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HYDROGEN STORAGE AND PURIFICATION SYSTEMS II

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I. Introduction

The use of metal hydrides as hydrogen reservoirs has been the subject of much research and speculation in recent years. This interest is due mainly to the fact that hydrogen is a promising medium for the storage of energy. It is a suitable fuel for both fuel cells and combustion engines; it produces little or no pollution on combustion; and it can be readily made from such other forms of energy as electricity (by the electrolysis of water). It has been proposed for use as an automotive fuel, for storage of solar energy, and for load-levelling at power plants. In all these applications there is need for a more convenient and less power-intensive storage mode than compression or liquefaction. Metal hydrides - or more generally, metal-hydrogen systems - suggest themselves because of their high hydrogen content, in terms of volume per cent. However, all of the systems known up until about ten years ago were unsuitable for storage purposes in one respect or another: cost, dissociation temperature, hydrogen content, etc. During the last decade, research at this Laboratory and elsewhere on previously untested hydrogen-metal systems, mostly alloys, has turned up several promising materials. None is perfect, however, and research in this field has therefore continued up to the present and will go on into at least the near future. At Brookhaven the basic research on metal-hydrogen equilibria and kinetics is supported both by the Atomic Energy Commission's Division of Physical Research and by the Army's Advanced Research Projects Agency (ARPA), operating through the Mobility Equipment Research and Development Center (MERDC).

This report, the preparation of which is supported by MERDC, summarizes the results of the fiscal years 1973 and 1974. It is the sequel to "Hydrogen Storage and Purification Systems", BNL 17136, which summarizes the work of

the preceding two-year period. All the material presented below appeared, sometimes in a different form, in bimonthly or quarterly progress reports addressed to MERDC. Some of the results were published in references 1 through 3.

II. Iron-Titanium Systems

By the beginning of the report period it had become apparent that the hydride $\text{FeTiH}_{1.9}$ was one of the most promising for stationary storage purposes, and it has even been considered for automotive use. Consequently it was important to obtain more detailed and precise information on the system and to find how the properties of the hydride were affected by such things as variations in the Fe-Ti ratio, the introduction of minor quantities of a third metallic element, oxygen contamination etc.

A. Equilibrium measurements

The greater part of the work consisted of determining relationships among the variables, pressure, temperature and composition ("P-T-C") for hydrogen gas in equilibrium with selected well characterized solid alloy phases. Data were obtained by the use of apparatus and procedures that have already been described (4) and only a brief synopsis will be given here. A stainless steel reactor was loaded with the granular alloy samples, sealed, evacuated, and then heated to 400-450° while outgassing continuously. Upon reaching temperature, hydrogen was admitted to the reactor until the pressure was ~7 atm. There was usually a slight drop in hydrogen pressure at this point due to some solution of hydrogen in the metal phase. After ~30 min. the reactor was evacuated and cooled to room temperature at which point H_2 was admitted to the reactor until the pressure was ~65 atm. Usually the metal-hydrogen reaction proceeded immediately with the evolution of heat. If no reaction took place over

a 15-min. period, the above procedure was repeated. It should be noted that if the alloy is in ingot form, rather than granular, the initiation of the reaction is somewhat more difficult and may require several such treatments. In order to obtain a highly active metal substrate, the sample was hydrided and dehydrided several times. Dehydriding was accomplished by outgassing and heating to $\sim 200^{\circ}$.

The procedure for obtaining the pressure-composition isotherms consisted of equilibrating the metal hydride with hydrogen at ~ 65 atm pressure and at a predetermined temperature. Hydrogen was then withdrawn in a measured amount from the system by venting to an evacuated reservoir of known volume. After equilibrium was reestablished as determined by no further pressure change over a period of ~ 3 hr, a further aliquot of hydrogen was withdrawn. This step was repeated in succession until the equilibrium pressure was below 1 atm, after which the sample was heated to $>400^{\circ}$ and any further hydrogen that evolved was measured. Finally, the sample was cooled to room temperature, removed from the reactor, and analyzed. The analysis for the metals was accurate to $\pm 0.5\%$ and total cumulative error for hydrogen was estimated to be $\pm 2.5\%$. Occasionally, the reverse procedure was followed in order to determine hysteresis effects.

