{0.1} Cu _{0.2} Zn _{0.05}										0.54	28	2.23	1.43
	282	271	266**	288	274	271								
107.92	Mg _{0.70} Ni _{0.1} Cu _{0.15} Zn _{0.05}										0.43	72	2.27	1.20
	274	282	268	268	268									
103.1	Mg _{0.83} Ni _{0.10} Sn _{0.02} Zn _{0.05}										1.24	106	2.09	3.79
	291	285	285											

Table 13 (Continued)

Alloy	T _D (°C) Run										H/M	ΔT, C°	\$/Kg	w/o H ₂
	1	2	3	4	5	6	7	8	9	10				
107.43	Mg _{0.81} Ni _{0.05} Cu _{0.075} V _{0.02} Zn _{0.045} 279 271 271 268 268 249* 249*										1.26	103	2.31	3.89
107.42	Mg _{0.81} Ni _{0.05} Cu _{0.075} Ca _{0.02} Zn _{0.045} 282 268 268 263 263 243* 235*										1.17	94	30.42	3.58
126	Mg _{0.81} Ni _{0.15} Si _{0.02} V _{0.02} 271 168 267 260 254* 254*										1.47	139	3.02	4.68
127	Mg _{0.8292} Ni _{0.15} Si _{0.0008} V _{0.02} 271 266 263 260 260 260*										1.42	150	3.04	4.56
128	Mg _{0.8092} Ni _{0.05} Cu _{0.075} Si _{0.0008} V _{0.02} Zn _{0.045} 285 274 267 266 263 238*										1.02	94	2.31	3.16
129	Mg _{0.8092} Cu _{0.05} Cu _{0.075} Si _{0.0008} V _{0.02} 332 310 307										1.09	64	2.77	3.37
130	Mg _{0.8292} Ni _{0.1} Cu _{0.05} Si _{0.0008} V _{0.02} 277 274 277 239* 238*										0.98	111	2.77	3.15
131	Mg _{0.845} Ni _{0.05} Cu _{0.10} Ce _{0.005} 296 277 262 274 272 238* 227* 232* 232*										1.23	100	2.93	3.91
132	Mg _{0.8} Cu _{0.1} Al _{0.05} Sn _{0.05} 316 343										0.23	3	2.95	0.69
133	Mg _{0.81} Ni _{0.05} Cu _{0.075} Ti _{0.02} Zn _{0.045} 296 293 293 266*										1.08	67	24.90	3.24
135	Mg _{0.84} Ni _{0.05} Cu _{0.1} Ce _{0.01} 291 282 N-R 260 274 264 259 229* 227* 232*										1.36	94	3.61	4.21
134	Mg _{0.81} Ni _{0.05} Cu _{0.075} B _{0.02} Sn _{0.045} 268 277 271 268 238*										1.12	83	2.11	3.56
107R	Mg _{0.85} Ni _{0.05} Cu _{0.1} 279 271 262 268 232* 271 237*										1.08	100	2.23	3.51
137	Mg _{0.7175} Ni _{0.15} Cu _{0.10} Ce _{0.01} Si _{0.0025} V _{0.02} 254 252 260 271* 254										0.52	94	4.07	1.46
139	Mg _{0.84} Cu _{0.15} Ce _{0.01} 343 321										0.47	6	3.30	1.49
140	Mg _{0.815} Cu _{0.1} Ni _{0.05} Sn _{0.02} Ca _{0.015} 296 277 249 257 277 254 232* 235*										1.04	83	4.57	3.03
142	Mg _{0.815} Ni _{0.05} Cu _{0.1} Sn _{0.02} MM _{0.015} 310 285 202 268 268 253 250*										1.06	81	2.98	3.69
143	Mg _{0.84} Ni _{0.05} Cu _{0.1} MM _{0.01} 293 277 279 266 266 238*										1.09	89	2.47	3.41
145	Mg _{0.8175} Ni _{0.1} Cu _{0.05} MM _{0.01} Si _{0.0025} V _{0.02} 288 279 279 271 271 257 271 254* 274 238*										1.26	122	2.95	3.89
146	Mg _{0.8475} Ni _{0.05} Cu _{0.05} MM _{0.01} Si _{0.0025} V _{0.02} B _{0.02} 307 288 282 279 243* 282 241* 279 235*										0.94	122	2.72	3.12
147	Mg _{0.803} Ni _{0.05} Cu _{0.1} Si _{0.002} V _{0.005} MM _{0.02} B _{0.02} 293 282 282 246* 246*										1.09	78	2.74	3.30
148	Mg _{0.81} Ni _{0.05} Cu _{0.1} MM _{0.02} B _{0.02} 307 291 279 279 279 241*										1.05	78	2.70	3.20

Table 13 (Continued)

