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Development of Lightweight Hydrides Annual Task Report

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August 1978 through September 1979

Prepared by
David A. Rohy
J.F. Nachman

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PREPARED FOR THE DEPARTMENT OF ENERGY
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SOLAR TURBINES INTERNATIONAL

An Operating Group of International Harvester

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INTRODUCTION

This report describes the results of the first years effort to develop light-weight hydrides for automotive storage of hydrogen under Contract DE-AC03-78CS52059. A test fixture to subject a magnesium alloy hydride to hundreds of hydriding cycles has been designed and is being constructed. Extensive testing of the magnesium lithium and magnesium aluminum alloy hydrides has been performed. Several alloys demonstrate significantly higher hydrogen dissociation pressures than the baseline alloy Mg_2Ni-Mg . No alloy has yet demonstrated one atmosphere of hydrogen pressure at the goal temperature of $200^{\circ}C$. Hydrogen capacity varies greatly with alloy composition. Alloys with high dissociation pressures have hydrogen capacities up to 3.6 percent by weight. Plans include the reduction of aluminum content in the alloys to increase the hydrogen capacity.

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TECHNICAL DISCUSSION

2.1 CYCLIC TESTING

Magnesium hydride properties are measured after approximately ten hydriding-dehydriding cycles. This number of cycles is sufficient to insure total saturation of the alloy with hydrogen but may not be sufficient to expose properties that would occur over the life cycle of an automotive fuel system. Two of those parameters are alloy comminution due to a large number of refueling cycles and contamination due to hydrogen impurities. One of the tasks of this program is to evaluate the properties of these alloys over hundreds of cycles. Since the test takes considerable time, it will be started when a clearly superior alloy is identified. At this writing, the planned startup period is February 1980.

The test will involve approximately two kilograms of magnesium alloy powder. This is significantly greater than the 15 to 20 gram samples regularly tested. The alloy will be installed in a two liter reactor. The temperature of the powder, while not yet determined, should be in the range of 250°C to 325°C. Hydrogen will be added to the reactor to fully hydride the powder. At the fully hydride condition, the powder will soak for approximately one-half hour. Subsequently the gas will be drawn off and disposed of until 90 percent of the stored hydrogen has been removed. The process will be repeated with new hydrogen. Each cycle should take approximately one hour. A sequence timer will allow unattended operation. Our initial goal is 500 cycles. At regular intervals the system will be cooled to room temperature to allow the removal of a small powder sample. The cycling test will resume while the small sample is measured and characterized in other apparatus.

The apparatus to perform this test is shown in Figure 1. All components have been specified. Fabrication should start when the longest lead item, the reactor is delivered in early January 1980.

2.2 TASK 2 - Mg ALLOY DEVELOPMENT

2.2.1 Mg-Li Base Alloys

The hydrides of magnesium and lithium have many desirable characteristics for automotive applications. Their densities are very low and both contain substantial quantities of hydrogen, 7.55 weight percent for MgH_2 and 12.68

Figure 1. Hydriding Cycling Apparatus

percent for LiH. Investigation of alloys combining the two elements appeared to be a logical step. The greatest disadvantage of both hydrides is their relatively high thermodynamic stability, with LiH exhibiting even a higher stability than MgH_2 .

One of the purposes of Task 2 was to attempt to decrease the thermodynamic stability of a Mg-Li base alloy hydride by the addition of ternary alloying elements consisting of Zn, Sn, Si, Ni, and Cu. Large differences in electronegativities between Li and the addition elements favor formation of stable compounds which in turn influence the interstitial hole size. The smaller the interstitial hole size the less stable the hydride (Ref. 1). The electronegativities of the alloy elements and possible compounds that might be formed are given in Table 1.

Table 1

Electronegativities of Alloy Elements and Possible Compounds

Element	Electronegativity (Ref. 3)	Possible Compounds (Ref. 4)	Temperature of Stability, °C
Li	0.95	--	--
Zn	1.50	Li_2Zn_3	520
Sn	1.61	Li_7Sn_2	783
Si	1.82	Li_2Si	752

Preparation of Hydriding Alloys

Melting of the alloys was by induction in a crucible of mild steel surrounded by argon. The lithium addition was made after the balance of the charge was molten, and just prior to solidification of the melt, to minimize oxidation of the lithium. By plunging the lithium below the molten surface, both oxidation and vaporization losses were held to a minimum. The melt was allowed to solidify and cool within the crucible before removal to the air.

