

**Best
Available
Copy**

AD/A-006 423

SOLID STATE HYDROGEN STORAGE MATERIALS
FOR APPLICATION TO ENERGY NEEDS

Charles E. Lundin, et al

Denver Research Institute

Prepared for:

Air Force Office of Scientific Research
Advanced Research Projects Agency

January 1975

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFOSR - TR - 75 - 0319	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER AD/A006423
4. TITLE (and Subtitle) SOLID STATE HYDROGEN STORAGE MATERIALS FOR APPLICATION TO ENERGY NEEDS		5. TYPE OF REPORT & PERIOD COVERED INTERIM 1 Oct 73-31 Dec 1974
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) CHARLES E LUNDIN FRANKLIN E LYNCH		8. CONTRACT OR GRANT NUMBER(s) F44620-74-C-0020
9. PERFORMING ORGANIZATION NAME AND ADDRESS DENVER RESEARCH INSTITUTE UNIVERSITY OF DENVER, 2450 S GAYLORD METALLURGY AND MATERIALS SCIENCE DIVISION DENVER, CO 80210		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS ARPA 2552 --1 4D10 61101E
11. CONTROLLING OFFICE NAME AND ADDRESS ADVANCED RESEARCH PROJECTS AGENCY DEPARTMENT OF DEFENSE 1400 WILSON BOULEVARD ARLINGTON, VIRGINIA 22209		12. REPORT DATE Jan 1975
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) AIR FORCE OFFICE OF SCIENTIFIC RESEARCH/NA 1400 WILSON BOULEVARD ARLINGTON, VIRGINIA 22209		13. NUMBER OF PAGES 43 64
		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) Reproduced by NATIONAL TECHNICAL INFORMATION SERVICE US Department of Commerce Springfield, VA. 22151		
18. SUPPLEMENTARY NOTES		
PRICES SUBJECT TO CHANGE		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) HYDROGEN STORAGE METAL HYDRIDES		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) During the first year of the program, five separate areas of study of solid state hydrogen storage materials were initiated, of which three were completed. These were (1) literature survey and field trips relating to studies of unstable metal hydrides; (2) safety characteristics of LaNi₅; (3) general hydriding characteristics of LaNi₅; (4) study of high pressure kinetics of desorption of LaNi₅; and (5) studies of characteristics of LaNi₅ as a catalyst. The properties of LaNi₅ were fully evaluated in terms of the properties of powders. The powder properties determined were: ignition temperature, relative combustibility,		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

flammability, shock sensitivity, impact sensitivity, spark sensitivity, and explosibility. Studies of dispersed dust clouds were conducted in which ignition minimum ignition energy, minimum explosive concentration, maximum explosive pressure, and maximum rate of pressure rise were determined. From these data, an index of explosibility was obtained, which indicated a "weak" rating. The general hydriding characteristics included data on activation, effects of repetitive cycling, hysteresis effects, surface poisoning effects, and more precise pressure-temperature-composition relationships of the system than have been available in the literature. The kinetics studies of hydrogen desorption from LaNi_5 were initiated during the latter part of the report period and are continuing into the next period. Enhancement studies of hydrogen absorption in new systems were also carried out. The binary systems, V-Cr and Nb-Mo at 30, 40 and 50 weight percent of Cr and Mo additions in their respective systems were initiated. Screening of the pressure-temperature-composition relationships are underway.

ia

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

UNIVERSITY OF DENVER
(COLORADO SEMINARY)

FIRST ANNUAL TECHNICAL REPORT

SOLID-STATE HYDROGEN STORAGE
MATERIALS FOR APPLICATION TO ENERGY NEEDS

January 1975

-Submitted by-

University of Denver
Denver Research Institute
Denver, Colorado 80210

AFOSR Contract No. F44620-74-C-0020
AFPA Order 2552
Program Code 4D10

Effective Date 1 October, 1973
Contract Expiration 31 December 1974
Contract Amount - \$98,805

Sponsored By
Advanced Research Projects Agency
ARPA Order No. 2552

Prepared by:

Charles E. Lundin
Charles E. Lundin
Principal Investigator
(303) 753-2621

Franklin E. Lynch
Franklin E. Lynch
Research Engineer

TABLE OF CONTENTS

	<u>Page</u>
<u>I. TECHNICAL REPORT SUMMARY</u>	1
<u>II. INTRODUCTION</u>	4
<u>III. LITERATURE SURVEY</u>	6
<u>IV. CONFERENCE AND FIELD TRIPS</u>	7
<u>V. CHARACTERIZATION OF LaNi_5</u>	9
<u>A. As Received Material</u>	9
<u>B. Hydrided Powders</u>	10
<u>VI. SAFETY CHARACTERISTICS OF LaNi_5 HYDRIDE</u>	12
<u>A. Introduction</u>	12
<u>B. Bulk Powder Safety Studies</u>	12
1. Ignition and Combustibility Properties	13
2. Flammability Studies	14
3. Shock Studies	15
4. Impact and Friction Studies	16
5. Electrostatic Spark Susceptibility	16
6. Dust Explosion Test	17
<u>C. Dust Cloud Safety Studies</u>	17
1. Preparation of Samples	18
2. Determination of Ignition Sensitivity	19
3. Determination of Explosion Severity	19
4. Determination of Index of Explosibility	20

<u>VII. HYDRIDING STUDIES WITH LaNi_5</u>	22
<u>A. Equipment Description</u>	22
1. Design	22
2. Calibration	24
<u>B. Data Reduction</u>	24
<u>C. Determination of Pressure-Temperature-Composition Relationships</u>	24
<u>D. Determination of Van't Hoff Relationships</u>	25
<u>E. Analysis of Hysteresis Effects</u>	26
<u>F. Surface Poisoning Effects</u>	26
<u>G. Kinetics of Desorption</u>	27
1. Literature Survey	27
2. Equipment	31
3. Approach	32
<u>VIII. ENHANCEMENT STUDIES OF NEW SYSTEMS</u>	33
<u>A. Introduction</u>	33
<u>B. Approach</u>	33
<u>C. Experimental</u>	35
1. Studies of V-Cr System	35
<u>D. Design and Construction of Ultra-High-Pressure Hydriding Apparatus</u>	35
<u>IX. POTENTIAL APPLICATIONS FOR DOD</u>	37
<u>X. REFERENCES</u>	39

I. TECHNICAL REPORT SUMMARY

During this first annual report period, five separate areas of study were involved to get the program underway. These were: 1) a literature survey and field trips, 2) safety characteristics of LaNi_5 , 3) general hydriding characteristics study of LaNi_5 , 4) study of high pressure kinetics of desorption of LaNi_5 , and 5) studies of characteristics of new alloy systems.

The literature survey was conducted on properties of unstable hydrides such as LaNi_5 through the period from 1970 to 1974 by a computerized search of the Chemical Abstracts. Prior to 1970 a thorough analysis was already available. Also, as a part of this phase of survey, field trips were taken to those centers of hydride activity that are pertinent to this contract. Visits were made to Brookhaven National Laboratories, Los Alamos Scientific Laboratories, and the Institute for Gas Technology.

Two separate apparatuses were designed and constructed specifically for the needs of this program. A third was designed and is currently being assembled. The first system was intended to carry on general activation and hydriding studies, primarily pressure-temperature-composition (PTC) relationships and screening of new alloy systems. It will handle three experiments simultaneously and independently, while a fourth station can be used to activate samples. The second system was designed to conduct the kinetics of absorption or desorption on selected hydrides. The third system is an ultra-high pressure system designed to activate and hydride samples up to 30,000 psi and 500°C.

A study of some of the general characteristics of hydriding of LaNi_5 was first conducted. The characteristics sought were: 1) minimum activation pressure for hydriding, 2) effect of repetitive cycling by adsorption and desorption on kinetics and also on the comminution of hydride particles and their morphology, and 3) cursory effects of air exposure on hydriding kinetics between multi-cycles of adsorption and desorption (all experiments at room temperature). It was found the activation could be accomplished in a reasonable period of time at 150 psi and room temperature. After 20 cycles of absorption and desorption, the LaNi_5 particle size had stabilized early in the cycle experiment and remained at about 11 micron average particle size. These particles were observed by scanning electron microscopy. The fracture surface was typically brittle fracture morphology. The bulk of the particle was microfractured throughout, giving the particle a very sponge-like character. Cursory air exposure studies of these cycled fine particles did not appreciably affect the ability to absorb on subsequent cycles nor their kinetics of absorption. They would regain their full kinetics in another cycle. It was not necessary ever to reactivate at higher pressures as when one first initiates hydriding.

The safety characteristics of LaNi_5 were fully evaluated in a major study of this aspect. It was felt this study should be a high priority task before some of the subsequent major studies were initiated.

The 11 micron size material either in fully hydrided form or as dehydrided LaNi_5 was found to be a very safe material to handle in all respects. Certainly the storage of hydrogen in large quantities of LaNi_5 will be significantly more safe than in gas or liquid hydrogen form. The following bulk powder properties were analyzed: 1) ignition and combustion properties in air and oxygen, 2) flammability in air and oxygen, 3) flammability in an open system, in systems with partially restricted openings, and in systems with restricted openings, 4) shock properties as determined by the explosive card-gap test, 5) impact properties determined by the drop-test, 6) impact and friction properties as determined by the bullet test, 7) electrostatic spark susceptibility, and 8) the test of exploding bulk powder into a dust cloud. Another very complete and thorough analysis of the suspended dust cloud safety aspects was conducted through the cooperation of the Bureau of Mines. The following tests were conducted of dust clouds of both LaNi_5 and LaNi_5 hydride powders; 1) ignition temperature, 2) minimum ignition energy, 3) minimum explosive concentration, 4) maximum explosive pressure, and 5) maximum rate of pressure rise. From these data the explosion severity and ignition sensitivity were calculated. These, in turn, allow one to calculate the Index of Explosibility which is a comparative measure of this property. The LaNi_5 hydride dusts were both determined to have an Index of Explosibility of 0.1, or a "weak" rating.

On completion of the safety characteristics study, a technical paper was prepared, followed by the presentation of same at the first major international meeting devoted entirely to the Hydrogen Economy. The meeting was "The Hydrogen Economy Miami Energy Conference" held on March 18-20 in Miami Beach, Florida.

A careful and accurate determination of the pressure-temperature-composition (PTC) relationships of the LaNi_5 hydride system was conducted. The solubility boundaries of the solid solution of hydrogen in LaNi_5 and of the LaNi_5 hydride phase were established as a function of temperature. Hysteresis effects were examined. Van't Hoff plots for the plateau partial pressures as a function of temperature were established for both absorption and desorption by two independent techniques. From these, the enthalpy of the reaction across the constant pressure plateaus was determined for absorption and for desorption. Additional experiments were conducted to analyze the nature and possible cause of the hysteresis phenomenon.

Some preliminary evaluations were carried out on the poisoning effects at the surface of LaNi_5 hydride by various contaminants. In general, it was found that LaNi_5 hydride is surprisingly resistant to serious contamination which might grossly affect absorption and desorption or drastically shift the equilibria. Removal of the contamination and reactivation of the hydride would generally restore the absorption and desorption properties and the equilibrium relationships.

A literature survey was initially conducted for the kinetics of absorption and desorption study. Various techniques were analyzed and considered for this study. While the first apparatus was intended for use with either general pressure-temperature-composition (PTC) relationship studies or

kinetics studies, it was later decided to build a separate system for kinetics measurements. This would allow incorporation of more flexibility and better adaptability to the specific needs. Measurements of desorption are currently being made with new equipment.

A selection of new systems of interest for enhancement studies has been outlined. The enhancement studies have been initiated. The binary alloy systems, V-Cr and Nb-Mo, have been arc melted and experiments have been initiated with V-Cr alloy system. A 60% V-40% Cr alloy has been investigated and found to absorb at room temperature with only a pressure activation. The Cr seems to impart properties to the surface which allow ready absorption of hydrogen. Total absorptivity at 25°C was determined.

Some early consideration has already been given to applications for DOD use. Discussions have been conducted with personnel at the U.S. Army Tank and Automotive Command near Detroit, U.S. Army Fuels and Lubricants Research Laboratory in San Antonio, and the U.S. Army Mobility Equipment Research and Development Center at Ft. Belvoir. These discussions center around the use of hydrides for a fuel for either auxiliary systems or for primary motive power in armored vehicles. A new concept for combined composite armor and fuel systems has been proposed. Discussions are continuing to develop interest in feasibility studies.

II. INTRODUCTION

This Annual Technical Report is the first of such reports due under Contract No. F44620-74-C-0020, Air Force Office of Scientific Research, and sponsored by the Advanced Research Projects Agency, Department of Defense under ARPA Order No. 2552. The report period is 1 October 1973 to 31 December 1974.

The eventual application of hydrogen as an all-purpose fuel to phase in as fossil fuel supplies deplete is a distinct technological possibility. The embodiment of such a concept is exhibited by the growing advocacy of the "Hydrogen Economy" by many segments of the energy related industry. The most significant benefit is the clean, non-polluting mode of combustion, namely water. The environmental impact of its use compared to burning fossil fuels amounts to a near total solution to the World's current pollution problems. The combustion of hydrogen and air releases about three times as much energy per unit of weight compared to that of gasoline. Current limitations in the use of hydrogen are its cost, availability, an economical energy source to dissociate water, and the storage and handling. The first three factors will diminish as fossil fuels use decreases and nuclear-energy produced hydrogen increases to the point where hydrogen will be a viable fuel. The storage and handling problems are limitations which are serious, but certainly subject to modification. The hazards of shipping and handling of pressurized hydrogen in steel tanks are obvious and severe. The alternate storage of liquid hydrogen in cryogenic containers is also prohibitive because of the large investment in refrigerative cooling and cryogenic dewars. The solution to the storage and handling problems is one of the significant incentives in the research program addressed in this report. The approach is to use metallic hydrides as the means to contain the hydrogen gas. Materials such as LaNi_5 have provided a breakthrough in this respect. The development of this and more enhanced solid hydride materials would greatly accelerate the use of the hydrogen in energy applications.