Alloy	T _D (°C) Run										H/M ^a	ΔT, C°	S/Kg	w/o H ₂
	1	2	3	4	5	6	7	8	9	10				
131R	Mg _{0.845} Ni _{0.05} Cu _{0.1} Ce _{0.005} 288 279 279 271 277 268 231* 271 263 231*										0.93	89	2.93	2.97
131M	Mg _{0.845} Ni _{0.05} Cu _{0.1} MM _{0.005} 271 268 268 281 274 279 274 274 229 229*										1.06	89	2.35	3.37
149	Mg _{0.845} Ni _{0.05} Cu _{0.1} Y _{0.005} 271 266 257 266 232* 274 223* 227* 277										1.06	94	3.48	3.41
150	Mg _{0.81} Ni _{0.05} Cu _{0.1} MM _{0.04} 299 288 282 288 279 238* 282										0.97	93	3.12	2.75
151	Mg _{0.845} Ni _{0.05} Cu _{0.1} Gd _{0.005} 277 274 271 285 271 274 260 277 231* 232*										0.99	103	4.43	3.16
152	Mg _{0.895} Ni _{0.10} Y _{0.005} 293 289 288 282 277 282 282 288 271*										1.39	136	3.98	4.74
153	Mg _{0.845} Ni _{0.05} Cu _{0.10} Nd _{0.005} 291 277 277 288 268 242* 283 235* 271										1.06	72	5.29	3.38
154	Mg _{0.84} Ni _{0.05} Cu _{0.10} Gd _{0.005} Y _{0.005} 279 271 268 264 263 252 246 243 282 238*										1.18	94	5.64	3.71
155	Mg _{0.775} Ni _{0.1} Cu _{0.1} Si _{0.005} Y _{0.02} 285 260 238* 254 254 224* 279 232* 229*										1.02	106	7.09	3.01
156	Mg _{0.78} Ni _{0.1} Cu _{0.1} Y _{0.02} 288 274 274 242* 282 235* 279 260 271 229*										0.80	100	7.10	2.38
157M4	Mg _{0.933} Ni _{0.0358} Si _{0.0044} Y _{0.0268} 338 307 296 288 288 282 288										1.07	89	9.76	3.80
158	Mg _{0.70} Ni _{0.1} Cu _{0.1} Si _{0.01} Y _{0.01} 279 266 279 260 277 254 277 254 263 232*										0.62	100	4.81	1.90
159	Mg _{0.83} Ni _{0.05} Cu _{0.1} Si _{0.01} Y _{0.01} 288 263 260 249 260 282 238* 282 254										0.98	89	4.70	3.11
160	Mg _{0.8} Ni _{0.08} Cu _{0.08} Ag _{0.01} Si _{0.01} Y _{0.02} 282 271 279 243* 249* 249* 268										0.97	86	11.56	2.93
162	Mg _{0.73} Ni _{0.12} Cu _{0.12} Si _{0.01} Y _{0.02} 227 235 227 190* 277**243 254 204* 207*										0.72	106	6.95	2.06
149YM	Mg _{0.845} Ni _{0.05} Cu _{0.1} YM _{0.005} 296 268 266 279 257 246* 226* 257										0.98	92	2.68	3.14
149YM-1	Mg _{0.845} Ni _{0.05} Cu _{0.1} YM _{0.005} 282 266 282 260 260 271 254 235*										1.08	100	2.68	3.44
149YM-2	Mg _{0.845} Ni _{0.05} Cu _{0.1} YM _{0.005} Homogenized 285 274 266 254 234* 282 296 260 260 235*										1.02	83	2.68	3.26
163	Mg _{0.73} Ni _{0.15} Cu _{0.09} Si _{0.01} Y _{0.02} 262 266 204* 199*										0.66	100	7.13	1.91
164	Mg _{0.62} Ni _{0.23} Cu _{0.12} Si _{0.01} Y _{0.02} 253 260 253 216* 260 221*										0.48	44	6.94	1.24

Table 13 (Continued)

Alloy	T _D (°C) Run										H/M	ΔT, C°	S/Kg	w/o H ₂
	1	2	3	4	5	6	7	8	9	10				
166	Mg _{0.667} Ni _{0.111} Cu _{0.222} 404 379 357 254* 296 254*										0.04	14	2.38	0.10
167	Mg _{0.6} Ni _{0.23} Cu _{0.13} Si _{0.02} YM _{0.02} 254 271 227 246 246* 246* 257 227*										0.43	67	4.32	1.09
168	Mg _{0.734} Ni _{0.172} Cu _{0.056} Si _{0.18} YM _{0.02} 282 277 274 260 260 260 241*										1.00	114	4.43	2.84
169	Mg _{0.78} Ni _{0.12} Cu _{0.06} V _{0.02} YM _{0.02} 285 282 266 271 254 257 257 277 241* 277										1.20	117	4.46	3.57
171	Mg _{0.825} Ni _{0.05} Cu _{0.1} V _{0.005} Ca _{0.02} 299 302 291* 299 296*										0.92	81	3.48	2.95
* Test period performed at equilibrium ** Open to atmosphere N-R not recorded														

Table 14

Typical Analysis of Yttrium-Mischmetal*

Element	Weight Percent
Y	62.3
Dy	7.3
Er	5.7
Yb	5.7
Ce	4.3
La	3.1
Nd	2.8
Gd	2.7
Ho	1.7
Sm	1.2
Tb	0.9
Tm	0.8
Pr	0.8
Lu	0.6
Eu	0.1
*Material and analysis obtained from Research Chemicals, Phoenix, Arizona	

was prepared as a possible high hydrogen capacity hydride former. The exact formulation was predicted with the use of multiple linear regression analysis using previous samples as data. Obviously this effort was not too successful. A hydrogen concentration of 1.07 H/M is routinely achieved with maximum quantities near 1.5 H/M. The cause for this poor performance is not known, but insufficient data for the MLR program is suspected as the cause. Alloy 162 was derived by computer prediction of optimum composition for lowest dissociation temperature. The alloy showed a significantly improved T_D , essentially meeting the goal of 200°C. However, it is more heavily alloyed than previously tested alloys and is consequently more dense, 2.9 gms/cc vs. 2.4 for Alloy 149. Another disadvantage, other than high strategic alloy content, is the relatively poor hydrogen capacity, H/M = 0.72.