Macrosegregation and/or completeness of melting of the 40-50 gram ingots was verified by radiographic examination. Those ingots containing undissolved elements were remelted and checked again by radiography.

Homogeneity on a macroscale was not a problem except in a few isolated instances. One of these was alloy No. 9L ($\text{Mg}_{0.67}\text{Li}_{0.2}\text{Si}_{0.125}$), where apparently the higher Li and Si contents caused the solubility limit to be exceeded.

Other problems of homogeneity were encountered with the Ni-containing alloys. In the case of the ternary $\text{Mg}_{0.7}\text{Li}_{0.2}\text{Ni}_{0.1}$ immiscibility appears to be the problem, which was not evident with alloys containing 10 atomic percent Li. This is not entirely unexpected as the binary system of Li-Ni exhibits essentially complete immiscibility (Ref. 1). Lowering the Li to 17.5 atomic percent did not appear to improve the immiscibility of the system to any great extent.

Those alloys containing 5 to 10 atomic percent Si appeared to have unmelted pieces present, indicating presence of some refractory silicides, possibly Ni_2Si or Ni_5Si_2 . The presence of unmelted refractory silicides was noted even though the NiSi master alloy was used, and the Si addition was reduced to 2.5 atomic percent.

Ingots free of macrosegregation were given a homogenization anneal at 400°C for a period of 48 to 72 hours to remove or minimize any microsegregation or

coring. Homogeneous ingots were then pulverized to -12 mesh with a steel mortar and pestle in argon.

Hydriding and Mini-PC Isotherms

Approximately 15 g of the pulverized alloy were placed in the Inconel 600 reactor and subjected to the standard hydriding procedure, except that the pressure was increased to 600 psi, instead of the usual 300 psi, to improve the hydriding kinetics.

After hydriding, mini-PC isotherms were determined on each alloy at 310°C. This procedure was adopted to permit screening large numbers of prospective alloys. Four points appear to be sufficient to indicate the plateau region and the general shape of the pressure-composition isotherm for each alloy.

For convenience, the alloy hydrides and their characteristics are discussed in separate categories, beginning with ternary and ending with multicomponent systems.

Mg-Li-X (X = Ni, Zn, Sn, Si, Cu)

The PC relationships are plotted in Figure 2. Highest plateau pressures were attained with $\text{Mg}_{0.8}\text{Li}_{0.1}\text{Ni}_{0.1}$ followed by $\text{Mg}_{0.8}\text{Li}_{0.1}\text{Si}_{0.1}$. Kinetics of hydrogen release were not as rapid as anticipated so that each point was equilibrated for 1-1/2 to 2 hours.

Hydriding characteristics of the ternary systems containing 10 atomic percent of the various addition elements are summarized in Table 2. The item listed in Table 2 as ΔT in °C is the change in temperature experienced during the hydriding and dehydriding cycle. It is listed because it is felt to be at least qualitatively related to the kinetics and hydrogen capacity of each alloy. The highest hydrogen content of 2.04 percent was achieved with Alloy No. 1L, containing 10 atomic percent Ni, followed by 1.70 percent for Alloy No. 3L ($\text{Mg}_{0.8}\text{Li}_{0.1}\text{Sn}_{0.1}$).

This series of alloys was designed to study the effect of doubling the Li content from 10 to 20 atomic percent on the ternary systems. The resulting mini-PC isotherms are shown in Figure 3. For the Si-containing alloy, doubling of the Li content to 20 atomic percent appears to increase the decomposition pressure abruptly.

Figure 2. Pressure-Composition Isotherms of Mg-Li-X at 310°C

In general, other than decreasing the density of the alloy, there appears to be no advantage in doubling the Li content. The hydriding-dehydriding kinetics are impaired, as indicated by the long time required for equilibration (approx. 2 hours), and the total hydrogen absorbed is considerably less than that of the ternary alloys containing 10 atomic percent Li. See Table 2 for a comparison of the hydriding characteristics of the various ternary alloys.

No data are available for Ni-containing alloys with 20 atomic percent Li because of the immiscibility of Ni in the presence of Li contents in excess of 10 atomic percent. Refer to section on Preparation of Hydriding Alloys.