The phenomenon of hydrogen absorptivity in LaNi_5 -type compounds was discovered by scientists at Philips in Eindhoven, Netherlands. In studies of the effect of hydrogen on the permanent magnetic properties of these compounds, it was found by H. Zijlstra and F. F. Westerdorp (1) that SmCo_5 would absorb 2.5 moles of hydrogen at a pressure of 20 atm at room temperature. By removing the pressure, the absorbed hydrogen was released. Further studies by van Vucht, et al. (2), extended this original work. They studied LaNi_5 , SmCo_5 , CeNi_5 , and alloys of $(\text{La}_{1-x}\text{Ce}_x)\text{Ni}_5$ and verified the phenomenon. Both LaNi_5 and $(\text{La-Ce})\text{Ni}_5$ alloys were found to absorb up to 6.7 and 7 hydrogen atoms per formula weight, respectively. The most important property of these compounds was their ability to absorb and desorb the large amount of hydrogen at room temperature and relatively low pressures (2.5 atm for LaNi_5). In each case the reaction was always initiated by a threshold pressure usually considerably higher than the equilibrium pressure of the isotherm. A gross lattice expansion and structural change accompanies the absorption. In LaNi_5 there is a 25% increase in the volume. This is accompanied by severe stresses which fracture the initially solid compound.

This factor can provide an extremely important side benefit. The new fresh surface and the increased surface area greatly speed up the kinetics of absorption and desorption. A loading-deload cycle of 10 times resulted in a fine powder with a subsequently constant active surface. Desorption rates were observed over a range of temperatures. At 25°C, about 100% of the hydrogen was removed in 5 min. The fully loaded LaNi_5 at room temperature and 2.5 atmospheres of pressure has a concentration of hydrogen atoms of 7.6×10^{22} atoms/cm³. This is nearly twice the density of liquid hydrogen. Furthermore, the desorption process allows only ultra-pure hydrogen to be released which is significant if only to provide an ultra-high purification process.

Further recent studies on LaNi_5 type hydrides (3-7) have still only cursorily delineated their properties and also their limitations as far as application. From additional studies on other hydrides of this same type, such as; Mg_2Cu , Mg_2Ni , and FeTi (8-15), one can see emerging a whole new class of metallic hydrides. Hydrides have generally been known and thoroughly studied for many decades, but of a different class; that is, they have been what one might term, stable hydrides. They are metal-hydrogen systems that have high heats of formation, that do not decompose unless heated to high temperature, and that have extremely low dissociation pressures at room temperature. Many of the elements of the periodic table form these hydrides; the alkali metals, the alkaline-earth metals, the lanthanide series of metals, the actinide series of metals, and Group III, IV, and V transition metals. On the other hand, the new class of "unstable" hydrides have low heats of formation, have very high equilibrium pressures (several atmospheres) near ambient temperatures, and rapidly absorb and desorb large quantities of hydrogen with only minor enthalpy transfer.

The specific objectives in this research program are to carry on a multiphase effort to investigate the potential and test the feasibility of employing unstable metallic hydrides to store hydrogen which could later be desorbed as a fuel for power or energy use. The materials under study will primarily consist of binary and ternary systems of both intermediate phases and complex alloys thereof. The concept of using such materials as an energy source will be explored in terms of several fundamental property characteristics. The characteristics of principal interest are:

1. Potential Safety Hazards
2. Pressure-temperature-composition (PTC) relationships
3. Kinetics of adsorption and desorption
4. Surface poisoning effects

A systematic investigation of the hydriding characteristics of various alloy combinations will be made to develop better criteria for the prediction of the existence and extent of hydrogen occlusion in hydrides that are classified as unstable types. It is intended that a better understanding of this class of hydrides will result. Also, the development of enhanced properties for more efficient application will be sought in alloy hydrides that are to evolve during the study.

III. LITERATURE SURVEY

A collection of the hydride literature up through 1970 already exists in our facility because of the previous extensive interest and research investigations carried on since 1955. This collection has been and will continue to be an extremely useful source of information. Much of this was used as reference material for the book "The Metal Hydrides" authored by Mueller, Blackledge, and Libowitz.

Representing the period from 1970 to date, a computer-aided literature survey was conducted early in this report period in the subject area of "metal hydrides and kinetics of desorption". A new service is now available employing probably one of the most thorough abstract services, the Chemical Abstracts. The Chemical Abstracts have been completely placed in computer retrievable storage and made available selectively by means of key-word searching with the computer. In this way the Chemical Abstracts were searched through the computer readable files. The service was rendered through the System Development Corporation in California by an on-line searching system via telephone couple and teletype machine.

Another literature survey was conducted through the NASA Technology Application Center at the University of New Mexico at Albuquerque. Three areas were sought; 1) hydrogen generation and absorption by hydrides, 2) hydride utilization, and 3) general information on hydrides and hydrogen. The TAC group is one of the most comprehensive information centers in the United States. It draws from 50 data banks of government, industrial, and foreign sources. Most of the data banks are on computer terminals at TAC.

The current and future literature search in this area will be continued by means of reference to the Current Contents.

IV. CONFERENCE AND FIELD TRIPS

During this report period a conference was attended at which a technical paper was presented. The technical paper was entitled, "The Safety Characteristics of LaNi_5 " and represents one of the first major studies completed under the terms of this contract. The conference was "The Hydrogen Economy Miami Energy Conference" in Miami Beach, Florida, on March 18-20, 1974, sponsored by the Advanced Research Projects Agency, the National Science Foundation, and the University of Miami. The paper submitted will be published in a proceedings to be available in the near future.

Three field trips were scheduled and completed to facilities early in this report period that have either been conducting studies on hydrides for storage or have great interest in such materials. The individuals and facilities visited were:

- a. Dr. J. D. Farr at Los Alamos Scientific Laboratories in New Mexico.
- b. Dr. Derek Gregory at the Institute for Gas Technology in Chicago, Illinois.
- c. Dr. R. H. Wiswall at Brookhaven National Laboratories on Long Island, New York.

All three visits were very useful in appraising the current status of studies in this field. Dr. Farr has conducted studies on rare earth- Ni_5 and Co_5 compounds and had just completed an internal report, which was obtained. This work was conducted to develop a system of gettering of hydrogen in weapons application. The study was purported by Farr to be cursory and had to be terminated short of their goals and interests due to the pressure of other studies. He does not plan any studies in this area in the immediate future. Their conclusion indicated that "there does seem to be a real possibility of using AB_5 compounds for the storage and transport of hydrogen". Dr. Farr does have other studies to prepare hydrogen by thermochemical means for energy needs.

Dr. Gregory has great interest in solid hydrides to store hydrogen. He is the chief proponent of the "hydrogen economy"; however, he had nothing underway in-house in this area. He is anxious for the development of inexpensive solid storage materials. Those already available, such as LaNi_5 , are too expensive and heavy for his purposes, and the Mg-Ni or Mg-Cu types require high temperatures, are pyrophoric, and require too much energy to desorb. He referenced several other sources where studies are either underway or are contemplated. These are:

- a. Brookhaven National Laboratories - AEC Support
Dr. R. Wiswall - Metal Hydrides.
- b. Allied Chemical Co. - Internal Support;
Dr. G. Libowitz - Metal Hydrides.

- c. University of Miami - RANN Support;
Dr. T. Veziroglu - Hydrogen Economy.
- d. Stanford Research Institute - RANN Support;
Dr. E. Dixon - Hydrogen Economy.

Dr. Gregory has many programs underway to study various aspects of the hydrogen economy and it will be useful to remain in contact with him.

Dr. Wiswall has conducted practically all of the recent studies in the area of metal hydrides for energy storage. He has continuing programs going on currently as follows:

- a. A grant from EPA in Ann Arbor to assess hydrogen storage for automotive purposes. This is principally engineering oriented.
- b. An AEC program to determine the isotope effects of absorbing and desorbing H_2 , D_2 , or T_2 in solid occluders.
- c. A program with the Electric and Power Co. of New Jersey to test the feasibility of storing off-peak power by means of electrolyzed hydrogen in FeTi.
- c. A continuing program with Ft. Belvoir (and possibly ARPA) to prepare solid hydrides to operate remote fuel cells. They will be screening new alloys.

Dr. Wiswall indicated that Stanford Research Institute may also be undertaking an ARPA supported program on hydride materials by Dr. Sirette.

The laboratory facility was toured and their equipment inspected. The visit was useful because we were in the midst of the design of our equipment.

V. CHARACTERIZATION OF LaNi_5

A. As Received Material

The LaNi_5 alloy was ordered in the form of crushed granules of about 10 mesh average size from the Molybdenum Corporation of America from induction melted stock. Both metallographic and X-ray analyses were performed on the original ingot. Metallographic analysis demonstrated that the ingot was homogeneous. The microstructure consisted of very large grains containing a faint sub-grain structure. X-ray analysis was conducted and the system was found to consist of LaNi_5 plus a trace amount of second phase. Experimentally determined values for the lattice parameters and the density agreed with the published values. The data obtained were:

$$a = 5.012 \text{ \AA} \pm 0.01 \text{ \AA}$$

$$c = 3.978 \text{ \AA} \pm 0.009 \text{ \AA}$$

$$\rho = 8.290 \text{ gm/cc}$$

The most recent data by K. H. J. Buschow and H. H. Van Mal (5) compare favorably, in that, $a = 5.019 \text{ \AA}$, $c = 3.986 \text{ \AA}$, and $\rho = 8.256 \text{ gm/cc}$ for a composition of 67.61 weight percent nickel.*

A chemical analysis was conducted on the nickel content and the impurity content. The following data were obtained:

<u>Nickel Analysis, Wt%</u>	<u>Impurity Analysis, Wt%</u>
(1) 67.50	Al 0.01
(2) 67.59	Cr 0.005
(3) <u>67.75</u>	Co 0.01
Ave 67.61	Cu 0.002
	Fe 0.02
	Mg 0.001
	Mn 0.001
	Hg --
	Nb --
	Si 0.005

All other elements are below limits of detection.

* See Section VII, C, for further discussion of lattice parameters as a function of nickel content.

The theoretical composition for LaNi_5 is 67.88 weight percent.

B. Hydrided Powders

The first consideration prior to commencing the safety studies and the general hydriding studies was to characterize and understand the physical nature of the powders one would be dealing with. It was established in the pioneering studies of van Vucht, et al. (2) that LaNi_5 absorbs large quantities of hydrogen up to 6.7 atoms per formula weight of the compound. In the process the unit cell expands 25 vol. percent. In turn, the volume expansion creates such large strains in the bulk that the fracture stress is exceeded. This results in the material breaking up into fine particle size comminution as a function of the number of cycles of hydriding. This was accomplished in three ways: 1) by classification with screens, 2) by measurement of the average particle size with optical microscopy, and 3) by observing the particle topography, shape, and fracture surfaces with scanning electron microscopy. The LaNi_5 granules were first broken down to grains in the size range of 20 mesh for hydriding. Three portions of hydrided LaNi_5 were then prepared: one cycle, 10 cycles, and 20 cycles. The apparatus used to conduct the hydriding of these samples will be described in detail in Section VII. The screen classification of the three hydrided samples is presented below. The three screens that were employed were: 200 mesh, 325 mesh, and 400 mesh. The 400 mesh screen has an opening size of 37 micron.

One Cycle

<u>Screen Classification</u>	<u>Weight Percent</u>
+ 200 mesh	0.5
+ 325	26.5
+ 400	10.5
- 400	62.5

Ten Cycle

+ 200	0.1
+ 325	0.1
+ 400	0.2
- 400	99.5

Twenty Cycle

+ 200	0.1
+ 325	0.1
+ 400	0.1
- 400	99.7

As one observes, most of the size reduction occurs in the first cycle where 99.5% of the material is already less than 7 μ microns. After that the size of the particles appears to stabilize in spite of the additional number of cycles. The average particle size as determined by the ASTM optical method also demonstrated that there isn't much change in size after the first cycle. The average size was found to be 15 microns after the first cycle, 12 microns after 10 cycles, and 11 microns after 20 cycles. It was very interesting to observe the particles by scanning electron microscopy. Figure 1a shows particles of the unhydrided LaNi₅ at 133x. Figure 1b shows LaNi₅ particles at 666x. In Figure 1c one sees particles of hydrided and dehydrided LaNi₅ after one cycle at 133x. Figure 1d shows the same particles after one cycle at 666x. Figure 2a is a view of LaNi₅ particles after ten cycles of hydriding and dehydriding at 133x. Figure 2b is similar to 2a except at 666x. Figure 2c is the particle configuration after twenty cycles at 133x. Finally, Figure 2d shows the same particles in 2c except at 666x. Note the extensive microfracturing within individual particles after the first hydriding cycle. This almost gives the material a sponge-like capability because of the extensive surface area of the exterior surfaces of the particles plus the unexpected interior surface areas.



a. Particles of Unhydrided LaNi_5 at 133x.



b. Particles of Unhydrided LaNi_5 at 666x.



c. Particles of Hydrided and Dehydrided LaNi_5 after one Cycle at 133x.



d. Particles of Hydrided and Dehydrided LaNi_5 after one Cycle at 666x.

Figure 1. Structure of LaNi_5 Powders, Unhydrided and Hydrided.



a. Particles of Hydrided and Dehydrided LaNi_5 after Ten Cycles at 133x.



b. Particles of Hydrided and Dehydrided LaNi_5 after Ten Cycles at 666x.



c. Particles of Hydrided and Dehydrided LaNi_5 after Twenty Cycles at 133x.



d. Particles of Hydrided and Dehydrided LaNi_5 after Twenty Cycles at 666x.

Figure 2. Structure of LaNi_5 Powders, Dehydrided and Hydrided.

VI. SAFETY CHARACTERISTICS OF LaNi_5 HYDRIDE

A. Introduction

Experimental studies were conducted to determine the limits of safety in handling, shipping, and usage of LaNi hydride. Emphasis was given to the accident-oriented safety problems such as punctured containers, impact, explosion, shock, and external fire. Although it is presumed this type of hydrogen storage system is relatively safe to handle compared to high-pressure tank hydrogen or liquified hydrogen, the safety characteristics have never been thoroughly assessed. It was the objective of this study to completely analyze the safety characteristics of LaNi_5 hydrides.

Various aspects of hazards were evaluated for bulk powders; the ignition temperature, the relative combustibility, flammability, shock sensitivity and potential explosibility. Since the LaNi_5 hydrides break down to powders after repeated absorption and desorption of hydrogen, the ultimate interest in the safety considerations is with fine powders. A characterization study of the particles and particle size was reported in the previous section that is also pertinent to the interests of this investigation. Another independent study was also made of the safety of dust clouds of LaNi_5 hydrides. The ignition sensitivity and explosion severity were determined, and an index of explosibility of dust clouds was established.