By the use of such methods, P-T-C relationships for a large number of alloys in hydrogen were studied. Our experimental results are summarized graphically below, in Figures 1 through 15. These graphs are either isotherms, which show the dependence of equilibrium pressure on the hydrogen content of the solid phase, at a specified constant temperature; or isochores, in which the logarithm of the equilibrium hydrogen pressure at a given composition is plotted against the reciprocal of the absolute temperature.

Figure 1 shows the uptake of hydrogen by samples of the equiatomic composition, FeTi, when the alloy is made from high-purity iron and titanium in an arc furnace. The curves are desorption isotherms; that is, they were obtained by our usual procedure of making the highest possible hydride and then removing the hydrogen in small aliquots. When the reverse procedure is followed, and one starts with the unhydrided metal and adds increasing amounts of hydrogen, a different curve is obtained. Figure 2 illustrates this hysteresis effect for FeTi at a single temperature, 40°. Chiefly for reasons of experimental convenience we have standardized on desorption isotherms, and all the other P-T-C results in this report refer to desorption.

The largest class of alloys that were tested in hydrogen consisted of FeTi in which part of the iron was replaced by another metal of similar atomic size, such as its neighbors in the periodic table. Although complete phase diagrams are not available for all such ternary alloys, it is known that in many such cases it is possible to effect such a replacement without causing the appearance of a new phase. In at least one case, $\text{Fe}_x\text{Co}_{1-x}\text{Ti}$, there is a complete series of solid solutions; x goes from 0 to 1. Figures 3 through 11 graph the hydrogen sorption isotherms of a number of alloys of this type. It should be emphasized that no great precision is claimed for these data. A quick survey of the field was the goal of this series of experiments, and the isotherms would undoubtedly differ in detail if the alloy preparation procedure had been more painstaking, or if more time had been allowed for the pressure at each point to come to desorption or absorption "equilibrium". The salient features of the various systems are probably correct, however.

Comparison of the curves of the ternary alloys with the isotherms of pure FeTi shows that small changes can produce profound effects. While none of these

systems appears better than FeTi for practical storage purposes, the results have proven of practical as well as theoretical interest. In some applications, a decomposition pressure rather less than that of FeTi hydride is wanted; the desired lessening can, it now appears, be achieved by adding a small quantity of manganese or chromium.

Another group which it is convenient to consider together consists of a series of alloys in which the Fe-Ti ratio was varied. Figure 13 shows P-C data at 408 for three systems. In examining these it should be borne in mind that the only stable phases in the Fe-Ti system at room temperature are Ti, FeTi, Fe_2Ti and Fe (containing a little dissolved Ti). The FeTi phase is homogeneous in the composition region extending from 45.9% Ti to 48.2% Ti. The equiatomic composition is 46.17% Ti; thus an appreciable amount of Ti can be dissolved in the intermetallic phase. This fact may be responsible for the behavior illustrated in Figure 13, curve B. Here, the starting alloy was enriched in Ti to the extent that its initial composition was slightly above that corresponding to the single phase region. The isotherm has been significantly distorted, the equilibrium dissociation pressure markedly decreased and the boundary between the lower and higher hydride almost indistinguishable. Such a situation is not without precedent and a somewhat similar effect occurs in the LaNi_5 -hydrogen system when excess nickel is added to the starting alloy. Thus, in order to obtain reproducible behavior it is advisable to control the intermetallic composition as closely as possible. Upon increasing the Ti content to 63.2 wt/%, the pressure-composition isotherm (C) is greatly distorted. This alloy was annealed at 1000° for 12 hours, and then quenched in an unsuccessful attempt to prepare metastable FeTi_2 ; but only FeTi and Ti were produced. After hydriding, an x-ray diffraction

pattern of the product indicated the presence of $\text{FeTiH}_{\sim 2}$, $\text{TiH}_{\sim 2}$, FeTi and Ti . The increased amount of residual hydrogen in the solid is undoubtedly due to the presence of the stable titanium hydride.

Upon departing from the single phase region in the opposite direction, i.e. that of higher iron content, there appears to be no significant effect other than a reduction in the amount of hydrogen sorbed. The starting alloy was a two-phase mixture, Fe_2Ti and FeTi , having an overall composition of 60.5 wt/% Fe and 39.5% Ti. The isotherm (A) is essentially congruent with that obtained with FeTi , indicating little interaction between the two phases or solid solubility of Fe in FeTi ; an observation which is in accord with the known homogeneity range of FeTi . The amount of hydrogen actually sorbed is somewhat less than that expected from the proportionate amount of FeTi present in the alloy, which may be due to the mere physical presence of Fe_2Ti .