To determine the basic effect of the lower Li content and to have a direct comparison with the 10 atomic percent Li ternary series, a ternary series containing 5 atomic percent Li was investigated. Figure 4 shows the mini-PC isotherms obtained with the lower Li content. These can be directly compared with the isotherms shown in Figure 2. The hydrogen contents are about half and the decomposition pressures are considerably lower than the 10 atomic percent Li ternary series. See Table 2 for the hydriding characteristics of both the five and ten atomic percent Li systems.

Table 2

Hydriding Characteristics of Mg-Li-X

Alloy	Composition	ΔT , °C	% H ₂ Absorbed	Approximate Plateau Pressure @ 310°C (atm)
1L	Mg _{0.8} Li _{0.1} Ni _{0.1}	44	2.04	1.2
2L	Mg _{0.8} Li _{0.1} Zn _{0.1}	19	1.63	0.6
3L	Mg _{0.8} Li _{0.1} Sn _{0.1}	10	1.70	0.8
4L	Mg _{0.8} Li _{0.1} Si _{0.1}	18	1.26	0.8
5L	Mg _{0.8} Li _{0.1} Cu _{0.1}	14	0.86	0.6
9L	Mg _{0.675} Li _{0.2} Si _{0.125}	11	1.64	0.4
20L	Mg _{0.7} Li _{0.2} Zn _{0.1}	11	1.10	0.6
21L	Mg _{0.7} Li _{0.2} Sn _{0.1}	22	0.60	0.5
22L	Mg _{0.7} Li _{0.2} Cu _{0.1}	18	0.69	0.5
38L	Mg _{0.85} Li _{0.05} Ni _{0.1}	44	1.38	1
39L	Mg _{0.85} Li _{0.05} Zn _{0.1}	9	0.59	0.3
40L	Mg _{0.85} Li _{0.05} Sn _{0.1}	14	0.77	0.5
41L	Mg _{0.85} Li _{0.05} Cu _{0.1}	9	0.51	0.4

Mg-Li-Ni-X (X = Cu, Zn, Sn, Si)

Since the best ternary hydride results were attained with Mg_{0.8}Li_{0.1}Ni_{0.1}, Alloy No. 1L was used as a base for the quaternary alloy hydrides which are shown in Figure 5. It should be noted that the addition of 0.1 atomic fraction of Cu increased the decomposition pressure materially. The most dramatic improvement in hydriding characteristics was achieved by the addition of 0.1 atom fraction of Sn. A plateau pressure greater than two atmospheres and an H/M ratio greater than 0.8 were observed for this hydride.

Figure 3. Pressure-Composition Isotherms of Mg-Li_{0.2}-X at 310°C

Figure 4. Pressure-Composition Isotherms of Mg_{0.85}Li_{0.05}X_{0.1} System at 310°C

Figure 5. Pressure-Composition Isotherms of Mg-Li-Ni-X at 310°C

Hydriding characteristics of all the alloys studied are summarized in Table 3. Note also the much higher ΔT (89°C) for $\text{Mg}_{0.7}\text{Li}_{0.1}\text{Ni}_{0.1}\text{Sn}_{0.1}$. The temperature rise, ΔT , observed during hydriding is felt to be a good qualitative measure of hydriding kinetics.

Although encouraging results were obtained with the 10 atomic percent Sn quaternary system, the heavy metal content is rather high. This particular series of alloys was an attempt to limit the Cu, Sn, and Zn additions to five atomic percent.

Hydriding results on this series of quaternary alloys are summarized in Figure 6 and Table 3. The alloy containing five atomic percent Sn still appears to give the better results over the Cu and Zn additions. The isotherm for five atomic percent Cu, on the other hand, exhibits a somewhat better plateau, and a higher hydrogen content than the previously run alloy containing ten atomic percent Cu.

Earlier hydriding studies indicated that larger amounts of Li (20 atomic percent) limited the total amount of hydrogen absorbed. To check this out