B. Bulk Powder Safety Studies

The definition of bulk powders are those that exist in loose compaction in the bulk due to their own weight as opposed to a dust cloud of powder which is greatly dispersed. All of the powder studies were conducted with $\text{LaNi}_5\text{H}_{6.7}$ that had been hydrided at least through four cycles, so the average particle size was down in the range of 12 microns. Therefore, one has several factors which affect the safety properties of these powders. First, the properties of the solid powder itself can present problems from the reactivity of the surface with air. Secondly, the hydrogen in the gas phase, either equilibrated or emanating from the surface, is a problem in itself which has been well characterized (16) if one just considers it as hydrogen gas. Thirdly, one may have a reaction at the surface of the particles in the combination of oxygen with hydrogen (and/or the surface) in a catalytic manner. Nickel-rich surfaces are well known for this characteristic. In safety matters one must take each of these factors into consideration when one determines the type and geometry of container system and the contained hydride. Although one cannot simulate in laboratory tests all the conditions that might be met in the storage, shipment, handling, or use of these hydrides, it was felt that the following studies represented the salient safety factors.

The method of preparation of the fully hydrided powders just prior to their various tests was designed to maintain full saturation until the test was readied. The samples were fully hydrided until saturation was assured. Then the container, either stainless steel or copper, was immersed in liquid nitrogen to keep the powder cold and the hydrogen equilibrium pressure very low. This would insure maintenance of composition as the hydriding chamber

was opened to air to unload the chamber and load the safety system. When the powders were in place for the respective tests, they were allowed to rise to ambient temperature at which time the test was conducted.

1. Ignition and Combustibility Properties

For reactive metals, a strongly exothermic reaction occurs with the oxygen in air. Ignition of metal powders is the temperature at which the rate of heat generated with the air-surface reaction exceeds the heat loss to the surroundings. The reaction is then carried on autocatalytically, and the powder continues to combust as long as the supply of air is sufficient and the reaction products on the particles are not impenetrable to oxygen. Since the intermetallic compound, LaNi_5 , is nickel-rich, one would not expect the unhydrided material to be too reactive. Nickel has a low free energy of formation of its oxide, whereas lanthanum has a high free energy of formation.

The ignition and combustion apparatus is seen in Figure 3. The ignition and combustion measurements were carried out in a Y_2O_3 -coated graphite crucible. A chromel-alumel thermocouple was placed in a well in the center of the crucible. The crucible was surrounded by an Inconel tube which could be provided either with an air or pure oxygen atmosphere. The tube was then placed into a furnace at 600°C , and the temperature of the crucible was monitored on a strip chart recorder. The ignition temperature was seen as an abrupt rise. The relative combustion energy of the sample was determined from the area under the curve compared with a blank run. Figure 4 is a portion of the strip chart recording for a sample of pure Ce carried on in a pure oxygen atmosphere. Cerium was included to demonstrate a very reactive material. In all of these experiments, the powder size was $-100/+200$ mesh. Note the very abrupt temperature rise for Ce which is the ignition temperature. The following temperature excursion is that during subsequent combustion. A blank run gives only a smooth S-curve. Thus, the area between these two curves gives the relative combustion energy. Figure 5 is the recording of a sample of pure La in pure oxygen. Its ignition and combustion properties are reduced from those of Ce because of the more protective oxide on its reacting surface. A sample of pure Ni was run in the same manner in pure oxygen. However, no ignition or combustion occurred. It would track the blank run. Figure 6 shows the ignition and combustion characteristics of LaNi_5 hydride. Note that it has a very gentle ignition point and combustion energy. Table I presents the results of these tests. In pure oxygen, LaNi_5 is ignited at a lower temperature and with more energy of combustion compared to LaNi_5 in air. In air, the energies of both LaNi_5 and LaNi_5 hydride are reduced compared to those in oxygen. In general, the hydrides either in air or in oxygen are ignitable at lower temperatures and have greater combustibility. However, compared to a reactive metal like cerium, they are considerably less ignitable and combustible. In no case did the hydrogen desorbing from the hydride react explosively with either air or oxygen in the enclosure. The kinetics of the burning, once ignited, were very slow compared to a reactive metal such as La or Ce.

13a

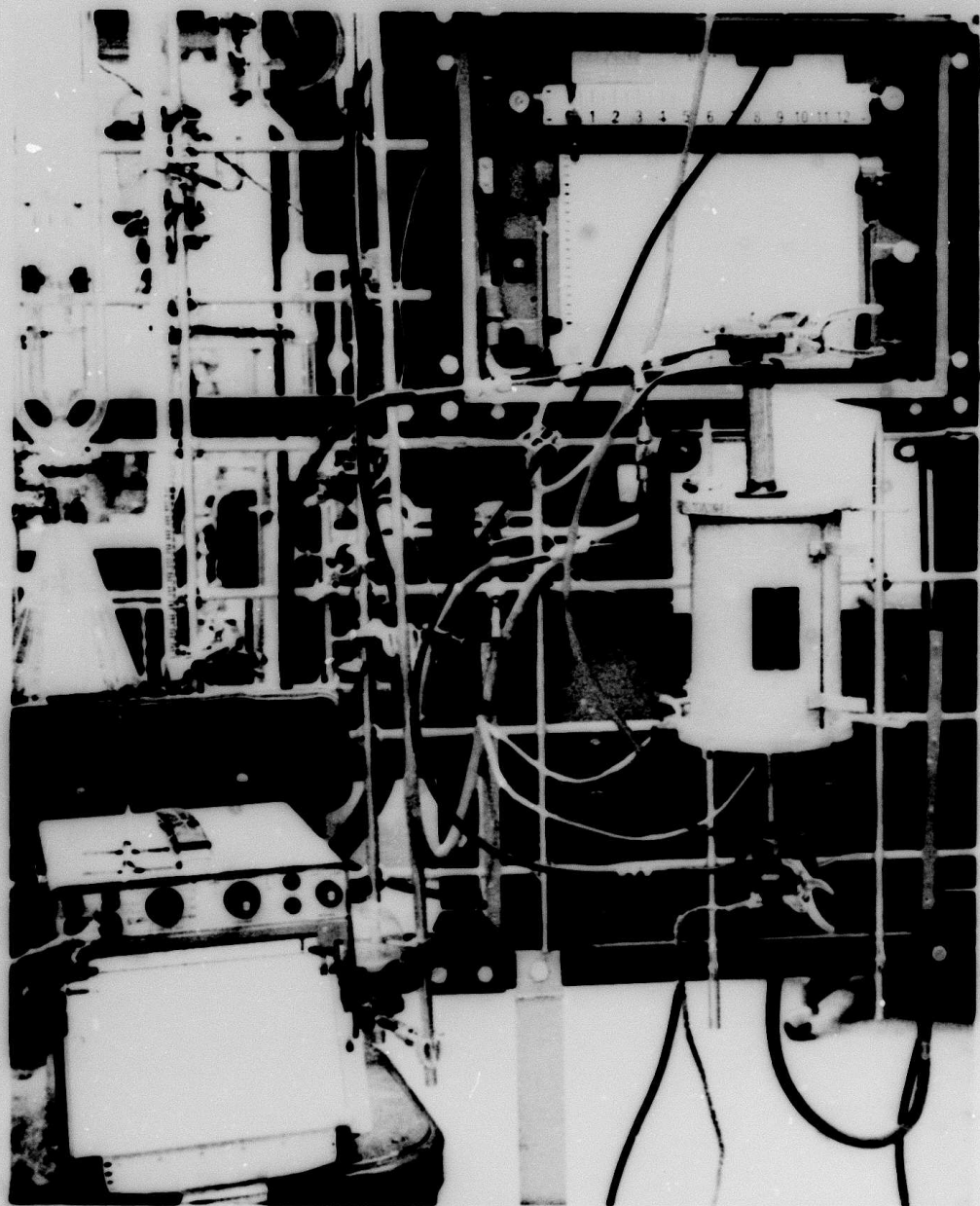


Figure 3. Overall View of Ignition and Combustibility Apparatus.

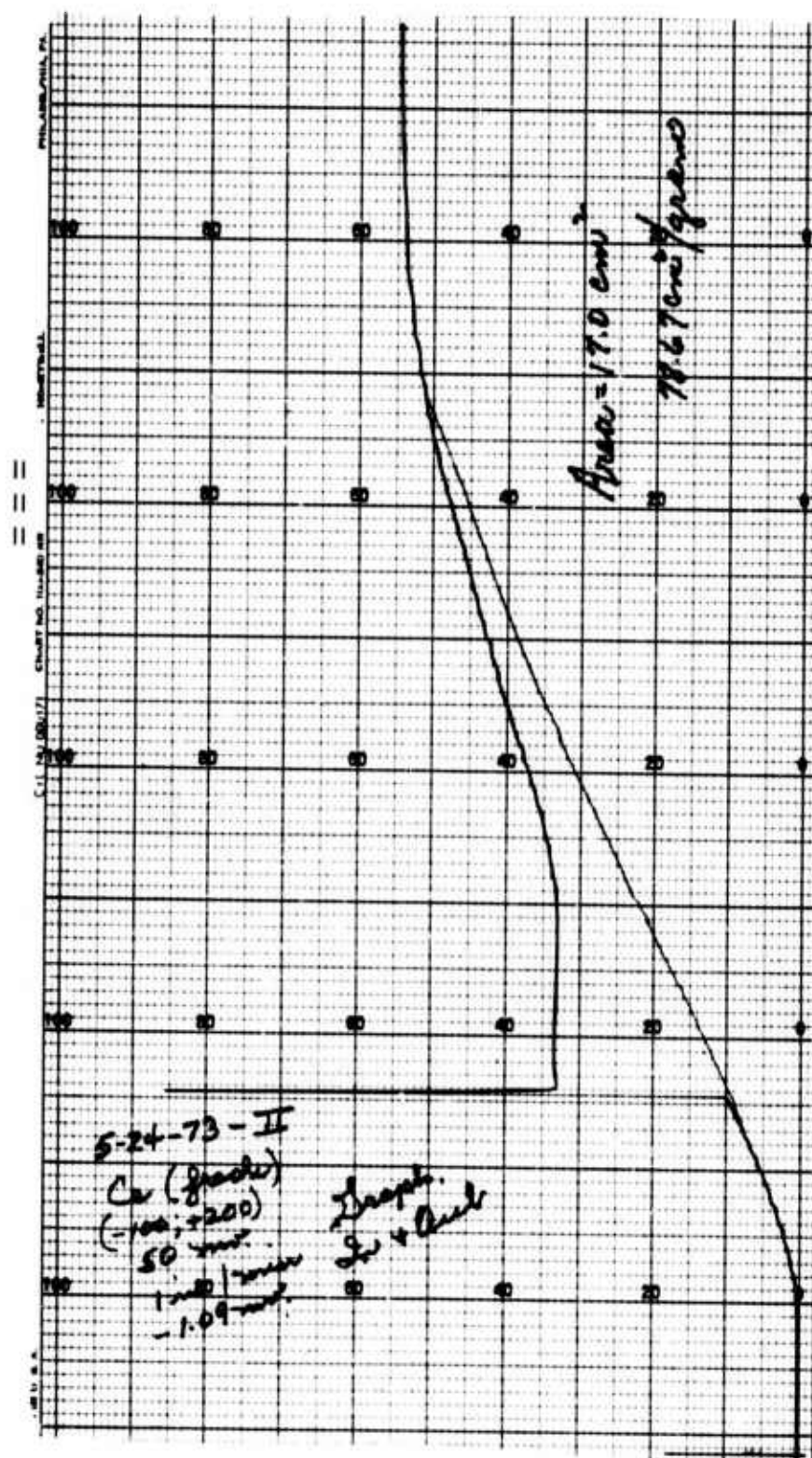


Figure 4. Ignition and Combustion Characteristics of Ce.

13c

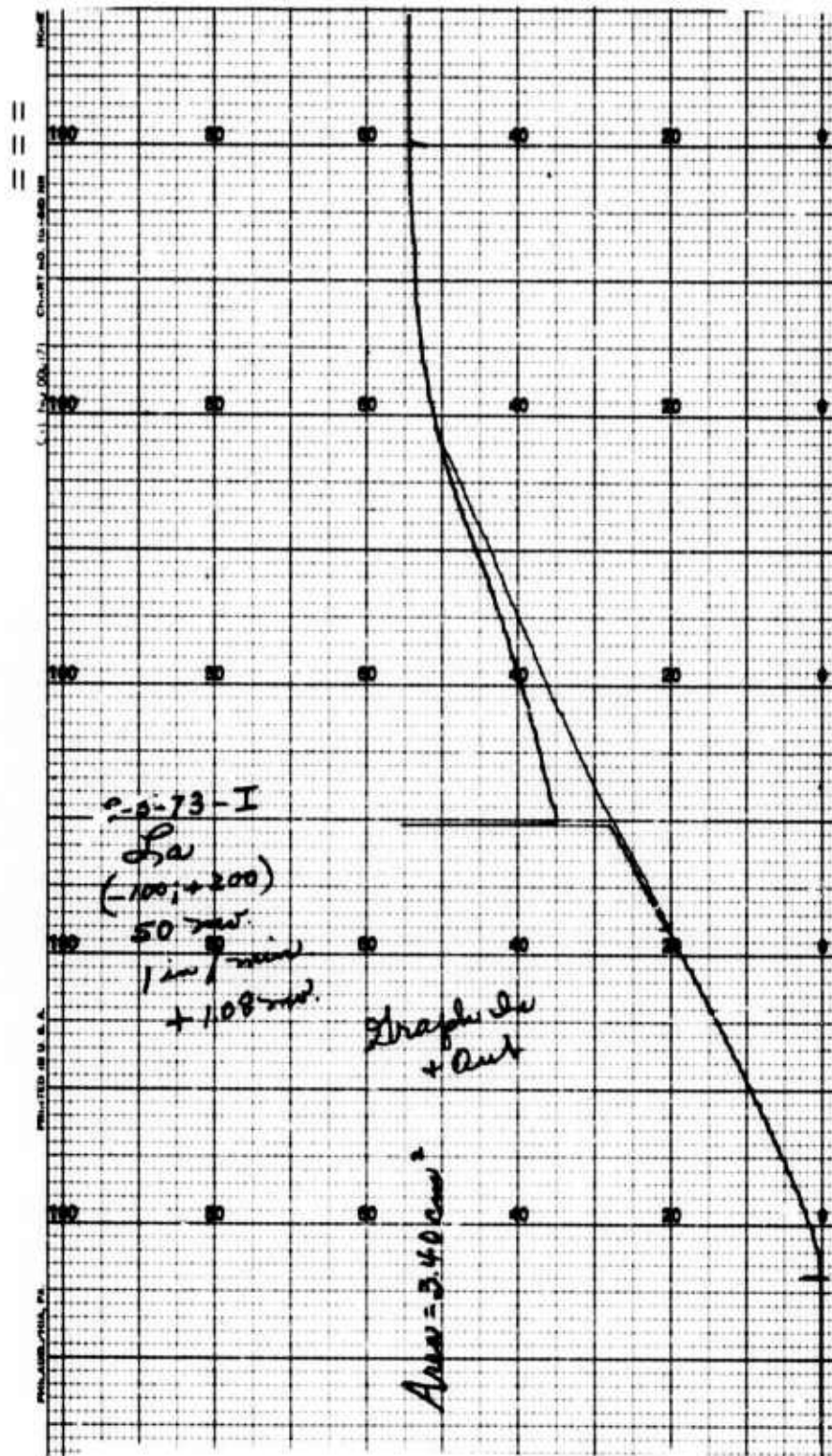


Figure 5. Ignition and Combustion Characteristics of La.