The impurity most likely to be found in commercial-grade FeTi is oxygen. Several hundred-pound batches that were made to order for us from pure iron and titanium proved to be contaminated in varying degrees with oxygen. This had a deleterious effect on their hydriding behavior, as is shown by curves A, B and C of Figure 14. These were obtained on three samples taken from the large batches, which happened to have the oxygen concentrations that are listed on the figure. The analyses from which these concentration figures were obtained were very imprecise, but the order of magnitude of the effect is clear. The presence of oxygen diminishes the maximum hydrogen uptake at high pressures, tends to eliminate the upper plateau and raises the lower plateau.

Finally, the reactions of hydrogen with a number of alloys of the basic formula Ti_2M were studied. As was mentioned above, the phase Ti_2Fe is not stable at room temperature; although the closely-related Ti_2Ni exists. It has

been reported that small amounts of Al stabilize the Ti_2Fe phase (5). In the hope that increasing the proportion of the hydride-forming element (Ti) to the non-hydride-former (Fe, Ni etc.) would result in an alloy capable of taking up more hydrogen, samples of aluminum-stabilized Ti_2Fe and a number of related materials were made up and tested in hydrogen. Table 1 shows the compositions of each, the amounts of hydrogen that were yielded by the hydrided alloy at each of several temperatures when the back pressure was 10 mm, and, in some cases, the maximum hydrogen uptake. It is seen that none of the systems fall in the class of "low-temperature hydrides", decomposable at or near room temperature.

B. X-ray data and phase diagram

The shape of the isotherms in the system $FeTi-H_2$ suggests the existence of two distinct hydride phases. It was of interest to verify this by x-ray diffraction methods, and to characterize whatever phases existed. X-ray studies posed something of a problem because of the high dissociation pressure of hydrided material. Fortunately, it was found that a brief exposure to air had the effect of producing a superficial change in the material which had the effect of greatly slowing down the decomposition without affecting the bulk of the solid. It was thereby possible to obtain diffraction pictures at room temperature on compositions as high in hydrogen as $FeTiH_{1.9}$. To obtain a suitable sample, iron titanium hydride was prepared in the usual manner. The reactor was then cooled to -196° and evacuated to remove gaseous hydrogen. Air was admitted into the reactor after which it was immediately warmed to room temperature. The reactor was disassembled and a sample for x-ray analysis was taken. The remainder, which was the bulk of the material, was analyzed for hydrogen content by heating it and collecting the evolved hydrogen. If a less than fully hydrided

sample was desired, the dihydride was prepared as outlined, but at room temperature (25°C) a measured amount of hydrogen was removed from the system to give a sample of the approximate composition desired. The hydride was permitted to re-equilibrate at 25°C and then was treated as above. Following this procedure we have been able to obtain x-ray diffraction patterns of a number of hydrided samples whose measured compositions ranged from $\text{FeTiH}_{0.106}$ to $\text{FeTiH}_{1.93}$.

The lower of the two hydrides has, from inspection of the pressure-composition isotherms, a formula near to $\text{FeTiH}_{1.0}$. Diffraction patterns were obtained on a sample with a composition corresponding to $\text{FeTiH}_{0.89}$. After subtracting the lines due to FeTi ("α phase"), the "β-phase" FeTiH was indexed as having tetragonal symmetry with $a = 3.18 \text{ \AA}$ and $c = 8.73 \text{ \AA}$; $c/a = 2.74$. Table 2 shows the observed and calculated d spacings.

In addition, the density of $\text{FeTiH}_{0.80}$ was measured under benzene as 6.003. Since this is a mixture of two phases, hydrogen-saturated FeTi and FeTiH_1 , and the density of FeTi is known (6.50), the density of FeTiH_1 was calculated to be 5.88. Knowing the density and using the lattice parameters given above, the number of molecules in a unit cell was calculated to be 2.99, or 3. That the calculated value is so very close to an integral number is substantial evidence that the indexing treatment is correct.