Table 3

Hydriding Characteristics of Mg-Li-Ni-X

Alloy	Composition	$\Delta T, ^\circ\text{C}$	% H ₂ Absorbed	Approximate Plateau Pressure at 310°C (atm)
11L	Mg _{0.75} Li _{0.1} Ni _{0.1} Cu _{0.05}	60	1.95	1.6
12L	Mg _{0.7} Li _{0.1} Ni _{0.1} Cu _{0.1}	45	1.64	1.0
13L	Mg _{0.7} Li _{0.1} Ni _{0.1} Zn _{0.1}	48	0.95	--
14L	Mg _{0.7} Li _{0.1} Ni _{0.1} Sn _{0.1}	89	2.32	2.4
28L	Mg _{0.75} Li _{0.1} Ni _{0.1} Sn _{0.05}	91	1.92	1.8
29L	Mg _{0.75} Li _{0.1} Ni _{0.1} Zn _{0.05}	41	1.03	--
35L	Mg _{0.8} Li _{0.05} Ni _{0.1} Sn _{0.05}	81	2.48	2.0
36L	Mg _{0.8} Li _{0.05} Ni _{0.1} Cu _{0.05}	40	1.11	0.9
37L	Mg _{0.8} Li _{0.05} Ni _{0.1} Zn _{0.05}	37	1.63	1.8

Figure 6. Pressure-Composition Isotherms of Mg-Li-Ni-X at 310°C

further, a series of quaternary alloys were investigated and were based on $\text{Mg}_{0.8}\text{Li}_{0.05}\text{Ni}_{0.1}\text{X}_{0.05}$, where X represents Sn, Cu, or Zn. Figure 7 summarizes the pressure-composition relationships obtained with this system. The hydriding characteristics are given in Table 3. It is interesting to note that the hydrogen content and plateau pressures of the alloy containing five atomic percent Sn (35L) are about the same as were obtained with $\text{Mg}_{0.7}\text{Li}_{0.1}\text{Ni}_{0.1}\text{Sn}_{0.1}$, which has best plateau pressure and one of the highest hydrogen contents attained to date on the quaternary systems (refer to alloy 14L in Table 3 and Figure 5).

Multicomponent Alloys

In this section, the discussion lumps together all alloys of five or more components. Initially a study was conducted on multicomponent systems, using $\text{Mg-Li}_{0.1}\text{Ni}_{0.1}\text{Sn}_{0.05}$ as a base. Additions of a fifth component were made to determine what, if any, synergistic effects may exist between the multiple addition elements. Figure 8 shows the mini-PC isotherms obtained with the addition of approximately 5-6 atomic percent of Si, Cu, and Zn. Additions of Cu and Zn appear to produce higher decomposition pressures at the higher H/M ratios, and also a somewhat flatter plateau region. Hydriding characteristics of these quinary alloys are listed in Table 4.

Figure 7. Pressure-Composition Isotherms of $\text{Mg}_{0.8}\text{Li}_{0.05}\text{Ni}_{0.1}\text{X}_{0.05}$ Systems at 310°C

Figure 8. Pressure-Composition Isotherms of Mg-Li-Ni-Sn-X at 310°C

Table 4

Hydriding Characteristics of Mg-Li-Ni-Sn-X and Mg-Li-Ni-Sn-X-Y

Alloy	Composition	ΔT , °C	% H_2 Absorbed	Plateau Pressure at 310°C (atm)
25L	$\text{Mg}_{0.67}\text{Li}_{0.11}\text{Ni}_{0.11}\text{Sn}_{0.06}\text{Si}_{0.06}$	30	0.67	--
26L	$\text{Mg}_{0.67}\text{Li}_{0.11}\text{Ni}_{0.11}\text{Sn}_{0.06}\text{Cu}_{0.06}$	60	1.30	2.0
31L	$\text{Mg}_{0.7}\text{Li}_{0.1}\text{Ni}_{0.1}\text{Sn}_{0.05}\text{Zn}_{0.05}$	55	1.48	2.0
32L	$\text{Mg}_{0.725}\text{Li}_{0.1}\text{Ni}_{0.1}\text{Sn}_{0.05}\text{Cu}_{0.025}$	61	1.67	2.0
33L	$\text{Mg}_{0.75}\text{Li}_{0.1}\text{Ni}_{0.05}\text{Sn}_{0.05}\text{Cu}_{0.05}$	53	1.31	--
34L	$\text{Mg}_{0.725}\text{Li}_{0.1}\text{Ni}_{0.1}\text{Sn}_{0.025}\text{Zn}_{0.025}\text{Cu}_{0.025}$	42	1.36	--

Other quinary alloys along with a six-component alloy (34L) were also included in this study to determine the effect of a number of small additions (2.5 atomic percent) of Sn, Zn, and Cu. The results of these hydriding studies are summarized in Figure 9. It was concluded that there were no particular advantages or synergistic effects with these multicomponent systems. Hydriding characteristics of these alloys are listed in Table 4.