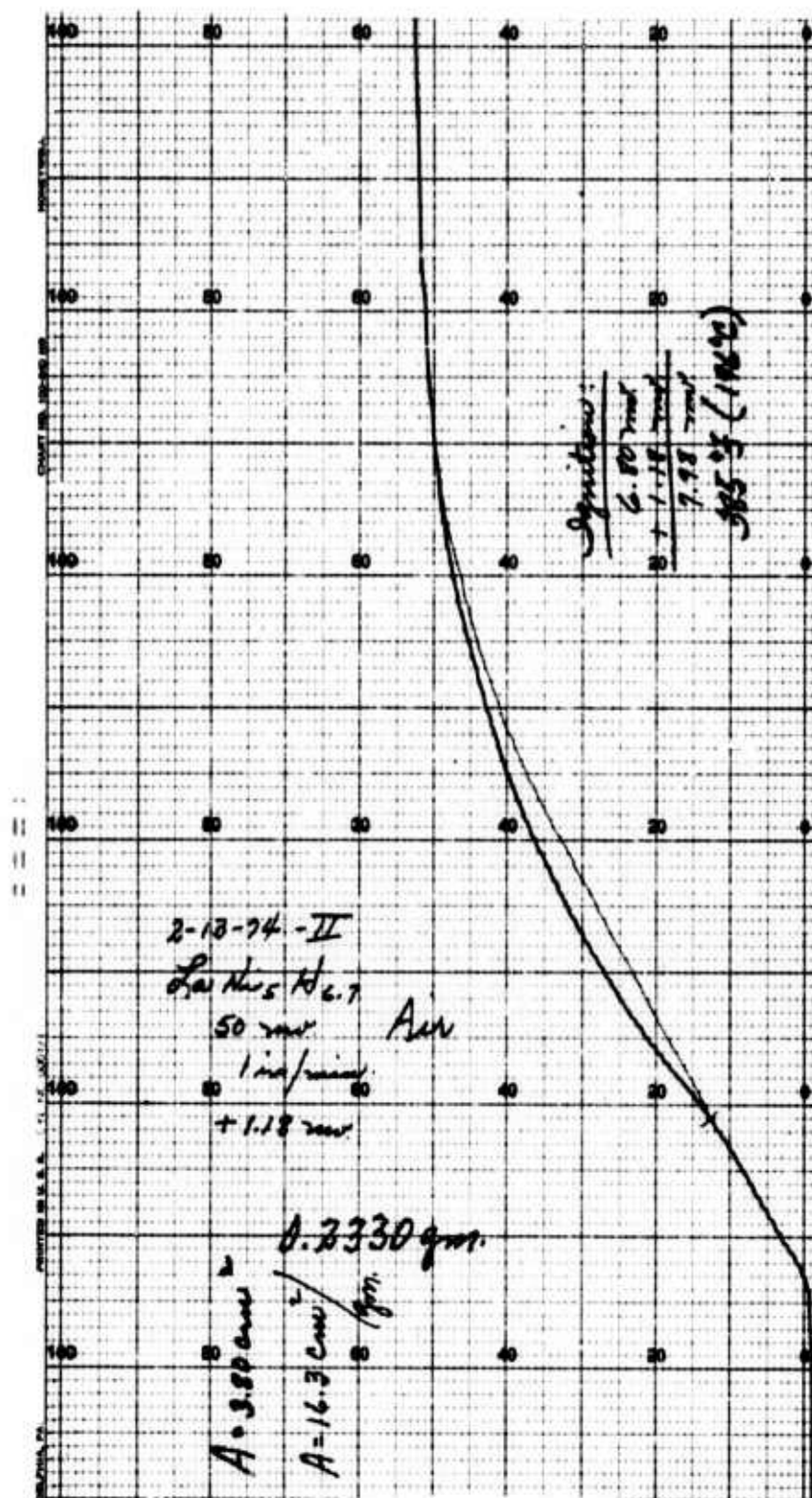


Figure 6. Ignition and Combustion Characteristics of LaNi_5 Hydride.

TABLE I
IGNITION AND COMBUSTIBILITY DATA

<u>Condition</u>	<u>Metal or Alloy</u>	<u>Relative Combustion Energy (area/gm)</u>	<u>Ignition Temp. °C</u>
In O ₂	Ce	90	149
In O ₂	La	13	376
In O ₂	Ni	--	---
In O ₂	LaNi ₅	28	323
In O ₂	LaNi ₅ Hydride	38	228
In air	LaNi ₅	4	360
In air	LaNi ₅ Hydride	17	192

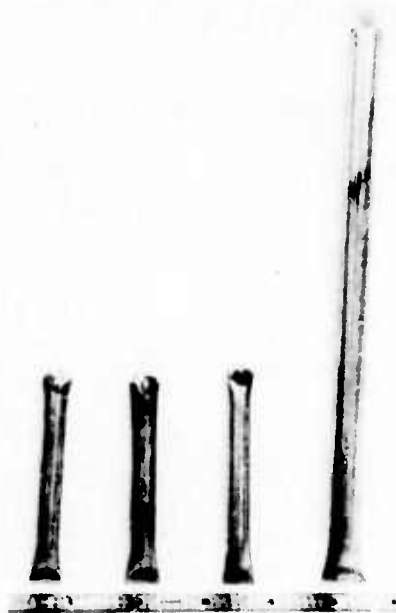
2. Flammability Studies

Flammability is defined as the combustion properties when a flame is intentionally employed to ignite the hydrogen which is desorbing or emanating from the hydride powder. Three tests were conducted: 1) with a completely open system, 2) with an enclosed system having a partially restricted opening, and 3) with an enclosed system having a restricted opening. Figure 10 shows the systems that were employed. The completely open system was prepared by simply pouring 100 grams of powdered LaNi₅ hydride onto aluminum foil in air. One sample was allowed to sit for at least 24 hours. Although hydrogen was desorbing, there was no spontaneous ignition and combustion. It was noted that the temperature within the bed of powder in the first 10 to 20 minutes raised to about 60°C. This was attributed to the hydrogen reacting slowly with the oxygen in air by catalytic reaction at the surface of the LaNi₅ hydride. A second sample was ignited at one spot on the surface of the pile with a torch. No violent reaction was noted. The LaNi₅ hydride burned with only a slightly visible flame at first immediately above the powder. The reaction spread slowly across the surface of the powder. This was observed by the blackened reaction product compared to the silvery grey luster of the unreacted material. The partially reacted surface can be seen in Figure 7. The reaction continued slowly until the surface was reacted and then started reacting from the surface inward. The flame disappeared in about 5 minutes. The total time for the reaction was about 30 to 40 minutes. If one would uncover the surface layer, one could see a dark red glow any time during this period. Several reactions were occurring which involved enthalpy transfer. One was the endothermic desorption of hydrogen at about 7.4 kcal/molH₂. The net result was heat generation, but with a moderating effect due to the endothermic reaction and the

14a



a. Open System



b. Restricted Systems

Figure 7. Flammability Tests of LaNi_5 Hydride.

diffusion time for the hydrogen to come to the surface and desorb. It was believed that most of the hydrogen and oxygen reaction occurred at the surface catalytically.

The enclosed system with a partially restricted opening consisted of a 9 in. length of 1/2 in. diameter copper tubing, closed at one end. A charge of 25 grams of LaNi_5 hydride was loaded into the tube, filling the tube half full. As the powder was desorbing hydrogen nothing occurred. A torch was then set to the open end of the tube. No explosion occurred because the air had been swept out by the desorbing hydrogen. The hydrogen simply burned at the mouth of the 1/2 in. diameter tubing until it was completely desorbed. The tube is seen in Figure 7.

The enclosed systems with very restricted openings consisted of 3/8 in. diameter copper tubing loaded with about 10 grams of LaNi_5 hydride each. Each tube was sealed at both ends and then drilled with 1/32, 1/16, and 1/8 in. diameter drills, respectively. The desorbing hydrogen was ignited with a torch. In no case did an explosion reaction occur. The hydrogen burned at each opening until all of the hydrogen was desorbed.

The rate of desorption was such that the open volume within the respective system was kept free of air to prevent buildup of a dangerous air-hydrogen mixture (between 4 and 75 vol. percent). Also, flow out of the openings was such that no chance for flash back within the container could occur.

3. Shock Studies

It is well known that explosives and reactive materials, including mixtures of oxygen and hydrogen (18 to 59 vol. percent), can be sensitive to shock. The standard test in the Department of Defense to characterize explosive sensitivity to shock is the card-gap test (17). The schematic design of the card-gap test is seen in Figure 8. It is used to compare the shock sensitivity of various explosive materials. Basically, it consists of a donor charge set off by an electric cap, a barrier of plastic sheet, the acceptor charge, and a means to detect the degree of explosibility due to shock. A test of this type was conducted using the LaNi_5 hydride as the acceptor. The DRI ballistics range was the site of the test. A tetryl pellet 3 in. in diameter by 2 in. high was the donor charge. The plastic barrier was set at a minimum with only one sheet of plastic. On top of this was placed a steel tube, 4 in. high by 1-1/4 in. ID in which the hydride powder was placed. The means of measurement of explosibility or sensitivity to shock was a standard means, termed, a witness plate. This was a sheet of mild steel plate, 3/8 in. thick, placed at the end of the hydride filled, steel tube. If exploded, the acceptor charge would blast a hole through the plate. The gap is usually varied with layers of plastic until a point is reached where the acceptor charge is not set off. In this particular case, the gap was a minimum, representing the most severe conditions. The test was completely negative. No damage was observed in the witness plate. The shock did not even ignite the hydride powder.

15a

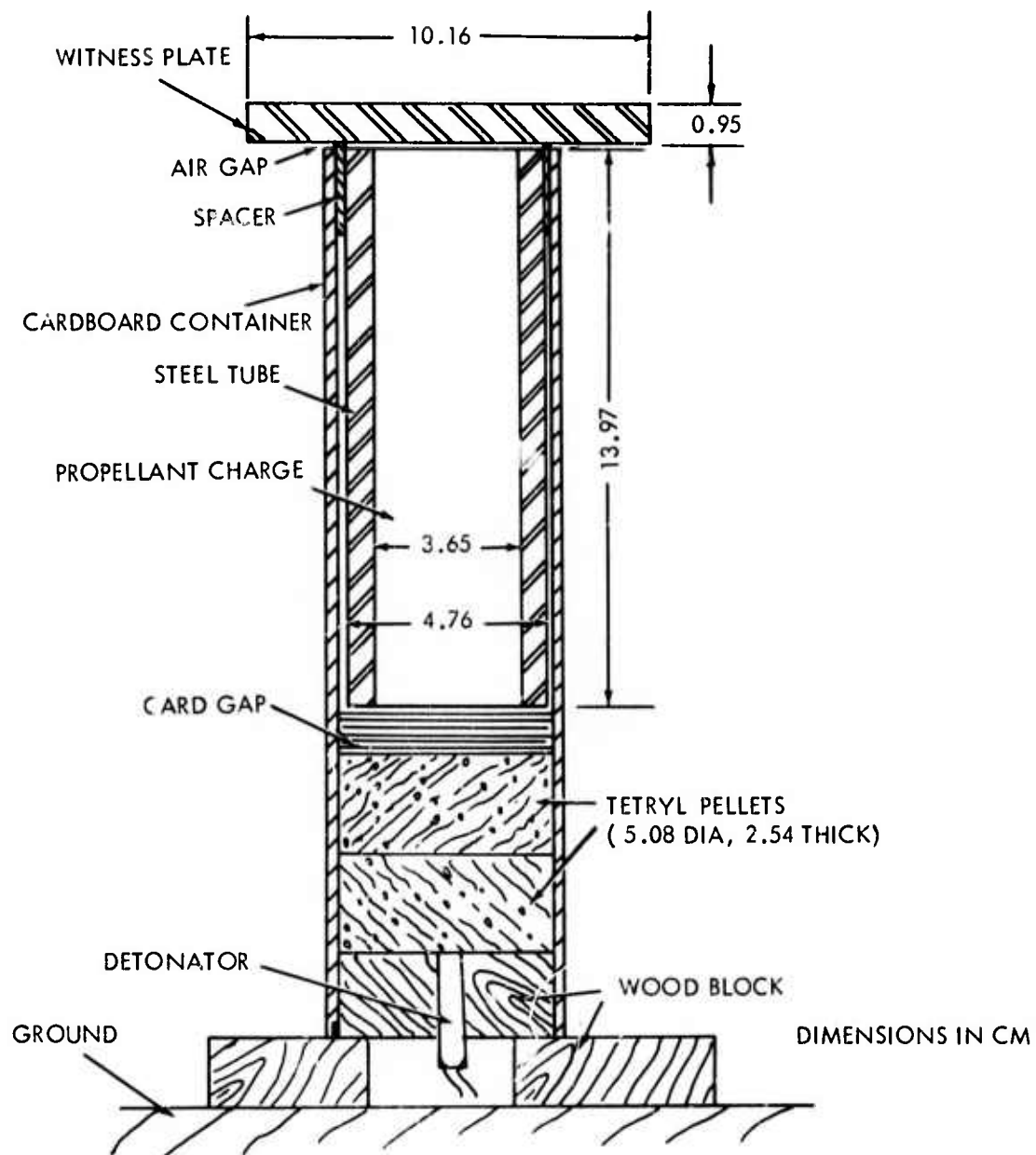


Figure 8. Schematic View of Card-Gap Shock Device.