The higher of the two hydride phases seems to approach the composition FeTiH_2 as a limit. Diffraction data were obtained on a sample of composition $\text{FeTiH}_{1.93}$. The structure was found to have cubic symmetry. The lattice constant was 6.61 Å at the composition taken; the phase has a range of composition and the lattice constant is likely to change slightly with hydrogen content). Several of the reflections were very weak and long exposures (~24 hr) were required

to define them. It was necessary to use CoK_α radiation, since CuK_α gives an appreciable amount of fluorescent radiation with iron-containing materials which results in a background on the film against which weak reflections are difficult to detect and measure. The observed and calculated d spacings for the dihydride phase are shown in Table 3. Reflections 4 and 6 also appear in the monohydride pattern, but since there is no other evidence of the presence of the monohydride phase they have been considered to be a genuine part of the dihydride pattern. The density of $\text{FeTiH}_{1.93}$, as measured under benzene, was determined to be 5.47 g/cm^3 ; using this value and lattice constant quoted, the number of molecules per unit cell was calculated to be 9.00.

Independent evidence drawn from x-ray diffraction patterns of a number of iron titanium hydride samples, of varying hydrogen content, has supported the validity of the FeTi-H phase diagram previously derived from pressure-composition relationships. This is shown in Fig. 15.

C. Thermal conductivity

Design of a practical hydride-hydrogen reservoir requires knowledge of the thermal conductivity of the medium, since the rate of decomposition will generally be limited by the heat input. Apparatus was therefore built to measure this property in iron titanium and other hydrides. The method, using the transient line source technique⁽⁶⁾, is rapid and adaptable to determinations at various temperatures and pressures with various gases. It yields the thermal conductivity directly. The present development was done with the specific objective of measuring the thermal conductivity of beds of granular metal hydrides to be used as hydrogen storage media.

The determination is made with an axial electrical heat source placed in a tube of the powder. The rate of temperature rise of the source is measured at

a known heat input. The temperature is plotted as a function of $\ln$ time, and from the slope of the straight-line portion of that plot and the power input, the thermal conductivity of the powder can be calculated. The relationship used is

$$T_2 - T_1 = \frac{2}{4\pi k} \ln \frac{t_2}{t_1}$$

where q = heat input, watts/meter

T_1 = temperature, °C, at t_1 seconds

T_2 = temperature, °C, at t_2 seconds

k = thermal conductivity, watts/meter · °C

The slope of the curve is $\frac{T_2 - T_1}{\ln \frac{t_2}{t_1}}$

and $k = \frac{2}{4\pi \times \text{slope}} \times 0.578 \text{ Btu/hr} \cdot \text{ft}^2 \cdot ^\circ\text{F/ft}.$

It was thought desirable to avoid the use of thermocouples to measure the source temperature, as they would increase the size of the heating unit and complicate the experimental setup. Accordingly, it was decided to use for the heat source a material that has a high temperature-resistance coefficient, and to measure the temperature rise by measuring the change in resistance of the heater. A survey of available materials indicated that Alumel would satisfy the requirements, having both a satisfactory T-R coefficient and a low thermal expansion coefficient, thus minimizing dimensional changes within the unit. Also, end effects can be avoided by using a relatively long tube, and connecting the heater wire to low-resistance leads well within the bed of powder.

The experimental equipment setup is a $3/4$ in. O.D. $\times$ 0.049 in. wall stainless steel tube, 27 in. long, with filling and pressure-vacuum taps 1 in. from either end. Copper leads are brought in through insulated vacuum-tight end connections, and silver-soldered to an Alumel wire 0.009 in. in diameter about 1 in. from the tube ends. The effective length of the resistance wire is 64.5 cm. Power is supplied to the wire at a closely controlled and recorded current level, and the voltage required to produce that current is recorded with time. The resistance of the wire can thus be calculated at any instant, and its temperature determined from a temperature-resistance curve.

For this technique to be used, the change of resistance with temperature must be accurately known. The thermal coefficient of resistance of Alumel is not constant with temperature, and a sufficiently accurate curve could not be obtained from the supplier. It was necessary, therefore, to determine such a curve. This was done by placing a length of Alumel wire in a thermostat and using the same measuring equipment set up for the powder measurements, but under conditions that would not heat the wire during the measurement. The test wire was taken from the same coil as that used for the powder bed, and resistances determined at about $1/5$ the normal power input, low enough so the readings did not change with time. Measurements were made over the range from 20°C to 200°C , at 5° intervals, and the change plotted as the percent increase of the resistance at 20°C . With the resistance of the axial wire accurately known at 20°C , then, the temperature can be readily determined from the resistance measurements.

In actual practice, best results are obtained when the power input is kept low enough to avoid a temperature rise greater than about 50°C in a 2-minute test. The straight-line portion of the temperature-time plot is usually passed in about 30 seconds. Thus, 2 minutes is ample running time for a single determination of bed thermal conductivity.