In general, a comparison of the hydriding characteristics of the five- or six-component systems (Table 4) with the quaternary system (Table 2) shows higher decomposition pressures at higher H/M ratios and lower hydrogen contents than the quaternary alloys.

2.2.2 Mg-Al ($Mg_{17}Al_{12}$) Base Alloys

With the completion of work on the Mg-Li base hydride alloys, attention was directed toward the Mg-Al system as a prospective starting base material. Initial investigations were centered around the $Mg_{17}Al_{12}$ intermetallic compound, whose hydride was reported by Brookhaven National Laboratory to contain 3.31 percent hydrogen (Ref. 5). The available data on hydriding of $Mg_{17}Al_{12}$ and other alloys of the Mg-Al system are summarized in Table 5. Interest in this particular system has been stimulated to a great extent by the existence of the complex hydride $Mg(AlH_4)_2$, containing 9.3 weight percent hydrogen. It should be pointed out, however, that preparation of this com-

Figure 9. Pressure-Composition Isotherms of Multicomponent System at 310°C

pound to date has been possible only through indirect synthesis by complicated organo-metallic reactions. Processes of this type are not suitable for vehicular use because of their irreversibility.

Hydriding and dehydriding of Mg-Al alloys is generally characterized by poor kinetics. This prompted Brookhaven to use hydriding pressures of 1000 to 5000 psi plus very fine powder of -200 mesh. The higher hydrogen content reported by Douglass on the 90Mg-10Al alloy listed in Table 5 was also achieved by hydriding at 400 to 450°C under a pressure of 600 psi for periods of time up to 20 hours (Ref. 6).

As stated before, one of the purposes of Task 2 is to attempt to decrease the thermodynamic stability of magnesium-base alloy hydrides by single or multiple additions of alloying elements consisting of Ni, Cu, Zn, Sn, Si, as well as Li and rare earths. These latter active elements, particularly the rare earths, should behave as scavengers to prevent oxidation of aluminum, which is believed to be responsible for the poor hydriding kinetics of the aluminum-containing alloys.

The first experiments were designed to investigate the effect of a change of lattice parameter upon hydriding characteristics of the gamma-phase ($Mg_{17}Al_{12}$), which is isotypic with the complex cubic structure of α Mn. Lattice constants vary linearly from $a = 10.469$ Å. at 51.6 at. percent Mg to $a = 10.591$ Å. at 61.5 at. percent Mg (Ref. 4). Recent work (Ref. 1) indicates that a decrease in lattice parameter suggests a smaller interstitial hole size with a decrease in thermodynamic stability of the resulting hydride (lower decomposition temperature).

2.2.3 Preparation of Hydriding Alloys

The Mg-Al alloys were prepared around the ideal composition of $Mg_{17}Al_{12}$ ($Mg_{0.59}Al_{0.41}$), using the standard induction melting and radiographic inspection procedures described in Section 2.2.1.

Alloying additions, consisting of Ni, Cu, Sn, Zn, Li, Y, and La, were made to the $Mg_{17}Al_{12}$ intermetallic with the basic composition of $Mg_{0.62}Al_{0.38}$ (4A). The ratio of Mg/Al of approximately 1.63 was kept constant in these alloys based upon the $Mg_{0.62}Al_{0.38}$ composition.

Previously, we had encountered difficulty in the preparation of magnesium alloys containing both Ni and Al additions due to the formation of the refractory compound NiAl. By the use of a master alloy containing 74 percent Al - 26 percent Ni (M.P. approx. 850°C) we have found it possible to prepare homogeneous alloys. To keep the melting temperature of the master alloys at 850°C, and at the same time maintain the Mg/Al ratio at approximately 1.63, it was necessary to limit the Ni addition to five atomic percent.

Radiography indicated no macrosegregation or unmelted phases in any of the newly prepared alloys. Alloys containing addition elements were given a homogenization anneal to minimize microsegregation prior to hydriding. All alloys, except the low-melting ones containing Zn, Li, and Cu, were homogenized at 400°C. The annealing temperature was lowered to 300°C for the latter.