4. Impact and Friction Study

Two separate tests were conducted to determine the effect of impact and friction on the LaNi_5 hydride powder. These were: the drop test and the bullet test, which again are standard Department of Defense tests for explosives (18). Both of these tests were carried out at the DRI facilities.

The drop test represented in Figure 9 consists of dropping a 2.5 Kg weight from a predetermined height. A steel die cup is filled with the powder. The die cup and anvil are seen in Figure 10. A sample of about 0.1 gram was placed in the cup with a circular area of $3/8$ inch in diameter. A cylinder is placed on the top of the powder on which the 2.5 Kg weight impacts. The minimum height required for explosion is the measure of susceptibility. The property of impact is tested. This test with the LaNi_5 hydride powder was negative.

The bullet test, which is used for differentiating the sensitivity to frictional impact, was conducted on LaNi_5 hydride. It consists of firing a .30 caliber bullet through a distance of 30 yards into a container of the material to be tested. The container is a 2 in. diameter by 3 in. long malleable cast iron pipe, threaded and capped at both ends. The pipe is filled with the sample material. The bullet strikes at right angles and centered to the axis of the pipe. Figure 11 shows the device used for the bullet test and the results. Usually a visual test suffices to measure the sensitivity. The ratings are: 1) no effect, 2) emission of smoke, 3) emission of flame, and 4) explosion. In the case of the tested LaNi_5 hydride, the test was completely negative.

5. Electrostatic Spark Susceptibility

Electrostatic spark discharges are always prevalent and insidious sources for causing unexpected explosions. Static discharges will readily ignite hydrogen-air mixtures (18). A standard test was conducted through the cooperation of the Bureau of Mines (19). The electrical energy required for the ignition of a layer of powder is determined by discharge of a condenser at 400 volts through a $1/16$ in. layer. The energy can be varied and the minimum energy for ignition can be quantitatively measured. The value obtained for LaNi_5 unhydrided was 0.04 joules and that for LaNi_5 hydride was 0.16 joules. In other words, it took more energy to ignite the hydride by electrostatic spark. The table below gives some comparisons of other hydrides.

16a

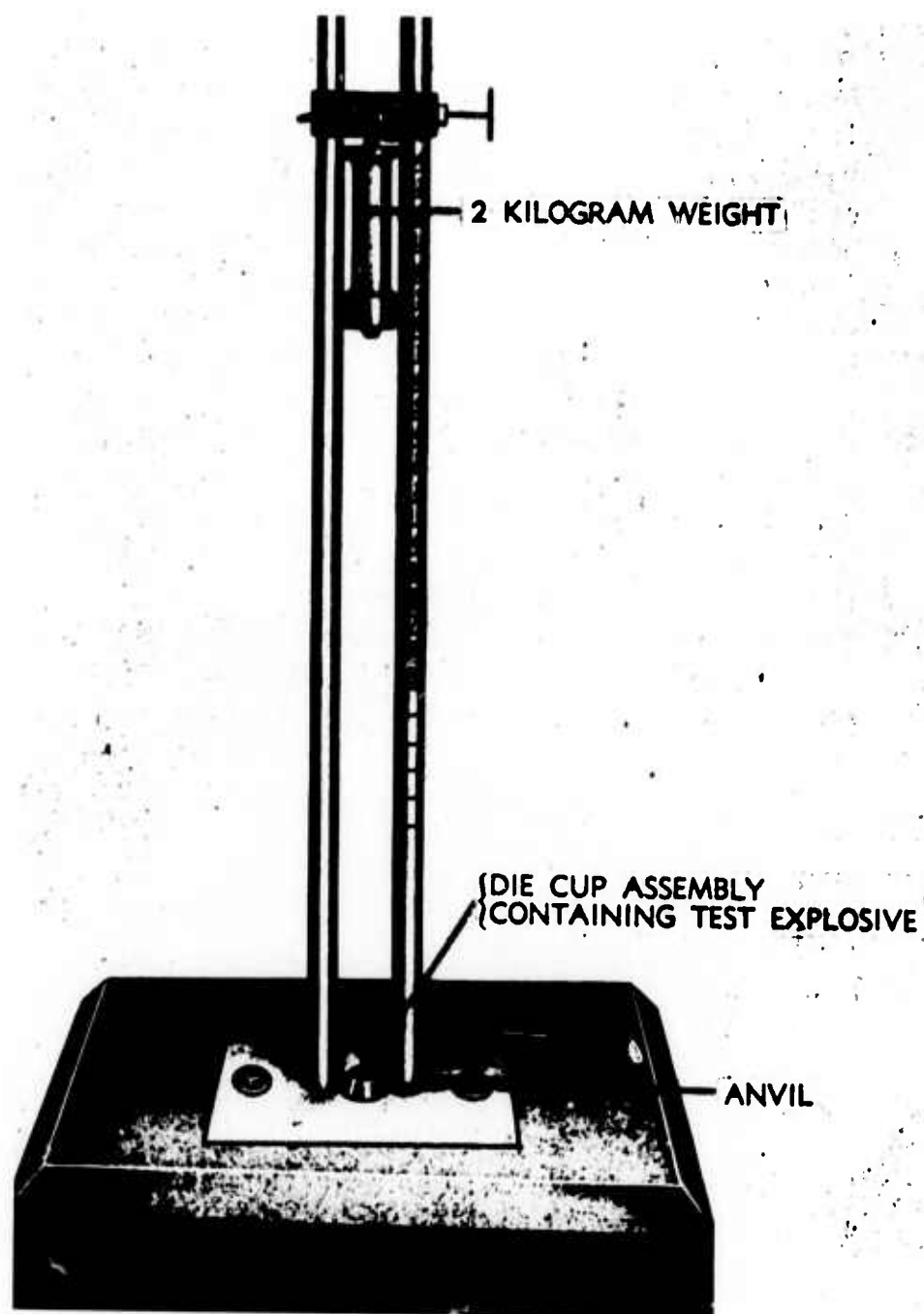


Figure 9. Drop Test Equipment.

16b

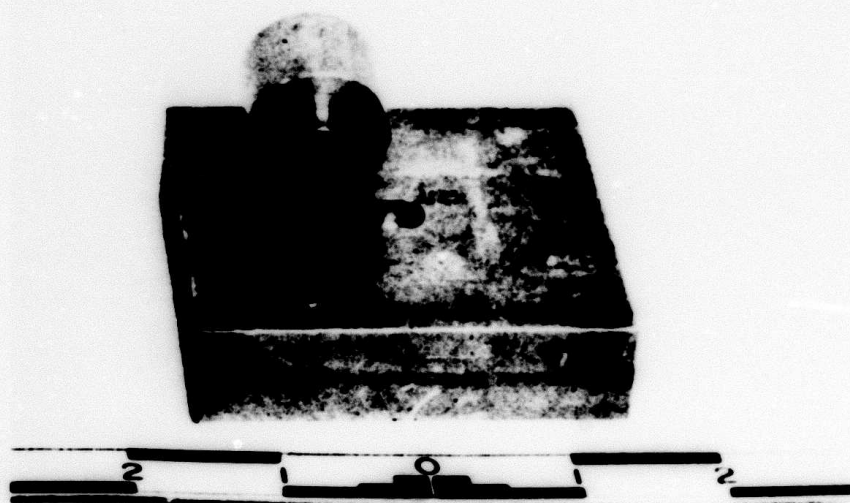


Figure 10. Drop Test Anvil.

16C

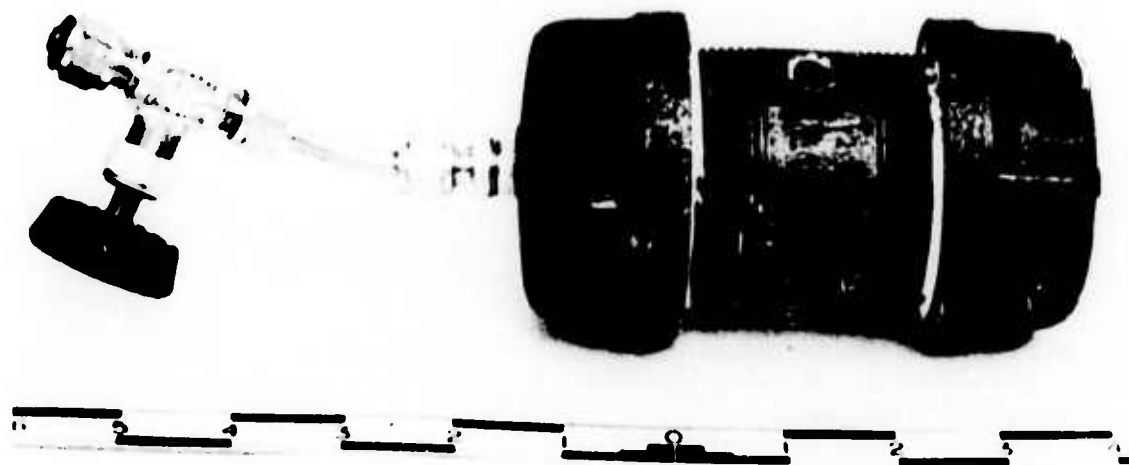


Figure 11. Results of Bullet Test.

It is interesting to note that the hydrides in general take more energy to ignite. The LaNi_5 in either hydrided or unhydrided form takes considerably more energy to ignite.

<u>Sample</u>	<u>Minimum Igniting Energy</u>
LaNi_5	0.04 joules
$\text{LaNi}_5\text{H}_{6.7}$	0.16
U	0.000004
UH_3	0.000032
Th	0.000004
ThH_2	0.000005
Ti	0.000024
TiH_2	0.024
Zr	0.000006
ZrH_2	0.00032

6. Dust Explosion Test

The effect of exploding a charge in the center of mass of a bulk amount of LaNi hydride powder was determined at the DRI ballistics range. A charge of 400 grams of powder was placed in a plastic container. Imbedded in the center was an electric blasting cap. The cap was exploded causing the bulk powder to be dispersed into a dust cloud in the air. The combined effect of the explosion and heat of the blasting cap was not enough to ignite the dust cloud.

C. Dust Cloud Safety Studies

A dust cloud consists of a levitation of bulk powders into an air suspension. A dust explosion is a rapid combustion of this cloud where heat is generated faster than it is dissipated. The explosion is a type which exhibits a rapid development of pressure. Many different materials that are combustible will, when powdered finely enough, explode on being dispersed in air and ignited. To cause a dust explosion to occur, one must raise a small portion of the cloud up to its ignition temperature. The dust concentration must be between a well-defined minimum and some less well-defined maximum.

Since the Federal Bureau of Mines of the U.S. Department of Interior has set-up equipment and procedures to conduct measurements of the parameters necessary to effect a dust explosion, it was felt necessary to contact them and request their cooperation in testing LaNi_5 and LaNi_5 hydride dust explosive susceptibilities. They were most helpful in obliging. Their techniques have been described in the U.S. Bureau of Mines publications (19, 20).

1. Preparation of Samples

Arrangements were made with the U.S. Bureau of Mines Industrial Safety Group at their Pittsburgh Technical Support Center, Pittsburgh, Pa., to determine the Explosibility Index for both LaNi_5 and LaNi_5 hydride in powder form. A series of 40 weighed samples of LaNi_5 hydride was requested by Bureau personnel to perform the necessary tests. Room temperature (25°C) equilibrium hydrogen pressure over saturated LaNi_5 hydride is approximately 37 psi. A description of the technique and apparatus used to prepare these samples and guarantee stoichiometry is given below.

A 5 station gas manifold was assembled using $3/8$ inch O.D. copper refrigeration tubing and Hoke, Inc., brass Gyrolok tube fittings. The manifold was valved for vacuum (Welch mechanical vacuum pump) and for hydrogen gas. Appropriate pressure and vacuum indicating devices were also attached. Sample containers were fabricated from $3/8$ inch O.D. copper refrigeration tubing by flattening and sealing one end of a $3-1/2$ to 4 inch long section of tubing with Varian Vacuum Division flattener and pinch-off tools respectively. If the inside of the tubing is clean, the pinch-off operation cold welds the copper, and the resulting seal will withstand an internal pressure of at least 220 psi.

Each sample was prepared by weighing the desired amount of LaNi_5 powder into a sample container. The powder used had been hydrided-dehydrided one time, and all weighings were done in air. The loaded container was then attached to the gas manifold using a Gyrolok nut and ferrules. The system was evacuated to a vacuum of less than one micron before hydriding was started. Five samples were prepared at one time by admitting hydrogen to the evacuated manifold. Samples were equilibrated at 220 psi hydrogen pressure for one hour to assure saturation. After equilibration the pressure was reduced to approximately 40 psi, and each sample was removed from the manifold with the flattener and pinch-off tools. This procedure produced a copper capsule sealed at each end with the contained sample under 40 psi hydrogen pressure. The seal can be opened easily with a pair of pliers. The capsule can be cooled in liquid nitrogen before it is opened, and the cold hydride sample can be exposed to the atmosphere for 2 to 3 minutes before appreciable hydrogen is evolved.

2. Determination of Ignition Sensitivity

Ignition sensitivity is assumed to be a function of ignition temperature, minimum ignition temperature, and minimum explosive concentration. It is defined as unity for a dust similar to Pittsburgh seam coal and is calculated as follows:

$$\text{Ignition Sensitivity} = \frac{(\text{Ign. temp.} \times \text{min. ign. energy} \times \text{min. conc.}) \text{ Coal Dust}}{(\text{Ign. temp.} \times \text{min. ign. energy} \times \text{min. conc.}) \text{ Sample Dust}}$$

Briefly, the ignition temperature is determined by dispersing a known amount of dust (usually 0.1 grams) in a tube furnace at differing levels of temperature. Ignition is determined when the appearance of a flame is observed in the mouth of the furnace.