The applicability of the method was tested with two granular materials, sand and alumina, with air as the interstitial gas. The sand is sharp sandblasting sand, screened to a +16-20 mesh cut and oven dried. While the k of this particular material is not accurately known, handbooks give a figure of $0.19 \text{ Btu/hr}\cdot\text{ft}^2\cdot^\circ\text{F/ft}$ for "river sand"; three determinations in this apparatus gave 0.186 , 0.211 and $0.228 \text{ Btu/hr}\cdot\text{ft}^2\cdot^\circ\text{F/ft}$.

The alumina was obtained from NRTS (National Reactor Testing Station, Idaho Falls, Idaho), and is spherical and of a fairly uniform size, about 12 mesh. It was produced by fluidized bed calcination of simulated ICPP waste, and its thermal conductivity was determined by NRTS to vary linearly from $0.08 \text{ Btu/hr}\cdot\text{ft}^2\cdot^\circ\text{F/ft}$ at 100°F to $0.27 \text{ Btu/hr}\cdot\text{ft}^2\cdot^\circ\text{F/ft}$ at 1500°F . Extrapolation back to the 25°C at which our tests were run gives $0.077 \text{ Btu/hr}\cdot\text{ft}^2\cdot^\circ\text{F/ft}$. Four tests with this equipment gave results of 0.0710 , 0.0769 , 0.0770 and $0.0830 \text{ Btu/hr}\cdot\text{ft}^2\cdot^\circ\text{F/ft}$. This method, therefore, seems to give results closely comparable to those obtained by far more complicated and time-consuming methods.

The first experiments on materials of hydrogen-storage interest were done with unhydrided FeTi alloy, broken into approximately 10-to 20-mesh granules. The exact size distribution was as follows:

Size Range U. S. Sieve	Fraction Wt %
-10+20	86.4
-20+30	12.0
-30+40	1.2
-40	0.4

A technical difficulty was caused by the alloy's high electrical conductivity; this short-circuited the Alumel heater wire. The problem was solved by giving the wire a thin, even coating of clear Glyptal varnish, which was baked for over

24 hours at 120°C. This provided adequate electrical insulation, and, by repetition of the runs with alumina, was shown to have no detectable effect on the determination of thermal conductivity. The wire temperature was not allowed to exceed about 75°C, which is well below the curing temperature of the insulating coating.

A hydrogen atmosphere was maintained over the granular alloy, and the thermal conductivity was obtained as a function of hydrogen pressure. Results are presented in Table 4 and Figure 16. Even at the highest pressure, the FeTi was not converted to the hydride form, since it had not been previously activated.

Later, experiments were done on material which had been hydrided. The results, which will be published elsewhere, gave almost the same values as for the metal.

D. Reaction rates

(a) Decomposition

Earlier work on other hydrides had shown rates of decomposition to be adequate for practical purposes, and that the rate of recovery of hydrogen from a hydride reservoir would generally be limited only by the rate at which the heat of decomposition could be supplied. A few experiments were carried out on the hydride of high-purity iron-titanium, to compare its behavior in this respect. The procedure, as before, was to allow gas to expand from a container of the hydride into a region of much lower pressure. The lowered pressure resulted in decomposition of the hydride; the system being a closed one, the pressure built back up toward the equilibrium pressure corresponding to the temperature of the solid. The course of the build-up was followed by measurements at close intervals. A source of possible error is the local cooling of the hydride resulting from the endothermic character of the decomposition process. To minimize this, the 0.5 g

hydride sample was mixed with about 20 g of 1/8-in. diameter steel balls which served to increase the thermal inertia of the system. The size of the evacuated vessel into which the hydrogen expanded was such that the pressure never built up to more than a small fraction of the equilibrium pressure, to minimize the effect of the back reaction. That the back reaction is indeed unimportant in this range is suggested, though not proven, by the fact the kinetics are first-order over a considerable time period. This is demonstrated by the long linear sections of the curves in Figure 17, which graphs the decomposition data for three temperatures. The divergences from linearity at short times may be due to a difference in behavior between the higher and lower hydrides of FeTi. The linear parts correspond to compositions below $\text{FeTiH}_{1.0}$. From their slopes the following rate constants may be calculated: 0° , 0.015 sec^{-1} ; 19.4° , 0.040 sec^{-1} ; and 29° , 0.059 sec^{-1} .