Table 5

Mg-Al System Summary*

<u>Alloy Composition</u>				
Atomic Ratio	Wt. Percent	Mesh Size	Maximum Hydrogen Wt. Percent	Results
Mg _{0.91} Al _{0.09} (Ref. 2)	90Mg-10Al	-25 +32 -32 +42	7.0	Kinetics hyd./dehyd. poor <

2.2.4 Hydriding and Mini-PC Isotherms

The homogeneous Mg-Al alloys were subjected to the standard hydriding procedure at a pressure of 600 psi (Section 2.2.1). Because the Brookhaven results on Mg₁₇Al₁₂ were obtained with -200 mesh powder and the relatively poor hydriding kinetics of these alloys, a decision was made to use -100 mesh powder. Normally we tend to avoid such fine powders because of the greater chance of losing part of the sample during alternate pressurization and evacuation of the reaction chamber.

After hydriding, mini-PC isotherms were determined on each alloy at 310°C. As in Section 2.2.1, the discussion is facilitated by organizing the results according to alloy category, i.e., binary, ternary, etc.

Binary Variations of $Mg_{17}Al_{12}$

As mentioned earlier, the lattice parameters vary linearly from $a = 10.469$ Å. at 51.6 atomic percent Mg to 10.591 Å. at 61.5 atomic percent Mg. Hydriding studies were conducted on the gamma-phase alloys containing these two extremes in composition.

In general, the alloys are comminuted to -12 mesh in an argon flow. However, since -100 mesh powder is being used, several alloys were powdered, screened, and loaded into the reactor in the dry box in an argon atmosphere and are so identified. As mentioned earlier, Douglass' work (Ref. 6) indicated that up to 20 hours were necessary to fully hydride the 90Mg-10Al alloy. Alloy 4A was therefore hydrided for approximately 12 hours at 400°C under a pressure of 600 psi. The PC relationships are plotted in Figure 10. Hydriding characteristics are tabulated in Table 6.

Hydrogen absorption by earlier alloys (2A and 3A) is about 30 percent of that reported by Brookhaven. This can probably be attributed to much higher pressures employed by the Brookhaven investigators (1000 to 5000 psi), as well as to the much finer powder (-200 mesh) used in their studies.

Some minor improvement in hydrogen absorption was obtained by sample preparation in the dry box. Compare Alloy 2A with and without dry box preparation in Table 6. The most dramatic improvement in hydrogen absorption was obtained with Alloy 4A, which was prepared in the dry box and held at 400°C for

Figure 10. Pressure-Composition Isotherms of Mg_xAl_y at 310°C

Table 6

Hydriding Characteristics of Mg-Al Systems

Alloy	Composition	ΔT , °C	%H ₂ Absorbed	Plateau Pressure at 310°C (atm)	Remarks
2A	Mg _{0.52} Al _{0.48}	15	0.55	--	-100 mesh
3A	Mg _{0.6} Al _{0.4}	7	0.95	0.7	-100 mesh
4A	Mg _{0.62} Al _{0.38}	19	0.88	1.3	-100 mesh (dry box)
2A	Mg _{0.52} Al _{0.48}	12	0.77	--	-100 mesh (dry box)
4A	Mg _{0.62} Al _{0.38}	20	2.30	1.4	-100 mesh (dry box plus 12 hours at 400°C plus 600 psi)

approximately 12 hours under a hydrogen pressure of 600 psi. Total hydrogen absorbed was two and one-half times that of the standard hydriding procedure.

The highest plateau pressure of about 1.5 atmospheres at 310°C was also observed with Alloy 4A, which has the largest lattice parameter of the gamma phase (see Fig. 10). This result appears to run counter to van Mal's rule of "reversed stability" (Ref. 7) and the observations of Lundin, et al. (Ref. 1). A recent communication with C. B. Magee of the University of Denver indicates that this is the reason why van Mal's rule is not always applicable. One must know the exact crystal structure and lattice parameter to determine interstitial hole size in order to predict the thermodynamic stability of hydrogen (Ref. 8).

Ternary Gamma-Phase Mg-Al Alloys

In this section are described studies carried out on ternary additions of Ni, Sn, Si, Li, Cu, Y, and La to the basic Mg_{0.62}Al_{0.38} composition, keeping the Mg/Al ratio constant at 1.63.

Note that the kinetics of hydriding were greatly improved by the addition of five atomic percent Ni (Alloy 5A). Hydrogen content and hydriding characteristics were nearly identical to Alloy 4A, which required 12 hours of hydriding under 600 psi as described in the previous sections. Compare the PC isotherms in Figure 11 and hydriding characteristics in Table 7.

On the other hand, addition of five atomic percent Sn to the basic alloy 4A causes a deterioration of the dissociation pressure and hydrogen content. See Table 7 and Figure 13.