Variants of Alloy 162, such as 163, 164, 167 and 168 were included primarily to further define the upper limits of nickel and copper additions, for purposes of computer interpolation between known values. A comparison of data for these alloys suggests both the negative effect of copper on hydrogen capacity, and the existence of a maximum nickel content beyond which the dissociation temperature begins to increase.

Alloy 166 was synthesized to represent one of the phases tentatively identified in Scanning Electron Microscope (SEM) and microprobe analyses as having the greatest propensity for hydriding. Refer to Section 6.3, Metallurgical Analysis. Experimental results with this particular composition were not promising, however, as the alloy displayed minimal hydrogen capacity and a dissociation temperature above our previous minimum. See Table 13 for results.

After a review of all the available data from the alloy optimization studies, a decision was made to continue Task IV with Alloy 149. This alloy represents our best effort for a low dissociation temperature combined with a low nickel content. It was therefore, utilized in all of Task IV studies to establish baseline data.

6.3 METALLURGICAL ANALYSIS

During this program rather extensive metallurgical studies were conducted on Alloys 149 and 159 in both unhydrided and partially hydrided forms. The two main objectives of the Scanning Electron Microscope (SEM) study and microprobe analyses were (1) to identify visually the constituent phase(s) showing the greatest propensity for hydriding and (2) to ascertain the chemical compositions of these and all constituent phases through SEM/EDX analysis (not computer corrected for mutual radiation absorption). The nominal compositions of the subject hydriding alloys in atomic fractions were:

- (a) Alloy 149 - Mg (0.845) - Ni (0.050) - Cu (0.100) - Y (0.005)
- (b) Alloy 159 - Mg (0.830) - Ni (0.050) - Cu - (0.100) - Si (0.010) - Y (0.010)

These metallurgically similar Mg-Cu-Ni alloys were examined in the as-cast as well as in a partially hydrided condition.

Where Alloys No. 149 and 159 present essentially analogous structures, they are discussed as one alloy. Both Alloys 149 and 159 exhibit apparently hyper-eutectic as-cast microstructures; with approximately 10 volume percent in each consisting of primary proeutectic hard needle-like intermetallic(s). Scanning Electron Microscopy (SEM) analysis (uncorrected) indicates these spikes or needles are an Mg-Cu-Ni intermetallic; probably of the general type $\text{Mg}(\text{Cu,Ni})_{1.5}$ to $\text{Mg}(\text{Cu,Ni})$, with copper the predominant species. Silicon and yttrium levels are typically very low in this phase, probably <0.1 percent. The exact ratios of Mg-Cu-Ni are difficult to establish with a Scanning Electron Microscope/Energy Dispersive X-ray (SEM/EDX) program uncorrected for mutual absorption, but it is clear the proeutectic (and eutectic) intermetallics identified in this work are quite far from stoichiometric, possibly due to rather rapid and nonequilibrium cooling rates during solidification.

The balance of the cast structure(s) (~ 90 percent by volume) consists of a complex cellular or Chinese script eutectic, comprised of three distinct phases (see Figure 10). The most readily identified eutectic phase, because it is essentially a physical outgrowth with common boundaries of the above proeutectic intermetallic, is again $\text{Mg}(\text{Cu,Ni})_{1.5}$ to $\text{Mg}(\text{Cu,Ni})$. To facilitate discussion, this eutectic intermetallic phase is called Phase A. Phase A differs principally from its proeutectic variant (i.e., the needles, above) in appearing to have appreciably but indeterminately more copper and

Figure 10. SEM Photograph of $\text{Mg}_{0.845}\text{Cu}_{0.1}\text{Ni}_{0.05}\text{Y}_{0.005}$ (Alloy 149) Before Hydriding (200X)

less nickel in its makeup. Again, silicon and yttrium levels are very low and probably minimal. Phase A provides the outline or network for the cellular eutectic structure in the form of a thin-wall filigree or interconnected thin-wall maze. This intermetallic phase (Phase A) does not appear to hydride preferentially.

The second eutectic phase consists of the Mg-rich terminal solid solution, i.e., predominantly Mg metal, occupying intercellular positions in narrow bands typically parallel to the proeutectic needles discussed above. Total volume of this phase in banded form does not exceed ~10 percent. This metallic phase in banded form (see Fig. 12 with similar alloy) appears to be a secondary proeutectic network called Phase B (Refer to Fig. 11). Phase B appears to be the major reservoir for silicon and yttrium; but copper, nickel, silicon and yttrium levels are all low; probably ≤ 1.0 at. percent on an individual basis. Existing binary phase diagrams for Mg alloys would tend to support this. Phase B, which is essentially impure Mg metal, in addition to its banded form, also occurs in intimate mixture with the third eutectic phase (C), described below. In total, Phase B probably is the single, most voluminous phase in the microstructures of both Alloys 149 and 150.

The third eutectic phase (Phase C) is a relatively perishable, fragile and friable intermetallic, occupying (with Phase B in intimate mixture) the balance of the intercellular spaces, or volumetrically (the two phases together) about 40 to 60 percent of the total alloy volume(s). An estimate of the volume percentage occupied by Phase C is not readily made, because of the friability and apparent high reactivity of this mixed structure during metallographic mounting and polishing.