(b) Formation

The rate of formation of a hydride is a property of more practical concern than its decomposition rate, since the former is generally quite slow and limited by other considerations than heat transfer. From a fundamental kinetic standpoint, these systems are very complex. The primary variables that govern the instantaneous rate of hydrogen absorption in a given system may be taken to be temperature; hydrogen-to-metal ratio in the solid phase; and the hydrogen overpressure - i.e., the difference between the system pressures and the "equilibrium" dissociation pressure of the solid. When the absorption isotherm shows hysteresis, as it generally does, (see for example Figure 2) "equilibrium" is taken as the upper curve. A number of other factors may also affect rates of hydride formation; these include specific surface area of the solid, impurities in the gas, presence of catalysts, etc. A thorough elucidation of hydriding

kinetics will be a lengthy undertaking; the data presented here are preliminary in nature.

Hydriding rates were ascertained by following changes of system pressure with time, in a procedure that was essentially the reverse of that used for decomposition rates. The apparatus that was used to measure decomposition rates was modified by the installation of a differential pressure transducer having a range of 0 to 250 inches of water. Also, the total volume of the system was increased; this had the effect of making the pressure change during the hydriding reaction very small as compared to the total pressure. Nevertheless, the change could be accurately measured by the transducer. The advantage of this arrangement is that the difference in driving force for the reaction due to the pressure change is small and can be ignored without the introduction of serious error, yet the rate can be conveniently and accurately determined by measuring the pressure change.

The results of a number of rate experiments are shown in Figure 18, in which the moles of H_2 sorbed vs time are plotted at various temperatures and pressures. Several compositions, corresponding to the amount of hydrogen sorbed, are indicated on the ordinate. The pressures cited are those at the end of the reaction; the initial pressures were <3 psi higher. These results have not yet been examined for correlations between the rate and the temperature and pressure; however, some observations can be made. Curve F (400 psia, 15°C) exhibits an induction period; the others do not. Other rate experiments, not recorded here, have also shown an induction period at low temperatures and relatively low pressures (~400 psia). By contrast, at 900 psia even at 10°C there was no induction period. In the temperature and pressure ranges examined, the rate of formation of the lower hydride is more sensitive to temperature than to pressure and, although the data are sparse, the reverse seems to be true for the formation of the higher hydride. The rate drops rapidly as $FeTiH_2$ is approached.

III. Magnesium-Aluminum Systems

The hydrides of magnesium and aluminum are too stable and too unstable, respectively, for most practical purposes. The naive conclusion that an alloy of the two might therefore have interesting hydriding properties was tested by making up a series of alloys and reacting them in hydrogen by our usual procedures. In some of the runs a new apparatus was used that was capable of going to much higher pressures than before. A schematic of the layout is given in Figure 19. A novel feature of the system is the use of about 1 kg of Misch-metal nickel hydride to supply pure hydrogen at pressures up to 5000 psia; this pressure is generated by heating the hydride to 110°C. Hydriding experiments can be done at this pressure over the temperature range -77° to +200°.

Magnesium-aluminum alloy compositions were chosen to lie in the single-phase regions usually designated as β , ϵ and γ and having the approximate atomic compositions Mg_2Al_3 , Mg_4Al_5 and $\text{Mg}_{17}\text{Al}_{12}$; although the last has a rather wide homogeneous composition range. Alloy samples were crushed and classified as to particle size by screening, since it was found early in the experiments that the larger particles were unusually resistant to hydriding. Table 5 shows the maximum hydrogen content that could be achieved for a number of alloys. Further information, in the form of pressure-composition isotherms, was obtained on three systems; the results are graphed in Figures 20, 21 and 22. Part of an isotherm for MgH_2 is included in Figure 20 for comparison, and it is interesting to see that the alloy hydride pressures are indeed somewhat higher. These data, like those obtained on the $\text{Fe}_{1-x}\text{M}_x\text{Ti}$ systems, must be considered to be of a preliminary nature and subject to refinement by more painstaking procedures. Some accuracy was sacrificed in order to broaden the survey.