Figure 11. Pressure-Composition Isotherms for Mg-Al-X System

Previously the most dramatic improvement in hydrogen absorption for the binary series was obtained with Alloy 4A described above. Alloy 5A was also hydrided for 12 hours at 400°C under a pressure of 600 psi. The H/M ratio was increased markedly to approximately 0.9 with a plateau pressure of about 1.8 atm. See Figure 12 and Table 7.

The highest plateau pressure observed for the five atomic percent level of additions was 2.3 atmospheres at 310°C, achieved with Alloy 13A, which contains five atomic percent of yttrium. Kinetics of hydriding were also greatly improved by the yttrium addition. Compare the PC isotherms in Figure 13 and hydriding characteristics in Table 7. The improved kinetics can perhaps be attributed to the very stable oxide that yttrium forms, in effect scavenging the oxygen and preventing the formation of the impervious and stable Al_2O_3 , which is believed to act as a barrier responsible for the poor hydriding kinetics of Al-containing alloys. See Table 8 for a comparison of the thermodynamic stabilities of various oxides.

The relatively poor hydriding kinetics of Mg can also be attributed to the very stable oxide it forms. However, MgO is somewhat less impervious and protective than Al_2O_3 . It is possible that the Y addition is also beneficial in this case, as Y_2O_3 is a little more stable than MgO at elevated temperatures (Table 8).

Table 7

Hydriding Characteristics of Mg-Al Systems

Alloy	Composition	ΔT , °C	% H ₂ Absorbed	Plateau Pressure at 310°C (atm)	Remarks
5A	Mg _{0.59} Al _{0.36} Ni _{0.05}	28	2.16	1.3	-100 mesh (dry box)
8A	Mg _{0.59} Al _{0.36} Sn _{0.05}	8	0.45	0.5	-100 mesh (dry box)
6A	Mg _{0.56} Al _{0.34} Cu _{0.10}	27	0.81	--	-100 mesh (dry box)
5A	Mg _{0.59} Al _{0.36} Ni _{0.05}	--	3.36	1.8	-40 plus -100 mesh (dry box) plus 12 hours 600 psi at 400°C
10A	Mg _{0.59} Al _{0.36} Li _{0.05}	26	1.78	0.7	-40 plus -100 mesh (dry box)
13A	Mg _{0.59} Al _{0.36} Y _{0.05}	30	2.01	2.2	-40 plus -10 mesh (dry box)
9A	Mg _{0.59} Al _{0.36} Si _{0.05}	10	0.63	0.4	-40 plus -100 mesh (dry box)
14A	Mg _{0.56} Al _{0.34} Y _{0.1}	40	2.51	1.9-2.4	-40 plus -100 mesh (dry box)
14A	Mg _{0.56} Al _{0.34} Y _{0.1}	40	3.29	2.1-2.6	Same as above plus 12 hours 600 psi at 400°C
12A	Mg _{0.59} Al _{0.36} La _{0.05}	31	2.68	1.9	-40 plus -100 mesh (dry box)
12A	Mg _{0.59} Al _{0.36} La _{0.05}	31	3.04	2.9	Same as above plus 12 hours 600 psi at 400°C

The five atomic percent Li addition may also have some potential oxygen scavenging ability, as hydriding kinetics show some improvement and the hydrogen content (1.78%) after the standard hydriding procedure is considerably better than the Cu- and Sn-containing alloys. However, the dissociation pressure is too low (Fig. 13).

The addition of five atomic percent of Si appears to provide no benefits to the hydriding behavior of the basic Mg₁₇Al₁₂ intermetallic compound. See Figure 13 and Table 7.

Using the standard hydriding procedure, the highest H/M ratio of 0.85 was attained with Alloy 12A, which contains five atomic percent La (Fig. 13). La has a slightly higher free energy of formation of its oxide than Y (see Table 8), so that it would be expected to exhibit similar hydriding behavior to Y.