Figure 11. Optical Photomicrograph of Alloy 149 Before Hydriding (250X)

Phase C proved very difficult to isolate and identify by SEM/EDX, but one good run on Alloy 149 indicated a probable intermetallic formula of $Mg_2(Cu,Ni)$, with copper almost twice the level of nickel. Yttrium and silicon levels are negligibly low. Partial hydriding of Alloy 149 and 159 surfaces cause expansion and volume-induced cracking of the intimate mixture of Phase B and C, which appears to be hydriding preferentially (Figs. 12 and 13). Because Phases B and C are so intimately mixed, it was difficult to ascertain which of the two phases was hydriding initially. Based on other studies of the $Mg-Mg_2Ni$ system (Ref. 10) in which it was determined that the magnesium phase hydrided preferentially, it is presumed that Phase B (impure Mg) is the preferentially hydriding phase in this case also. Note the build-up of hydride nodules on the surface of Alloy 149 at 500X, SEM (Fig. 14).

One other very minor phase was detected, only in Alloy No. 159 (Fig. 12). This proved to be a nickel-yttrium silicide in tiny rodular forms associated with the proeutectic intermetallic needles of Phase A. This silicide occurred only rarely (<1.0 percent volume) and sporadically; and showed no tendency to hydride preferentially.

6.4 CHEMICAL ANALYSIS

A chemical analysis of Alloy 149 was performed to compare calculated and actual compositions. Table 15 compares the analytical results, determined by atomic absorption, with the calculated alloy composition. The agreement between the calculated and analyzed compositions is within five percent.

6.5 KINETICS OF HYDROGEN EVOLUTION

In a practical hydrogen storage system for an automobile, hydrogen must be evolved at a sufficient rate to maintain engine operation. Exhaust heat must be supplied continually to the hydride bed heat exchanger to maintain the flow. The exhaust heat must supply the energy for the hydride heat of dissociation and provide for normal thermal losses. The rate of heat transfer will have a large effect on the temperature of the hydride material and therefore the rate of hydrogen evolution. Thus, engineering design of the hydride bed and heat exchanger will have a significant effect on the hydrogen rate.

Experimental efforts were made to quantize the rate of evolution of hydrogen from the alloys. The data from these tests is important as a benchmark to compare with data from future alloys.

A simple test was made during alloy preparation on every sample. During pressure-vacuum cycling of the hydrides at temperature, a large temperature excursion can be noted for many of the alloys. This is recorded in Table 13 as ΔT , $^{\circ}C$, and is a function of the exo- and endothermic nature of hydrogen absorption and release, and is at least qualitatively tied to the kinetics and hydrogen capacity of the alloy.

Figure 12. Optical Photomicrograph of $\text{Mg}_{0.83}\text{Ni}_{0.05}\text{Cu}_{0.1}\text{Si}_{0.01}\text{Y}_{0.01}$ (Alloy 159) After Partial Hydriding (500X)

Figure 13. SEM Photograph of Alloy 149, Partially Hydrided (200X)

Figure 14. SEM Photograph of Alloy 149, Partially Hydrided (500X)

Table 15
Chemical Analysis of Alloy 149

Method of Determination*	Mg	Cu	Ni	Y
Calculated	67.8508	20.9858	9.6953	1.4682
Atomic Absorbtion	68.13 (by diff.)	20.0	10.31	1.56
*Expressed in weight percent.				

A second more exact test has been performed on Alloy 149, the alloy with the lowest dissociation temperature. The alloy is prepared in the normal fashion in the high pressure reactor. Dissociation temperature tests are made and the alloy is dehydrided. The entire reactor and hydrided sample are then brought up to the test temperature and held there for one hour. A valve is opened and the hydrogen is allowed to escape from the reactor to a Wet Test Meter, Precision Scientific Model 63119. That meter is a positive displacement design. Total hydrogen flow is measured as a function of time at a fixed temperature. The temperature is measured in the hydride powder. Results of the tests at 260 and 277°C are shown in Figures 15 and 16. (Similar tests have been performed on Alloys 127 and 128 and are shown in Figures 17 and 18. The 15.59 gram sample of Alloy 149 evolved hydrogen at only one half the rate of Alloy 127. When the test begins the powder temperature drops 3 to 6°C immediately and slowly recovers. This has an adverse effect on flow.

6.6 IMPURITY SENSITIVITY STUDIES

6.1 Oxygen Contamination

Alloy 149 ($\text{Mg}_{0.845}\text{Ni}_{0.05}\text{Cu}_{0.1}\text{Y}_{0.005}$) was used as the baseline material for these studies. The alloy was prepared and hydrided according to the standard procedure developed during the course of this program.

Figure 15. Hydrogen Evolved by Alloy 149 at 260°C

Figure 16. Hydrogen Evolved by Alloy 149 at 277°C

Figure 17. Dissociation Rate of Alloy 127

Figure 18. Dissociation Rate of Alloy 128

Two separate determinations of T_D yielded a value of 228°C, which is in good agreement with the range of 223 to 232°C previously obtained with this alloy.

Pure oxygen in increments of 0.1 weight percent was introduced to the reactor, containing the dehydrided alloy, at ambient temperature and allowed to remain for about 12 hours. Upon introduction of the oxygen, an immediate reaction was indicated by a slight rise in the temperature and drop in pressure within the reaction chamber. To make certain the alloy reacted completely with the oxygen, the reactor was heated up to about 200°C before the hydriding procedure was resumed. The effect of oxygen contamination upon the hydriding parameters is summarized in Table 16.