IV. Lanthanum-Nickel-Platinum Alloys

The reactions with hydrogen of a series of alloys of the general formula $\text{LaNi}_x\text{Pt}_{5-x}$, with x varying from 0 to 5, were studied. This series represents a variation of the well-known AB_5 group, where A is a rare earth and B is one of the transition elements Fe, Co, Ni or Cu. The rationale here was not so much the expectation of discovering a better material for hydrogen storage as to obtain information that would be useful in developing a theory of alloy hydrides. These alloys (without hydrogen) form a particularly interesting series with respect to their solid-state chemistry; see for instance "The $\text{LaNi}_x\text{Pt}_{5-x}$ System: Structural and Electronic Properties", by L. H. Bennett, I. D. Weisman, A. J. McAlister and R. E. Watson, given at the March 1974 meeting of the American Physical Society, with preprinted abstract. Certain properties show a maximum at the composition LaNi_2Pt_3 , and it was of interest to determine hydrogen absorption as a function of Ni:Pt ratio.

Samples of eight different compositions were made up by D. Fickle and L. Swartzendruber of the Bureau of Standards, who kindly supplied them for our experiments. We hydrided them by our usual procedures, with the results shown in Table 6 and Figure 23. It is seen that even the replacement of 5% (atomic) of the nickel by platinum has a marked effect on the hydrogen uptake, and that the five compositions highest in platinum absorbed only negligible amounts of hydrogen, even in the high-pressure apparatus.

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Table 1. Interaction of Hydrogen With Some Ti_2M Phases

Nominal Composition	Cumulative Amount of H Removed Below Temp. Cited; Wt %			Total H* Content Wt %
	150°C	300°C	450°C	
$Ti_2FeAl_{0.1}$	1.11	1.62		-
Ti_2Fe	0.61	0.64		-
Ti_2Co		1.13		-
Ti_2Ni	0.49	1.47		-
Ti_4Fe_2Al	0.50	0.85		1.58
Ti_4Mn_2O		0.87	1.77	1.96
$Ti_2MnAl_{0.2}$		0.79	2.06	3.17
$Ti_2CoAl_{0.1}$	0.89	1.37	1.99	2.19
$Ti_2NiAl_{0.1}$	0.49	0.85	1.53	1.76
$Ti_2MnAl_{0.2}$		0.74	2.11	-

* Includes H from thermal decomposition plus the residual H remaining in the alloy as determined by chemical analysis.

Table 2. d Spacings for FeTiH₁

<u>Relative Intensity</u>	<u>d obs.</u>	<u>d calc.</u>	<u>hkl</u>
40	2.2488	2.2488	110
20	2.1831	2.1831	004
100	2.1454	2.1472	103
10	1.9950	1.9990	112
50	1.5676	1.5644	201
20	1.2840	1.2840	204
20	1.2553	1.2474	007

Table 3. d Spacings for FeTiH_{1.93}

Cubic a = 6.61 Å

<u>Relative Intensity*</u>	<u>d obs. Å</u>	<u>d calc. Å</u>	<u>hkl</u>
80	2.320	2.337	220
100	2.194	2.203	{300 321}
50	2.091	2.090	310
10	1.994	1.993	311
15	1.755	1.766	321
10	1.562	1.558	{411 330}
15	1.416	1.409	332
20	1.344	1.349	422
10	1.268	1.272	{511 333}
15	1.210	1.207	521
10	1.168	1.168	440
10	1.104	1.102	{600 442}

* by visual inspection

Table 4. Thermal Conductivity of FeTi Alloy

<u>Hydrogen Pressure Absolute</u>	<u>Thermal Conductivity Btu/hr·ft²·°F/ft</u>
1 μ	0.00525
5 psi	0.502
10 psi	0.638
15 psi	0.740
75 psi	0.780
300 psi	0.929
500 psi	1.021

Table 5. Hydrogen Sorption by Mg-Al Alloys

Alloy Composition Wt. %	Probable Phase	Particle Size, U. S. Std. Mesh	Wt. % H	Formula
43.9 Al 56.1 Mg	γ	-100	2.25	$\text{Mg}_{17}\text{Al}_{12}\text{H}_{14}$
43.9 Al 56.1 Mg	γ	- 20	0.60	$\text{Mg}_{17}\text{Al}_{12}\text{H}_{4.5}$
43.9 Al 56.1 Mg	γ	-200	3.31	$\text{Mg}_{17}\text{Al}_{12}\text{H}_{25}$
52.0 Al 48.0 Mg	$\epsilon + \gamma$	- 20	0.38	$\text{MgAlH}_{0.2}$
52.0 Al 48.0 Mg	$\epsilon + \gamma$	-200	3.02	$\text{MgAlH}_{1.6}$
58.0 Al 42.0 Mg	ϵ	- 20	0.64	$\text{Mg}_4\text{Al}_5\text{H}_{1.5}$
58.0 Al 42.0 Mg	ϵ	-200	2.20	$\text{Mg}_4\text{Al}_5\text{H}_{5.2}$
58.0 Al 42.0 Mg	ϵ	-200	2.77	$\text{Mg}_4\text{Al}_5\text{H}_{6.5}$
62.4 Al 37.6 Mg	β	-200	3.28	$\text{Mg}_2\text{Al}_3\text{H}_{4.4}$
63.0 Al 37.0 Mg	β	-200	2.34	$\text{Mg}_2\text{Al}_3\text{H}_{3.1}$