Figure 12. Pressure-Composition Isotherms (310°C) for Mg-Al-X Hydrided for Extended Times

Table 8

Free Energies of Formation of Selected Oxides (Ref. 9)

Oxide	Temperature °C (°K)	ΔG_{of} , kcal/gm-atom O
Al_2O_3	400 (673)	-117
	1027 (1300)	-98
MgO	400 (673)	-126
	1027 (1300)	-106
La_2O_3	400 (673)	-129
	1027 (1300)	-115
Y_2O_3	400 (673)	-125
	1027 (1300)	-111
Li_2O	400 (673)	-121
	1027 (1300)	-97

Figure 13. Pressure-Composition Isotherms for Mg-Al-X Systems at 310°C (Standard Hydriding Procedure)

Because of the greatly improved hydriding characteristics of Alloy 13A, containing five atomic percent Y, hydriding studies were also conducted on a ten atomic percent Y alloy (14A). A comparison of the two in Figure 14 and Table 7 shows an even greater improvement in dissociation pressure and H/M ratio (0.84). The somewhat greater slope in the curve for the ten atomic percent Y alloy may indicate some microsegregation. It is possible that this could be minimized by annealing for a longer period of time, or homogenizing at a higher temperature.

Because of the substantial improvement in hydrogen capacity experienced by alloys hydried for a period of 12 hours, this procedure has now been adopted for most of the better alloys. Figure 15 summarizes the results on all alloys that have been subjected to the 12 hour procedure to date. Alloying of the gamma phase intermetallic has improved both the hydrogen capacities and plateau pressures. Again, the best results for plateau pressures and hydrogen capacities (H/M = 1.1) were obtained with the Y-containing alloys, in particular 14A containing ten atomic percent Y.

It should be noted that the curve for Alloy 14A is considerably flatter than in Figure 14. This could possibly be attributed to the effect of the additional 12 hours the alloy was held at 400°C.

Figure 14. Pressure-Composition Isotherms for Mg-Al-Y (Standard Hydriding Procedure)

Figure 15. Pressure-Composition Isotherms (310°C) for Mg-Al-X Hydrided for Extended Times

2.3 CONCLUSIONS

To date, the best hydride alloys have been observed to be the ternary Mg-Li-Ni base system with up to 10 atomic percent Sn($\text{Mg}_{0.07}\text{Li}_{0.1}\text{Ni}_{0.1}\text{Sn}_{0.1}$), and the gamma-phase Mg-Al alloys containing up to 10 atomic percent of rare-earths or related metal additions ($\text{Mg}_{0.56}\text{Al}_{0.34}\text{Y}_{0.1}$).

2.4 PLANS FOR CONTINUATION OF TASK 2

Because of the promising results achieved with the Y and La additions to the gamma-phase of the Mg-Al system, work is continuing with these additions, including combinations of these elements with each other and with Ni for possible synergistic effects.

Plans also call for studying a series of Mg-Al alloys with lower Al contents, perhaps in the range of about ten weight percent Al. Based on the work of Douglass, these alloys have the capability of absorbing seven weight percent hydrogen, and have the further advantage of resisting fragmentation during repeated hydriding (Ref. 6).

One of the major disadvantages of the Mg-10Al alloy is the rather poor hydriding kinetics. The results obtained to date in Task 2 indicate that the hydriding properties of Mg-Al alloys can be altered substantially by alloying additions.

3

CONCLUSIONS AND PLANS

At the end of the first year of this effort, magnesium alloys from two basic groups have been prepared and tested as hydride formers. These groups are Mg-Li-X and Mg-Al-X. Some of the alloys tested have better kinetics, higher dissociation pressure at a fixed temperature, and higher hydrogen capacity than any previously tested. While these advances are notable, no one alloy has the needed characteristics to operate alone as a hydrogen fuel carrier for automotive use. For that reason we will begin working on combined alloy testing (Task 3) in the next reporting periods.

The combined alloy concept involves the use of a low temperature hydride such as FeTi with a lightweight magnesium alloy. With that combination hydrogen evolutions should begin immediately at room temperature. The two alloys will be chosen for maximum hydrogen storage capacity consistent with supply of hydrogen gas at all driving conditions. Estimates of the relative quantities of each alloy and the schedule to which they will supply hydrogen will be made. At this time FeTi, vanadium alloys and rare-earth AB₅ alloys will be considered for the low temperature hydrogen storage material.

Cyclic testing of a magnesium alloy should begin in January 1980 when the rig is completed. One of the best magnesium alloy hydrides will be cycled for several hundred cycles. The critical parameters measured will be hydrogen capacity, comminution, kinetics and filter effectiveness. Cyclic testing on other alloys will continue through 1980.

There are no technical or administrative problems that should prevent us from meeting our program goals in FY 1980.

The Contract Management Summary Report and Cost Measurement Report are submitted separately.

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