The minimum ignition energy of a dust cloud is done in another combustion tube. Dispersion of a known amount of dust is accomplished through a solenoid valve by an air blast. The quantity of dust ranges from 5 to 10 times the minimum explosion concentration. A timed ignition spark is passed between two electrodes in the combustion chamber. The spark is obtained from condenser discharge. The energy of the spark can be calculated from the capacitance and voltage. The energy is varied for a series of dust levitations until a minimum energy for ignition is determined. This is observed when flame propagation is produced 4 inches or longer in the tube.

The minimum explosive concentration or lower limit of explosibility of a dust is determined in the same apparatus as that to obtain minimum ignition energy; however, an induction spark igniting source is used. Known amounts of dust are placed in a dispersion cup and levitated by a blast of air. Prior to levitation the spark is struck and the current adjusted to 23.5 milliamperes. A filter paper diaphragm in the top of the combustion tube must burst from the pressure from the explosion to comply with the minimum concentration as above. For more complete details refer to (20).

3. Determination of Explosion Severity

Explosion severity is assumed to be a function of maximum explosion pressure and rate of pressure rise. Again, it is defined as unity for a dust similar to Pittsburgh seam coal and is calculated as follows:

$$\text{Explosion Severity} = \frac{(\text{Max. exp. press.} \times \text{max. rate of press. rise}) \text{ Sample Dust}}{(\text{Max. exp. press.} \times \text{max. rate of press. rise}) \text{ Coal Dust}}$$

Briefly, the maximum explosion pressure and rates of pressure rise are determined in the same test in a closed steel tube. The dust is dispersed by releasing a known amount of compressed air. The dust is ignited by a continuous spark source. The explosion pressure is measured by electronic transducers and the maximum pressure and the average and maximum rates of pressure rise developed in the explosion are determined from the plot of pressure versus time. The dispersion pressure is subtracted from the peak explosion pressure to give the corrected maximum pressure. The average rate is obtained by dividing the maximum pressure by the time interval

between ignition and the maximum pressure. The maximum rate is the steepest slope of the pressure-time curve. Explosion tests were made with dust concentrations of 0.10, 0.20, 0.30, 0.50, 1.00, and 2.00 oz./cu.ft. For complete details refer to (20).

4. Determination of Index of Explosibility

The Index of Explosibility is measured as follows:

$$\text{Index of Explosibility} = \text{Ignition Sensitivity} \times \text{Explosion Severity}$$

Tests have been determined for many different metal powders during the past 25 years by the Bureau of Mines, so an extremely valuable comparison with many different types of elements and alloys is available (20). The relative hazards of dusts have been arbitrarily ranked as follows:

<u>Relative Explosion Hazard Index</u>	<u>Index of Explosibility</u>
None	0
Weak	< 0.1
Moderate	0.1 - 1.0
Strong	1.0 - 10.0
Severe	> 10

The data obtained for LaNi_5 and LaNi_5 hydride in all of the experiments just described are presented in Table II along with selected other materials for comparison. The Indexes of Explosibility for both LaNi_5 unhydrided and fully saturated LaNi_5 hydride were determined to be 0.1, or a rating of "weak". As can be observed, Ni is completely negative. Vanadium metal is comparable to LaNi_5 hydride. An example of a highly explosive dust is UH_3 which has an Index of Explosibility of 10.

TABLE II - EXPLOSIONABILITY OF DUSTS

Index of Explosibility	Ni 0	V 0.1	LaNi ₅ 0.1	LaNi ₅ H _{6.7} 0.1	UH ₃ 10
Ignition Temperature, °C: Dust Cloud	--	500	420	320	20
Minimum Energy Required for Ignition by Electric Spark from Condenser Discharge, Joule:Dust Cloud	--	0.06	0.56	0.28	0.005
Minimum Explosive Dust Concentration: oz/cu ft	--	0.220	0.300	0.100	0.060
Maximum Pressure and Rates of Pressure Rise (psi/sec) Developed by Explosions of Dust Clouds in a Closed Bomb at Concentrations of:					
0.10 oz/cu ft					
Maximum Pressure	--	--	NI ¹	5	--
Average Rate	--	--	--	--	--
Maximum Rate	--	--	--	--	--
0.20 oz/cu ft					
Maximum Pressure	--	--	NI	10	36
Average Rate	--	--	--	100	1400
Maximum Rate	--	--	--	100	3000
0.50 oz/cu ft					
Maximum Pressure	--	48	14	47	43
Average Rate	--	300	100	1300	2900
Maximum Rate	--	600	100	1600	6500
1.00 oz/cu ft					
Maximum Pressure	--	57	43	56	53
Average Rate	--	500	300	700	3500
Maximum Rate	--	1000	500	1000	7500
2.00 oz/cu ft					
Maximum Pressure	--	--	45	59	74
Average Rate	--	--	500	500	3500
Maximum Rate	--	--	600	700	9000

¹No ignition.

VII. HYDRIDING STUDIES WITH LaNi_5

A. Equipment Description

1. Design

The high-pressure hydriding apparatus was designed with flexibility of operation as the chief consideration. By a simple change of a pressure gauge, any one of the four hydriding connections to the main gas manifold can be used at pressures up to 2000 psi. The design allows three pressure-temperature-composition determinations to be run simultaneously. The valve arrangement allows a reaction chamber to be moved from one connection or station to another without atmospheric exposure.

It has been our experience that LaNi_5 can be activated initially at hydrogen pressures as low as 150 psi. Other materials may require much higher pressure capability. It is conceivable that some materials may require a very high activation pressure although their normal working pressures, once activated, may be in the range of pressures for LaNi_5 .

A constant temperature circulator was selected for the temperature range -30°C to $+150^\circ\text{C}$ because of its convenience and sensitive temperature control, $\pm 0.02^\circ\text{C}$. The reaction chambers are small, and it should be possible to operate three of them at one temperature by the use of the one circulator. At temperatures above 150°C , strip-chart recorder-controllers provide the sensitivity for adequate temperature control.

Construction and calibration of a pressure hydriding apparatus was completed. This apparatus has and will be used for screening new alloys and to determine the pressure-temperature-composition relationships for the various hydrogen host materials that will be investigated during the course of the programs. Figure 12 is an overall view of the apparatus without the furnaces or cooling units.

The apparatus has an ultimate pressure capability of 2,000 psi, but it is expected that most of the experimental work will be done at pressures below 1,500 psi. The main pressure manifold and the ten valves attached to it are fabricated from 304 and 316 stainless steel. The valves are Hoke, Inc., 4200 Series packless valves with 2,000 psi stainless steel bellows stem seals. All tube fittings have been TIG welded, and 304 seamless stainless steel tubing, 1/4 inch O.D., was used throughout the manifold.

Four reaction chambers can be attached to the manifold at one time. Each of these four connections to the manifold is equipped with a pressure gauge. Three of the connections have Marsh Instrument Co. Test Gauges attached. The pressure ranges covered are 0-200 psi, 0-300 psi, and 0-600 psi, and these gauges have an accuracy of $\pm 0.5\%$ full scale reading. The fourth reaction chamber connection has a Marsh standard gauge attached with a 0-2000 psi range. This connection will be used for initial high pressure activation of any material that will not hydride at a pressure of 600 psi or below.

22a

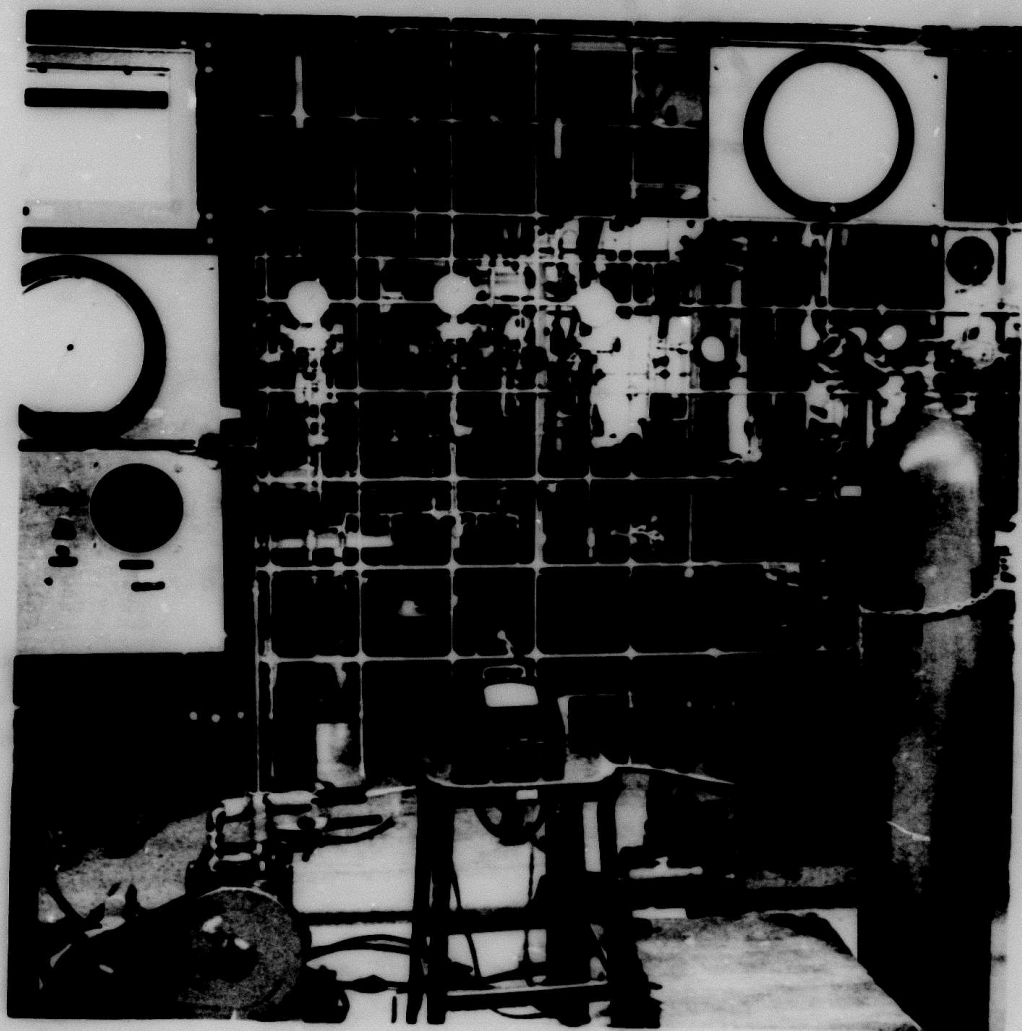


Figure 12. The High-Pressure Hydriding System.

Two Heiss gauges are attached to the manifold. The one gauge has a pressure range 0 to 600 psi and an accuracy of $\pm 0.1\%$ full scale reading. This gauge will be used to check the calibration of the three Marsh Test Gauges. The second Heiss gauge has a pressure range of 0-77 psi (0-4000mm. Hg) and an accuracy of $\pm 0.1\%$ full scale reading. This gauge can be used for low pressure equilibrium measurements or low pressure calibration of the Marsh Test Gauges.

The reaction chambers were fabricated from Cajon Company Model VCR vacuum couplings. These couplings are fabricated from 316 stainless steel as are the gaskets which make the vacuum seal. The chambers are 13/32 inch ID by 1-1/8 inch deep. The bottom of each chamber was made from 0.150 inch thick 304 stainless steel plate and welded to the body of the coupling. A thermocouple recess 0.130 inch diameter by 0.080 inch deep was provided in the bottom of each chamber. A Hoke 4200 Series stainless steel valve is attached to each reaction chamber. Each reaction chamber is attached to the main pressure manifold with a 1/4 inch Cajon VCR vacuum coupling with a stainless steel gasket.

The LaNi_5 intermetallic fractures during hydriding to a very fine powder. Some of the powder is so fine that it has a tendency to travel with a gas stream in a hydriding system. In order to confine the powder to the reaction chamber, the gaskets used to join the two halves of the chamber will be fitted with inserts of Pall Trinity Micro Corporation Grade II porous stainless steel filter material. The absolute pore size of this material is one micron; this filter should allow free flow of hydrogen gas and confine the hydride powder in the reaction chamber. Figure 13 is a photograph of a reaction chamber assembly with the filter medium inserted in the gasket.

Vacuum for the apparatus is provided by a Welch Model 1402B mechanical vacuum pump. High purity hydrogen gas is available from the National Bureau of Standards Cryogenic Laboratory in Boulder, Colorado. Although the purity of this gas is not certified by the Bureau, it has been used routinely by the Denver Research Institute for over 10 years for direct hydriding experiments with no purification required.

Temperature control for the reaction chambers in the range -30°C to $+150^\circ\text{C}$ will be provided by a Haake Instruments, Inc., Model FK-2 constant temperature circulator. In the temperature range above 150°C tube furnaces and strip-chart recorder-controllers will be used to provide constant temperature for the reaction chambers.

Sample preparation will be performed in an inert atmosphere (helium) glove box. The sample can be weighed and loaded into the reaction chamber in the inert atmosphere, and the valve attached to the chamber can be closed inside the glove box. When the chamber assembly is removed from the glove box, there will be a helium atmosphere protecting the sample surface until the assembly can be connected to the main manifold and evacuated. This procedure will guarantee a clean surface for any materials that may be particularly sensitive to atmospheric exposure.