After each increment of oxygen was added, the T_D increased by 45 to 50°C, and the ΔT decreased to a level of about 89°C. However, recovery of hydriding characteristics appeared to be fairly complete after three or four normal hydriding cycles (alternate pressure and vacuum) at a temperature of 340 to 370°C.

The general conclusion is that, although some deterioration of T_D occurs, the hydride can continue to function usefully. There appears to be no obvious explanation at this time for the increase in the H/M ratio of the alloy containing 0.4 percent oxygen. It is possible that the large number of hydriding-dehydriding cycles could have some effect upon the H/M ratio through increased comminution. This phenomenon should be investigated further.

Table 16
Effect of Oxygen Contamination Upon Hydriding
Properties of Alloy 149

Oxygen Increments, w/o	Total Added Oxygen, w/o	T_D , °C	H/M Ratio	ΔT , °C
0	0	228	1.09*	108
0.1	0.1	238	--	97
0.1	0.2	232	--	97
0.2	0.4	235	1.23	94
*Previous hydriding run for Alloy 149.				

6.6.2 Commercial Hydrogen

Since in all probability, hydriding on a large scale will be carried out with commercial gas, Alloy 149 was hydrided with Linde Commercial hydrogen, 99.95 percent minimum purity to determine the effect of these impurities on hydriding characteristics. Maximum moisture content of this gas is reported as 32 ppm.

After the normal five hydriding cycles, the hydride appeared to behave in a normal manner. To determine the effect of repeated cycling, thereby increasing contamination, fourteen hydriding cycles were completed before an equilibrium dissociation temperature was measured. A T_D of 227°C was observed after this sequence. After the 26th and 30th hydriding cycle, dissociation temperatures of 224°C and 227°C were obtained, respectively. New hydrogen gas was introduced for each hydriding cycle. The H/M ratio was observed to be 1.21. Thus the alloy appears to be affected very little by the minor amounts of impurities in commercial grade hydrogen.

6.6.3 Nitrogen Contamination

A similar experiment was performed using nitrogen in place of oxygen: a new sample of Alloy 149 was prepared in the normal manner. Several hydriding cycles were accomplished using ultra-pure hydrogen. A dissociation temperature of 226°C was established for this sample. All hydrogen was removed by pumping at elevated temperatures. Then nitrogen was introduced at room temperature. No temperature increase was noted as was the case with oxygen additions. After approximately 12 hours of exposure to nitrogen the sample

was heated to approximately 325°C in the presence of the nitrogen. Any nitrogen not absorbed was removed and the sample rehydrided. A schedule of the results is shown in Table 17.

Table 17
Effect of Nitrogen Contamination Upon Hydriding
Properties of Alloy 149

Nitrogen Increments w/o	Total Added Nitrogen w/o	T _D ; °C	H/M Ratio
0	0	226	1.09
0.1	0.1	226	--
0.1	0.2	229	--
0.2	0.4	231	1.14

The effect of nitrogen on the dissociation temperature and hydrogen capacity was expected to be relatively slight. In fact the dissociation temperature changed only slightly. The hydrogen capacity also showed only minor changes after the nitrogen additions.

As a further check for consistancy we decided to measure the hydrogen flow rate at fixed temperatures. In this experiment the hydrided chamber is again connected to a positive displacement meter. The sample is heated to a preset temperature and a valve to the meter is opened. Results for a typical Alloy 149 sample are shown in Figure 15. In this case we preheated the sample at 260°C, 277°C, 293°C and 315°C in four successive experiments. No significant amount of hydrogen was evolved until 277°C. At that temperature greater amounts of hydrogen were evolved than for a similar sample not exposed to nitrogen. At 260°C essentially no hydrogen evolved from the sample. This result is different from earlier data. The best explanation at this time is the formation of a surface film of a nitride (YN or possibly Mg₃N₂). The exact determination of the contaminant would require extensive analytical work and was not thought to contribute to the goals of this program. In actual vehicle operation the hydride would see nitrogen only during a refill and then accidentally. A properly designed procedure would remove a large percentage of the nitrogen. Flow test data at 293°C is shown in Figure 19.

Figure 19. Hydrogen Flowrate After Nitrogen Contamination

7

ADVANCED CHARACTERIZATION

The objective of the final phase of this program was to perform detailed advanced characterization of the best alloy developed at that time. Before initiating this final task, all equipment used in our experiments was first cleaned and calibrated to assure high quality data. Improvements were made, where possible, to increase the accuracy of the data. The cleaning process was very important since small amounts of powder from previous experiments could reside in the system. Through experiments conducted in this program, we are aware of the effects of trace amounts of certain elements on T_D and H_x . In order to insure unbiased data in the Advanced Characterization task, it was necessary to remove these residues. During this final task only Alloy 149 was thoroughly investigated.

The first element of this task was alloy preparation. Several melts of Alloy 149 were prepared and each was inspected by X-ray and set aside until the time of its use. To avoid oxidation or other contamination the ingots were crushed just before use.

The first sample of Alloy 149 was placed into the hydriding chamber and conditioned by cycling approximately sixteen times. Each cycle consisted of hydriding to maximum hydrogen capacity, cycling sample temperature, and then dehydriding the sample. An equilibrium T_D value of 227°C was obtained. This value corresponds well with previous measurements.