Table 6. Hydrogen Sorption by $\text{LaNi}_{5-x}\text{Pt}_x$ Alloys

Alloy	Max H ₂ Pressure psia	Max H Content (formula)
LaNi_5	~1000	$\text{LaNi}_5\text{H}_{7.5}$
$\text{LaNi}_{4.75}\text{Pt}_{.25}$	~1000	$\text{LaNi}_5\text{H}_{5.5}$
LaNi_4Pt_1	~1000	$\text{LaNi}_4\text{Pt}_1\text{H}_{3.0}$
$\text{LaNi}_{2.5}\text{Pt}_{2.5}$	~2100	$\text{LaNi}_{2.5}\text{Pt}_{2.5}\text{H}_{.03}$
LaNi_2Pt_3	~1000	$\text{LaNi}_2\text{Pt}_3\text{H}_{.01}$
$\text{LaNi}_{1.5}\text{Pt}_{3.5}$	~4000	$\text{LaNi}_{1.5}\text{Pt}_{3.5}\text{H}_{.02}$
LaNi_1Pt_4	~4000	$\text{LaNi}_1\text{Pt}_4\text{H}_{.02}$
LaPt_5	~4000	$\text{LaPt}_5\text{H}_{.02}$

Figure 1

Pressure composition isotherms (desorption)
in the system $FeTi-H_2$

Figure 2

Absorption-desorption hysteresis in the system FeTi-H₂, at 40°

Figure 3
Pressure-composition isotherms (desorption)
in the systems FeTi-H₂ (upper curve) and Fe_{0.95}V_{0.05}Ti_{1.0}-H₂, at 40°

Figure 4

Pressure-composition isotherm (desorption)
in the system $\text{Fe}_{1.0}\text{Cu}_{0.1}\text{Ti}_{1.0}\text{H}_2$, at 40°

Figure 5
Pressure-composition isotherm (desorption)
in the system $\text{Fe}_{0.9}\text{Mo}_{0.1}\text{Ti-H}_2$, at 40°

Figure 6
Pressure-composition isotherms (desorption)
in two (Fe, Cr, Ti)-H₂ systems

Figure 7

Pressure-composition isotherms (desorption)
in three (Fe, Mn, Ti)-H₂ systems

Figure 8

Pressure-composition isotherms (desorption)
in two (Fe, Mn, Ti)- H_2 systems

Figure 9
 Pressure-composition isotherm (desorption)
 in system $\text{Fe}_{0.8}\text{Mn}_{0.2}\text{Ti-H}_2$, at 61°

Figure 10
Pressure-composition isotherms (desorption)
in the system Fe_{0.9}Mn_{0.1}Ti_{1.0}-H₂

Figure 11
Pressure-composition isotherms (desorption)
for the system CoTi-H₂

Figure 12

Figure 13

Pressure-composition isotherms (desorption) for H₂ in three Fe-Ti alloys at 40°. A, 60.5 Fe, 39.5 Ti; B, 50.5 Fe, 49.2 Ti; C, 36.7 Fe, 63.2 Ti (all by weight)

Figure 14

Effect of oxide in FeTi on hydrogen desorption isotherms at 40°.

A, 7000 ppm O; B, 3700 ppm O; C, 1000 ppm O; D, FeTi from zone refined Fe and Ti.

Figure 15

Phase diagram of the FeTi-H system as derived from pressure-composition data. X-Ray diffraction patterns taken at positions indicated; ●, one solid phase; ○, two phases.

Figure 16

Thermal conductivity of granular FeTi as a function of hydrogen pressure.

Figure 17

Figure 18

Rate of formation of iron titanium hydride.

HIGH PRESSURE EXPERIMENTAL APPARATUS

Figure 19

Figure 21

Figure 22

Figure 23