23a

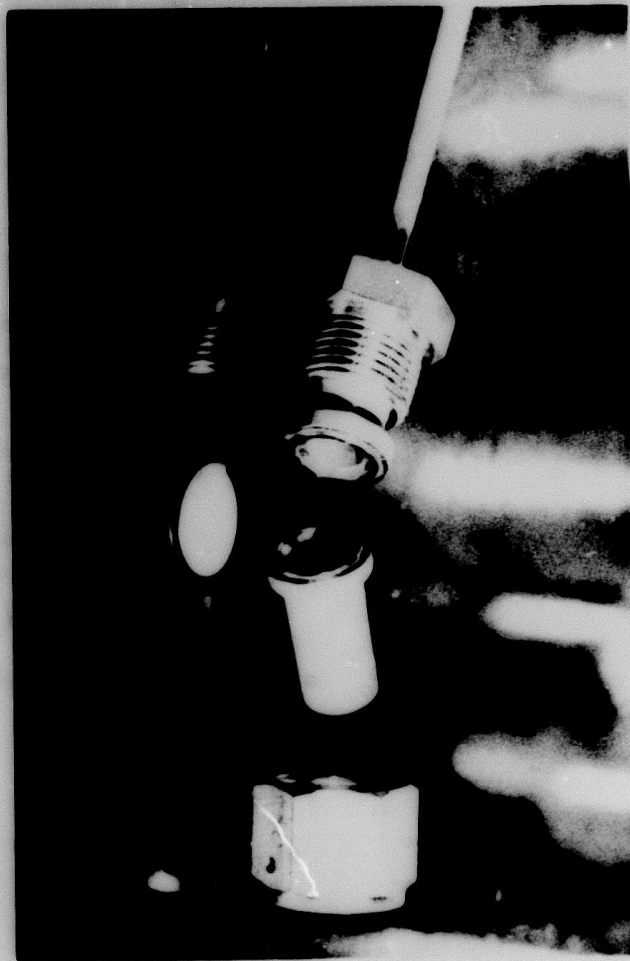


Figure 13. The Reaction Chamber.

2. Calibration

The primary volume standard is a stainless steel cylinder which displaces 97.06 cc as determined by analysis on a Sieverts apparatus. The accuracy of the Sieverts apparatus was verified as $\pm 0.02\%$ by comparison with a volume standardized by bromo benzene weighings.

The standard volume is connected to the gas manifold through a valve. The volumes of the various portions of the apparatus were determined using the standard volume, Boyles Law and pressure-density data from reference (21). Error propagation during this procedure should be less than 0.4% stemming mainly from the limitations of the Heise pressure gauges (0.1% of full scale).

Samples were weighed on a Mettler balance whose accuracy was verified as ± 0.0004 grams using Ainsworth Class SI standard weights certified as ± 0.00001 gram.

B. Data Reduction

The P-V accounting process required for the addition and withdrawal of hydrogen is made mathematically cumbersome by two factors which influence the mass of gas contained in a volume element; gas density and room temperature variations. The use of a Compucorp 324G desk model computer simplified the task.

The machine uses a modified assembly language and has a capacity of 160 programmed operations. All constants and coefficients were stored in the memory so that only raw data was entered during program execution.

C. Determination of Pressure-Temperature-Composition Relationships

The collection of pressure-composition isotherms has been hampered by a lack of repeatability in both the equilibrium plateau pressure and to a lesser extent in the saturation composition. Initially the apparatus and procedure were suspect as sources of the inconsistency, but thorough recalibration of the entire apparatus and analysis of methods and maximum instrumental indeterminacy provided no explanation of the apparently random behavior.

Recently a trend has been found which relates these variations to the history of the sample. These phenomena are discussed below in Section E.

Unlike the saturation composition and equilibrium pressures, the shapes of the P-C isotherms were very consistent, especially in the 25°, 35° and 45° tests. Figure 14 shows absorption and desorption isotherms for 25°C with all the data points included. The abrupt transition from solution in the metal phase to the two phase plateau region is remarkable.

Figure 15 shows the family of absorption and desorption isotherms. This figure is a composite of data determined by several approaches to avoid the random variations observed in direct data collection. The shapes of the

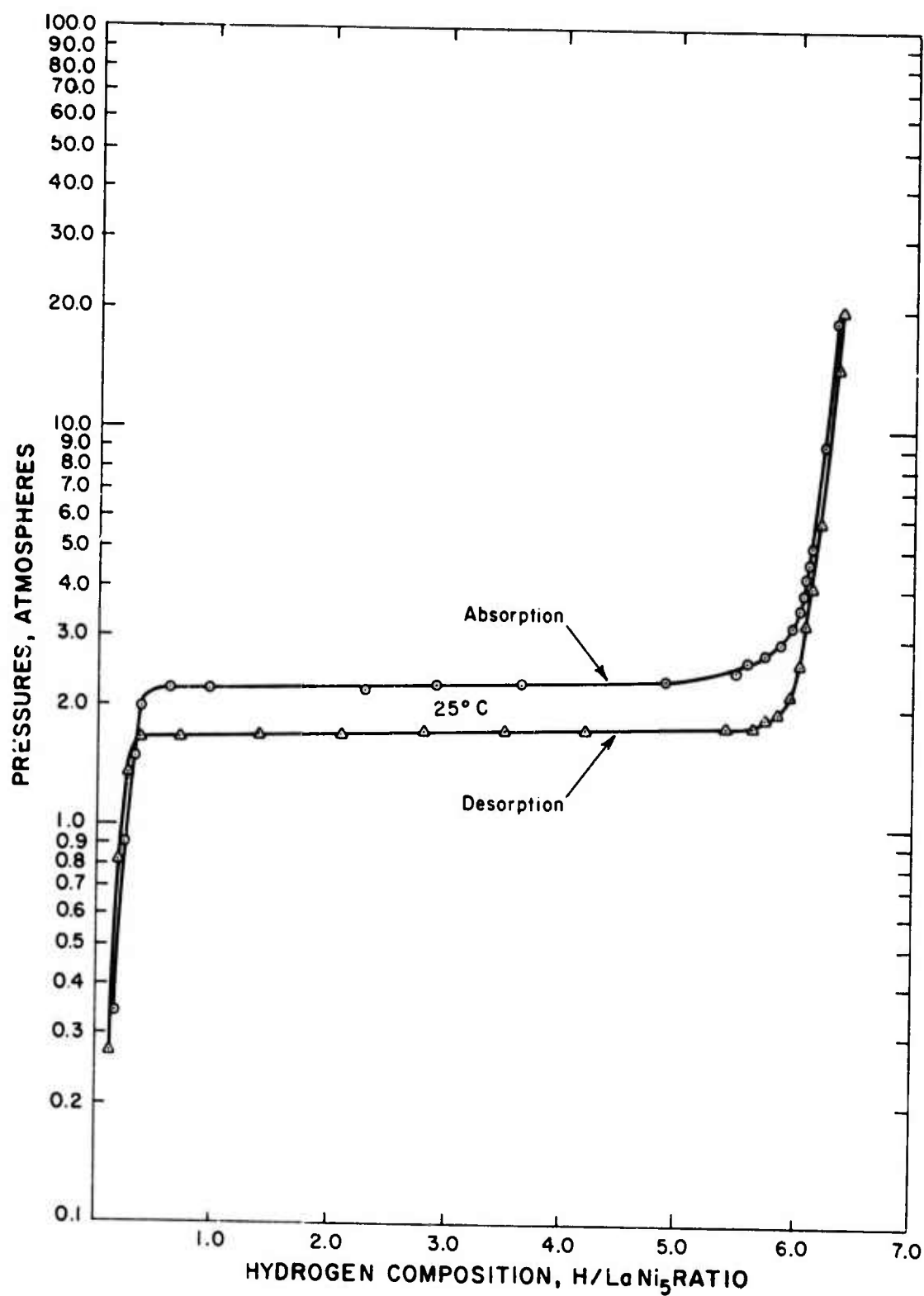


Figure 14. Plot Including Data Points of 25°C Absorption and Desorption Isotherms.

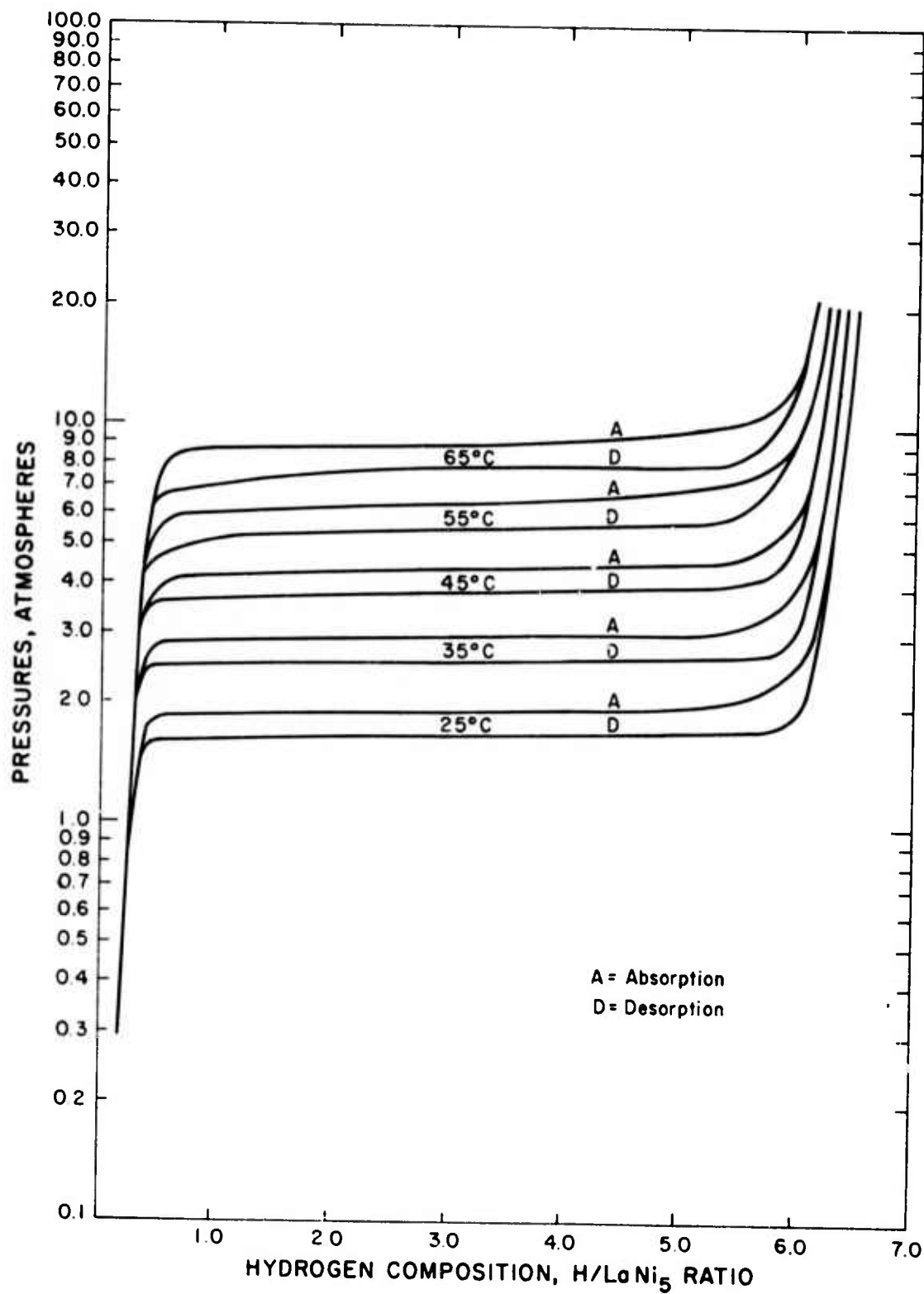


Figure 15. Family of Isotherms in Absorption and Desorption of the LaNi_5 -H System from 25 to 65°C.

curves are from actual isotherms taken at the respective temperatures. The heights of the plateaus were adjusted to those determined by an isothermal Van't Hoff experiment which has yielded the most self-consistent, pressure-temperature data obtained to date. The saturation compositions at 20 atm. were obtained from several single-addition saturation experiments performed at each temperature.

A correlation was made with the investigation of K. H. J. Buschow and H. H. Van Mal (5) on the dependence of the plateau pressure equilibria with the composition of the LaNi_5 alloy. The Dutch investigators found a relatively wide homogeneity range of the LaNi_5 phase at elevated temperatures. This, in turn, affected the plateau pressure equilibria as a function of the composition of LaNi_x at any isotherm, where x varied from 4.9 to 5.4. They specifically studied the 40°C desorption isotherm over these compositional limits. From this, they arrived at a plot of the natural logarithm of the plateau pressures versus x which resulted in a straight line. The line had the form, $\ln p = 2.4 x - 10.75$. They also observed that grossly sloping plateau pressures result from inhomogeneous samples, as one would expect from the above considerations. Note that the plateaus in this current data (Figure 15) are only slightly sloping, so the homogeneity of the material is very good. Using the analyzed value of 67.61 weight percent nickel for the LaNi_5 material used in this investigation, one calculates the stoichiometry to be $\text{LaNi}_{4.95}$. The 40°C pressure plateau as determined from the isothermally determined Van't Hoff relationship in the desorption mode in the current study is 3.1 atmospheres. The value calculated from the Dutch data is also 3.1 atmospheres. The correlation is excellent.

The X-ray diffraction lattice parameters were determined for the material in this study and also correlated with those of Buschow and Van Mal. The lattice parameters determined were

$$a = 5.012 \text{ \AA} \pm 0.01, c = 3.978 \text{ \AA} \pm 0.009$$

for the hexagonal, CaCu_5 type structure, and a calculated density of 8.290 g/cc. This compares with the Dutch data of this same composition, $\text{LaNi}_{4.95}$, of $a = 5.019 \text{ \AA}$ and $c = 3.986 \text{ \AA}$. The correlation is fair.

D. Determination of Van't Hoff Relationships

Van't Hoff data are obtained by plotting the natural logarithm of pressure as a function of inverse temperature. The slope of the plot yields the heat of reaction via the following relation:

$$\Delta H = -R \frac{d \ln P}{d T^{-1}}$$

where R is the universal gas constant.

Initially, since the pressure is nearly constant over a broad range of composition in the plateau region, data were obtained merely by recording equilibrium pressure at various temperatures without adding or removing any gas to maintain constant composition. The result was a random array of points which did not provide the precision desired in this study.

With the assistance of a computer program the composition was controlled at $\text{LaNi}_{5.3 \pm 0.1}\text{H}_{3.0}$ yielding the data of Figure 16.

A third method yielded the best plot with minimum hysteresis. The sample was brought to test temperature at zero hydrogen content and then charged to $\text{LaNi}_{5.3 \pm 0.1}\text{H}_{3.0}$ with a single gas addition for absorption experiments. For desorption experiments the sample was brought to the test temperature, saturated with hydrogen at 20 atm. and then brought to $\text{LaNi}_{5.3 \pm 0.1}\text{H}_{3.0}$ with a single withdrawal of gas. This data is shown in Figure 17.