7.1 PRESSURE-COMPOSITION ISOTHERMS (ALLOY 149)

Measurements of P-C-T data were taken with the high-pressure reactor used for preparation of the hydrides. Approximately 15 grams of the alloy was placed in the reactor and activated in the usual manner by cycling between ambient temperature and 400°C. The sample was evacuated during cool-down from 400°C to room temperature. Ultra high-purity hydrogen was then introduced at 300 psig, at which point an accurate pressure reading was recorded. Hydriding of the sample took place during heating to approximately 340°C. After holding at temperature for about half-hour, the sample was slowly cooled to room temperature and another pressure reading was recorded at the same temperature at which the sample was pressurized. With this ΔP and the system volume it is possible to calculate the total quantity of gas absorbed, and hence the total H/M ratio of the sample.

After allowing the temperature to come into equilibrium for at least one hour, hydrogen was allowed to escape into evacuated known volumes. The system pressure was measured after an equilibrium was obtained in approxi-

mately one hour. Temperature was controlled to within $\pm 2^\circ\text{C}$ during equilibration. The quantity of gas withdrawn for each increment was calculated according to the ideal gas law:

$$PV = n R T,$$

where

P = pressure in atmospheres

V = volume in liters

n = moles of hydrogen = $\text{g/M} = \text{wt. H}_2/\text{molecular wt.}$

R = gas constant = 0.08205 liter-atm

T = temperature in degrees Kelvin

Weight of desorbed hydrogen, g, in each increment was recalculated in terms of H/M ratio.

After several preliminary measurements, a modification was instituted in determining total hydrogen content of the hydrided alloys. It was noted that measurement of pressure, before and after hydriding, did not always yield hydrogen content consistent with total hydrogen withdrawn incrementally. To insure complete removal of the hydrogen the residual gas was driven out into a known volume by heating the sample to about 350°C , equilibrating the pressure, and calculating the quantity of gas by PVT relationships as indicated above.

This method was in good agreement with hydrogen content determined by both weighing the sample for weight gain and by weight loss after vacuum treatment at 350°C . For example, for the 310°C isotherm, summation of measured incremental volumes indicated a total H/M ratio of 1.06, compared to an H/M ratio of 1.05 by the vacuum weight-loss method. Pressure composition isotherms were determined at 271°C , 299°C , and 310°C . These are desorption isotherms (i.e., measured during hydrogen removal).

The experimental data for the determination of isotherms for 271°C , 299°C , and 310°C are summarized in Tables 18 through 20. Isotherms are plotted and shown in Figures 20 through 22. The isotherms appear to be very consistent and are typical of desorption isotherms in the family of magnesium alloy hydrides.

The effect of temperature upon plateau pressures is shown in the isochores of Figure 23 where log of plateau pressures at H/M ratios of 0.25, 0.50 and 0.75 are plotted versus $1/T$. Table 21 lists the data which were used to plot the isochores. The isochores for H/M of 0.5 and 0.7 practically coincide, while the isochore for H/M of 0.25 is slightly below the other two. All three curves appear to be parallel.

Although plateau pressures are not as high as anticipated, they are nevertheless higher than those for the heavier and more expensive hydrides presently available for use as automotive hydrides. By way of comparison, the

Table 18
Desorption Data on Alloy 149 - 299°C

Increment Withdrawn ml	Equil. Pressure		H ₂ Grams Removed	-Δ(H/M)	Remaining H/M in Sample
	psia	Atm.			
Run #1 (Data Point 0)					
0	69.2	4.71	--	--	0.909
1367.4*	28.2	1.92	0.2173	0.418	0.491
367.4	21.2	1.44	0.0405	0.071	0.420
367.4	19.7	1.34	0.0377	0.066	0.354
367.4	19.2	1.31	0.0374	0.071	0.283
367.4	18.7	1.27	0.0362	0.069	0.214
367.4	18.2	1.24	0.0354	0.068	0.146
367.4	17.7	1.20	0.0370	0.071	0.075
367.4	14.7	1.0	0.0310	0.059	0.016
Rerun of high pressure data (Data Point 0)					
0	74.7	5.08	--	--	0.912
67.4	66.7	4.54	0.0249	0.048	0.864
67.4	42.7	2.90	0.0159	0.031	0.833
367.4	23.7	1.61	0.0481	0.093	0.740
1367.4	22.7	1.54	0.1713	0.330	0.410
1367.4	20.7	1.40	0.1563	0.301	0.109
367.4	16.2	1.10	0.0331	0.064	0.045
367.4	7.3	0.5	0.0150	0.029	0.016
Heated to 350°C					
367.4	4.0	0.27	0.0082	0.016	~0
Run #3 (Data Point □)					
0	--	--	--	--	0.772
67.4	27.7	1.88	0.0105	0.020	0.752
67.4	27.7	1.88	0.0105	0.020	0.732
67.4	26.7	1.82	0.0102	0.020	0.712
367.4	25.7	1.75	0.0532	0.102	0.610
367.4	25.7	1.75	0.0532	0.102	0.508
1367.4	20.7	1.41	0.1596	0.305	0.203
Run #3 (Data Point +)					
0	--	--	--	--	0.920
67.4	60.7	4.13	0.0230	0.405	0.875
67.4	41.7	2.84	0.0158	0.031	0.844
Run #4 (Data Point X)					
0	41.7	2.84	0.0157	--	0.834
67.4	41.7	2.84	0.0157	0.030	0.814
67.4	28.2	1.92	0.0106	0.021	0.793
367.4	23.7	1.61	0.0484	0.094	0.699**
* Includes 27.4 ml of connecting tubing.					
** Taken out and weighed (H ₂ = 0.3655 g or H/M = 0.699).					

Table 19
Desorption Data on Alloy 149 - 271°C

Increment Withdrawn ml	Equil. Pressure		H ₂ Grams Removed	-Δ(H/M)	Remaining H/M in Sample
	psia	Atm.			
0	--	--	--	--	0.880
67.4	65.7	4.47	0.0246	0.047	0.833
67.4	44.7	3.04	0.0167	0.032	0.801
67.4	32.7	2.22	0.0122	0.024	0.777
67.4	24.2	1.65	0.0091	0.018	0.759
67.4	17.7	1.20	0.0066	0.016	0.743
367.4	9.8	0.66	0.0199	0.038	0.705
367.4	9.8	0.66	0.0199	0.038	0.667
1367.4	9.0	0.61	0.0681	0.131	0.536
367.4	9.0	0.61	0.0183	0.035	0.501
1367.4	9.5	0.65	0.0720	0.139	0.362
1367.4	8.4	0.57	0.0636	0.122	0.240
367.4	8.6	0.58	0.0174	0.034	0.206
367.4	9.2	0.63	0.0193	0.037	0.169
367.4	8.7	0.59	0.0177	0.034	0.135
367.4	8.6	0.58	0.0174	0.034	0.101
367.4	6.9	0.47	0.0142	0.027	0.074
367.4	5.6	0.38	0.0114	0.022	0.052
367.4	4.7	0.32	0.0095	0.018	0.034
Heated to 350°C					
367.4	8.6	0.58	0.0174	0.034	~0

Table 20
Desorption Data on Alloy 149 - 310°C

Increment Withdrawn ml	Equil. Pressure		H ₂ Grams Removed	-Δ(H/M)	Remaining H/M in Sample
	psia	Atm.			
0	--	--	--	--	1.06*
67.4	98.7	6.71	0.0368	0.071	0.989
67.4	67.7	4.61	0.0253	0.049	0.940
367.4	33.7	2.29	0.0685	0.132	0.808
1367.4	31.7	2.16	0.2403	0.462	0.346
367.4	30.2	2.05	0.0613	0.118	0.228
367.4	27.7	1.88	0.0563	0.108	0.120
367.4	20.7	1.41	0.0422	0.081	0.039
Heated to 350°C					
1367.4	2.7	0.18	0.0201	0.039	~0
* Summation of increments. H ₂ by wt. loss in vacuum = 0.5483 g = H/M of 1.05.

Figure 20. PCT Isotherm at 271°C for Alloy 149

Figure 21. PCT Isotherm at 299°C for Alloy 149. Different Points Represent Different Hydriding-Dehydriding Runs.

Figure 22. PCT Isotherm at 310°C for Alloy 149

Figure 23. Plateau-Pressure Isochores for Alloy 149 as a Function of H/M Ratio

Table 21

Effect of Temperature on Plateau Pressures of Alloy 149

Pressure (P) Atm.	Log P	Temperature (T) °K	1/T x 10 ³
H/M = 0.25			
2.10	0.322	583	1.715
1.40	0.146	572	1.748
0.60	-0.222	544	1.838
H/M = 0.5			
2.20	0.342	583	1.715
1.55	0.190	572	1.748
0.66	-0.181	544	1.838
H/M = 0.7			
2.27	0.356	583	1.715
1.52	0.182	572	1.748
0.66	-0.181	544	1.838

pressure-composition isotherm for the $\text{Mg}_2\text{Ni-Mg-H}_2$ (72.9 w/o Mg-25.2w/oNi) system is reproduced in Figure 24. This system has been extensively investigated at the Brookhaven National Laboratory (Ref. 12).

7.2 PCT DATA ON OTHER SELECTED SYSTEMS

To obtain some indication of PCT relationships on several of the better alloys previously investigated, several PCT data points were observed for each of the selected systems. The alloys were activated and fully hydrided according to standard procedures mentioned previously. Small increments of gas were withdrawn initially to determine the equilibrium pressures at the high hydrogen compositions, followed by larger increments to determine the plateau regions for a given temperature.

The results for each alloy and the pressure-composition relationships are summarized in Tables 22 through 25. Data points were plotted to provide partial P-C isotherms, which are shown in Figures 25 through 28.

The level of the observed plateau pressures were as expected, except for Alloy 107.4 ($\text{Mg}_{0.8275}\text{Ni}_{0.05}\text{Cu}_{0.0775}\text{Zn}_{0.045}$) which showed a slightly higher pressure of 0.8 atm compared to 0.66 atm observed for Alloy 149 at 271°C. No discernable advantage was observed for alloy 107.4 at 299°C.

Table 22
Desorption Data on Alloy 107.4
($\text{Mg}_{0.8275}\text{Ni}_{0.05}\text{Cu}_{0.0775}\text{Zn}_{0.045}$)

Increment Withdrawn ml	Equivalent Pressure		H ₂ Grams Removed	-Δ (H/M)	Remaining H/M in Sample
	psia	Atm.			
271°C					
0			--	--	1.20
67.4	102.7	6.99	0.0383	0.078	1.12
367.4	39.2	2.67	0.0797	0.162	0.960
367.4	16.7	1.14	0.0340	0.069	0.891
1367.4	11.8	0.80	0.0890	0.181	0.710
299°C					
0					1.20
1367.4	25.2	1.71	0.1909	0.388	0.812
367.4	24.7	1.68	0.0504	0.103	0.709
1367.4	23.2	1.58	0.1764	0.359	0.350
1367.4	16.7	1.14	0.1268	0.258	0.092
Heat to 350°C					
1367.4	5.9	0.4	0.0448	0.091	1.20+

Table 23
Desorption Data on Alloy 107R ($\text{Mg}_{0.85}\text{Cu}_{0.1}\text{Ni}_{0.05}$)

299°C					
Increment Withdrawn ml	Equivalent Pressure		H ₂ Grams Removed	-Δ(H/M)	Remaining H/M in Sample
	psia	Atm.			
0					0.957
67.4	129.7	8.82	0.0485	0.092	0.865
367.4	30.7	2.09	0.0626	0.119	0.746
1367.4	23.7	1.61	0.1800	0.317	0.429
<p style="text-align: center;">Taken out and weighed</p> <p>Remaining H₂ = 0.2252g or H/M = 0.429</p> <p style="text-align: center;">Total H/M = 0.957</p>					

Table 24
Desorption Data on Alloy 107.1 ($\text{Mg}_{0.75}\text{Zn}_{0.1}\text{Ni}_{0.05}$)

299°C					
Increment Withdrawn ml	Equivalent Pressure		H ₂ Grams Removed	-Δ(H/M)	Remaining H/M in Sample
	psia	Atm.			
0					0.956
67.4	82.5	5.80	0.0319	0.072	0.884
367.4	25.7	1.75	0.0524	0.119	0.765
1367.4	21.2	1.44	0.1607	0.363	0.402
<p style="text-align: center;">Taken out and weighed</p> <p>Remaining H₂ = 0.1777 g or H/M = 0.402</p> <p style="text-align: center;">Total H/M = 0.956</p>					

Table 25
Desorption Data on Alloy 140M ($\text{Mg}_{0.85}\text{Cu}_{0.1}\text{Ni}_{0.05}\text{Sn}_{0.02}$)

299°C					
Increment Withdrawn ml	Equivalent Pressure		H ₂ Grams Removed	-Δ(H/M)	Remaining H/M in Sample
	psia	Atm.			
0					0.744
67.4	75.2	5.12	0.0281	0.057	0.687
367.4	27.7	1.88	0.0564	0.114	0.573
1367.4	24.2	1.65	0.1836	0.371	0.202
<p style="text-align: center;">Taken out and weighed</p> <p>Remaining H₂ = 0.1001 g or H/M = 0.202</p> <p style="text-align: center;">Total H/M = 0.744</p>

Figure 24. Pressure Composition Isotherm for the Mg₂Ni-Mg-H₂ System

Figure 25. Partial Desorption: Isotherms at 214°C - Alloy 107.1

Figure 26. Partial Desorption Isotherm at 299°C - Alloy 107R

Figure 27. Partial Desorption: Isotherm at 299°C - Alloy 140M

Figure 28. Partial Desorption: Isotherms for Alloy 107.4

8

CONCLUSIONS AND RECOMMENDATIONS

8.1 CONCLUSIONS

The program goals of developing a light weight, low cost metal hydride with a low temperature of dissociation (200°C) led to extensive alloying studies of magnesium based systems, which included alloy additions of Ni, Cu, Zn, Sn, Ga, V, Si, B, Al, In, and rare-earth and related elements.

These studies, using Multiple Linear Regression (MLR) analysis as a backup, resulted in the development of the Mg-Ni_{0.05}Cu_{0.1}Y_{0.005} alloy (No. 149), exhibiting a low hydride dissociation temperature of 223°C. These investigations further indicate that the T_D of 223°C perhaps represents the lower limit attainable with the Mg-Cu-Ni alloy system.

It is further concluded that hydrided Alloy 149 has properties equivalent to or better than the more expensive Mg-Mg₂Ni-H₂ system extensively investigated and which contains more than 25 weight percent of the expensive and strategic element nickel.

8.2 RECOMMENDATIONS

Results of this study indicate a further need for investigating the following two areas of lightweight metal hydride storage: (1) decreasing the dissociation temperature, T_D , and (2) increasing hydrogen storage capacity, the H/M ratio.

Approaches to the solution of these problems should make use of the findings of recent work by Lundin et al. (Ref. 13), which shows a remarkably close relationship between interstitial hole size and the thermodynamic stability of the hydrides of AB₅ (LaNi₅) and AB (FeTi) intermetallic compounds. Figure 29 illustrates this correlation of stability and tetrahedral hole size for AB₅ hydrides of the LaNi₅ type.

It would be wise to continue the investigations of the Mg-Cu-Ni-X system in the light of the correlation of hole size and stability mentioned above. This may lead us to some important basic relationships.

New alloy systems recommended for study, adhering as closely as possible to the alloying principle discussed above, include the following:

- Mg-Li-(Zn, Sn, Si, Ni)
- Mg-Ni-Li (Zn, Sn, Si)
- Mg-Al-X
- Mg-Li-Al-X

Figure 29. Correlation of the Free Energy of Formation of Various AB₅ Hydrides (Temperature Specified) vs. the Radius of the Tetrahedral Hole (Ref. 13)

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