The various methods establish the heat of reaction as 7.6 ± 0.1 kcal/mole H_2 being the same for desorption as for absorption. This compares with a value of 7.2 kcal/mole H_2 as reported by van Vucht (2), and 7.3 kcal/mole H_2 as reported by J. Anderson, et. al. (22).

E. Analysis of Hysteresis Effects

One viewpoint from which to analyze the inconsistency of the isotherm plateau pressures is to focus on the hysteresis which exists between the absorption and desorption isotherms. Since the heats of reaction should be identical for the forward and reverse directions, the difference in the logarithms of the absorption and desorption pressures should be invariant with temperature. Otherwise, the Van't Hoff plots will not be parallel and the reaction heats will not be equal. The inconsistency observed in the plateau pressures resulted in variations of hysteresis of a factor of 2 or even 3. It is noteworthy that variations in hysteresis width are seen in the data of others (ref. 22).

The role of the history of the sample in causing this variation is not yet fully understood but, since hysteresis is thought to be a manifestation of surface chemistry, contamination is strongly suspect.

It was found consistently possible to expand and contract the hysteresis of a sample by controlling the degree of communication between the vacuum pump and the sample. Worst case conditions were produced by baking the sample at high temperatures while evacuating it to the 1 micron level. More studies will be conducted to determine the cause for the hysteresis and its variations.

F. Surface Poisoning Effects

Cursory evaluations were carried out on the poisoning effects at the surface of LaNi_5 hydrides by various contaminants. The contaminants were water vapor, air, and organic vapor (oil). No attempts were made to establish their quantitative partial pressures. In no case of exposure was the surface absorption or desorption of hydrogen completely blocked. The rates were only mildly affected throughout the hydriding range of approximately 25 to 65°C. Some effect was noted on the total saturation absorptivity and

26a

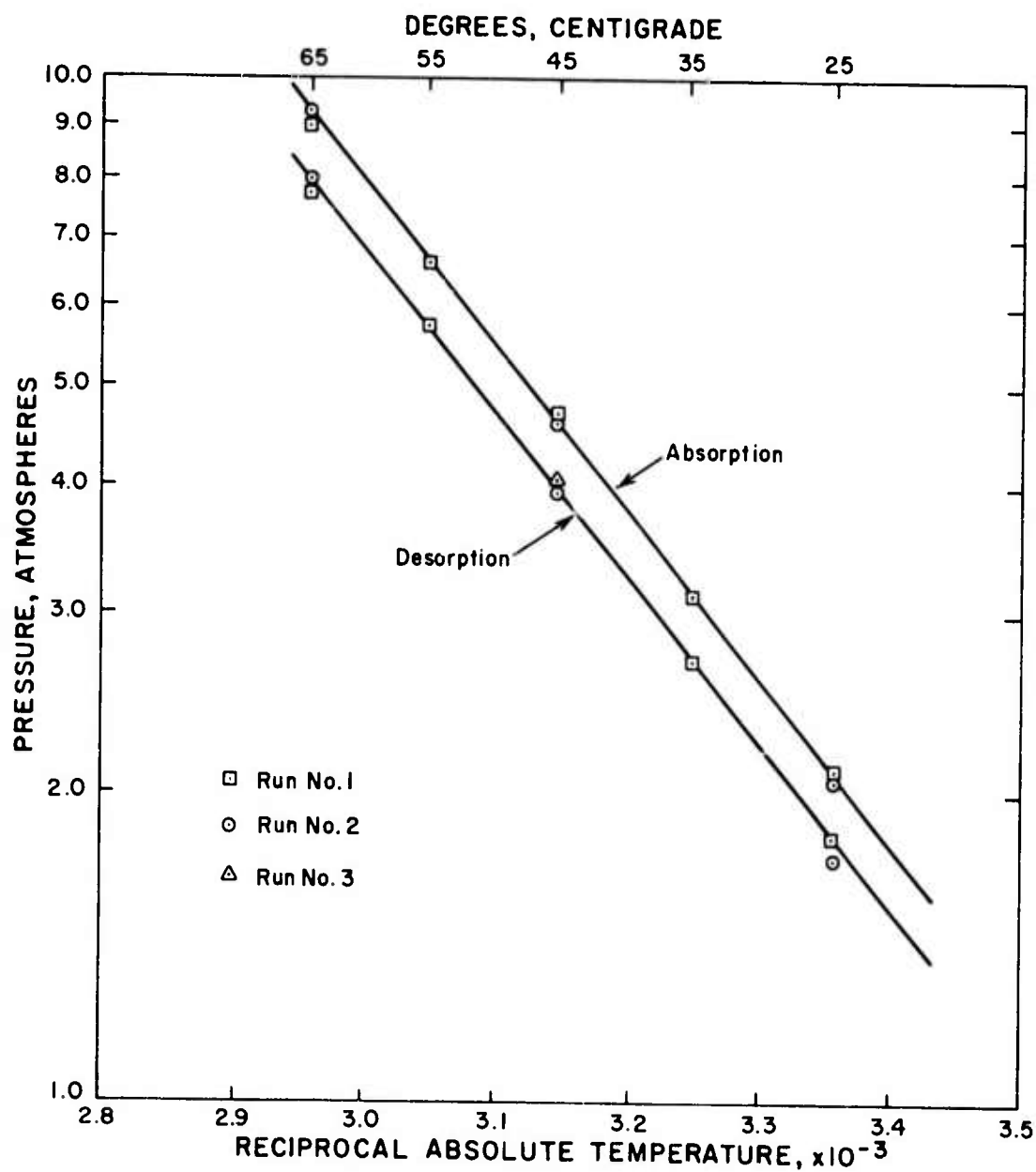


Figure 16. Van't Hoff Relationships for Absorption and Desorption Equilibria Determined at Constant Composition, 3.0 H/M in the LaNi₅-H System.

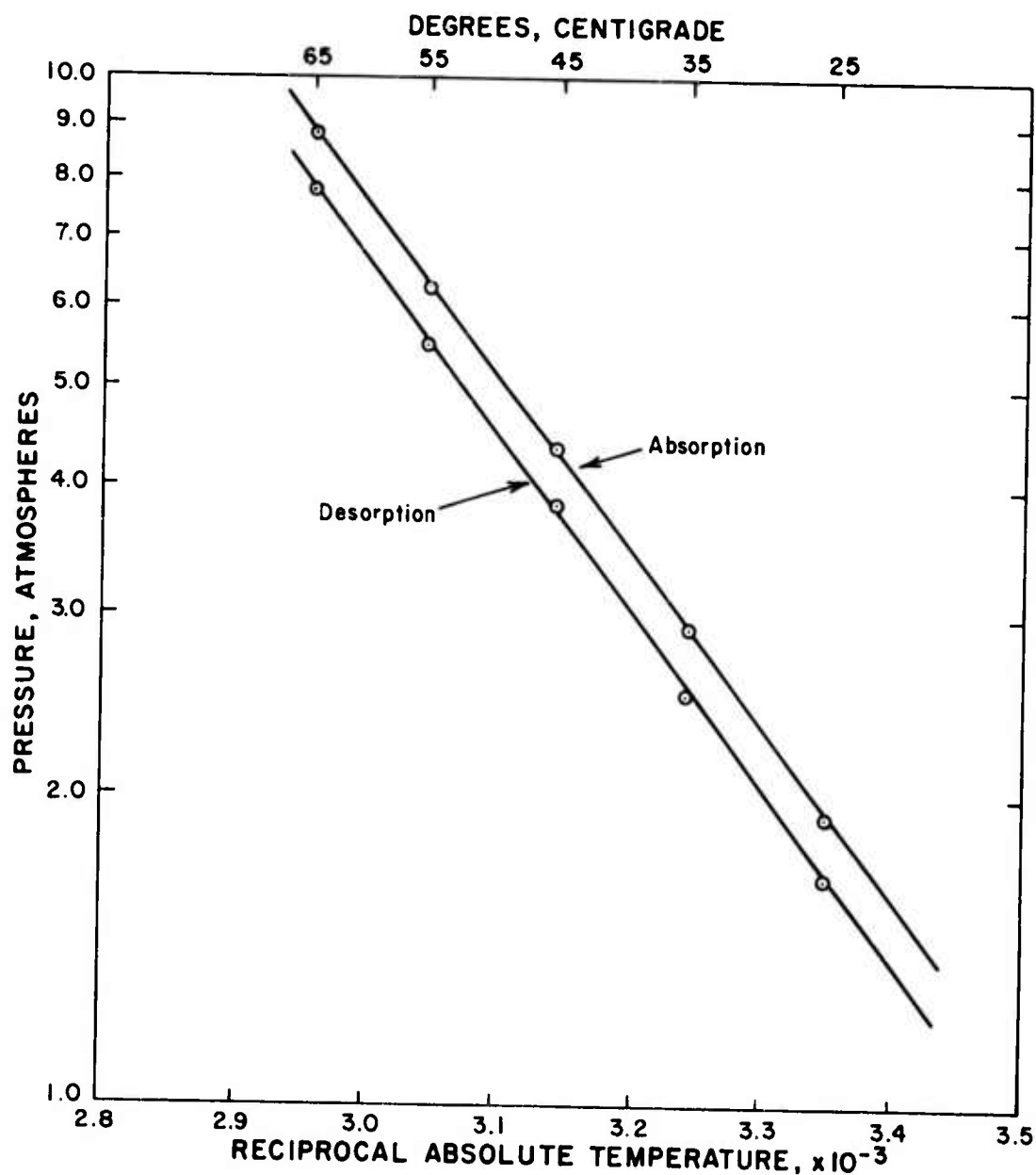


Figure 17. Van't Hoff Relationships for Isothermally Determined Absorption and Desorption Equilibria at 3.0 H/M in the LaNi₅-H System.

the reproducibility of the pressure plateaus. In the case of air exposure, tests were conducted to determine whether LaNi_5 hydride, reacted to full saturation, would passivate by removal from the hydriding apparatus. Samples were transferred at both room temperature and liquid nitrogen temperatures from the pressure hydriding apparatus to a Sieverts apparatus. The samples in either case continued to desorb at room temperature with rapid kinetics in spite of the complete air exposure. Very little reactivation to initiate hydrogen absorption was required when the LaNi_5 was placed back in the pressure hydriding apparatus.

In general, the LaNi_5 intermetallic compound demonstrated surprisingly good resistance to surface passivation to hydrogen passage by water vapor, air, or organic vapor contaminants. Additional studies will be conducted in the near future to more fully and extensively determine effects of vapor and gaseous contaminants.

G. Kinetics of Desorption

1. Literature Survey

In the sections that follow brief summaries are given of recent studies of the kinetics of hydrogen reactions with metal and intermetallic compounds to form solid solutions or hydride phases.

a. The Lithium-Hydrogen System (23)

In this system a hydride phase approaching the stoichiometry, LiH , is formed when hydrogen is reacted with lithium metal.

Experimental Method

A Sieverts apparatus was used with stainless steel reaction tubes. A known amount of hydrogen was added to the system, and the decrease in hydrogen pressure with time was observed.

Observations

Plots of $\log P$ (P =pressure of H_2 gas) versus t (t is the time) at various temperatures were linear for the initial time periods up to about 20 minutes. These data were fit to a first order rate equation of the form:

$$-\frac{dP}{dt} = mkP$$

where k is the first order rate constant and m is the weight of lithium used in the experiment. The inclusion of m in the rate expression takes account of differing surface areas in different experiments. Plots of $\log k$ versus $1/T$ gave an activation energy, E_a , of 6300 ± 2500 cal per mole of hydrogen, and an intercept of 2.09.

After about 20 minutes the rate decreased; this is attributed to the requirement for hydrogen diffusion through solid LiH.

Effects of Heats of Formation

It is mentioned in the report that the heat of formation of LiH caused local heating within the reaction tube. In one instance it was observed that the temperature rose from 150°C to 460°C in a time of two minutes. These local heating effects were not taken into account in the analysis of the experimental results.

b. The Niobium-Hydrogen System (24)

In this system the amount of hydrogen absorbed by niobium approaches a hydrogen to niobium ratio of 0.8. However, except at relatively low temperature and very low pressures, this is but a single condensed phase: a solution of hydrogen in niobium.

Experimental Method

A Sieverts apparatus was used in which cylindrical niobium specimens were suspended under vacuum. From thermodynamic data the temperature required to achieve a certain H/Nb ratio at one atmosphere pressure of hydrogen was determined. The reaction tube was heated to this temperature and hydrogen at one atmosphere pressure was admitted. The pressure was maintained at one atmosphere by adjusting the volume of the gas in the burette. The kinetic data were obtained by observing the burette volume change as a function of time.

Observations

At temperatures up to 550°C the initial reaction rate for all H/Nb ratios studied were observed to be linear. This means that a plot of hydrogen versus time is linear. In kinetic terms this translates to a reaction of the 0th order, i.e., the rate of reaction is independent of concentration. In the linear region the activation energy, which depends on the H/Nb ratio, is of the order of 35 kcal/mole.

At higher temperatures (600° - 700°C) the reaction is apparently diffusion controlled, i.e., the rate is called parabolic. In kinetic parlance this means that the rate is of the (-1)th order. The activation energy determined in this temperature range is 9370 ± 600 cal. per gram atom.

c. The Titanium-Hydrogen System Solid Solubility Region (25)

Titanium does form a hydride phase, but the study is restricted to the single condensed phase region of hydrogen solubility in the metal.

Experimental Method

A Sieverts apparatus was used in which cylindrical specimens of partially hydrided titanium were heated to temperatures from 650° to 1020°C under vacuum. The amount of hydrogen evolved as a function of time was measured.

Observations

The data were interpreted in terms of Fick's laws of diffusion (this implies a parabolic rate and a reaction order of (-1)'th. Diffusion (or "degasing") coefficients were determined from the experimental data.

d. The Titanium-Hydrogen System, Hydride Phase Region (26)

Unlike niobium, titanium forms a hydride phase different in structure from the solid solution phase observed above.

Experimental Method

In contrast to the volumetric methods described heretofore in this section of this study have been interpreted to be consistent with a rate equation of the following type:

$$\frac{dw}{dt} = kP^{1/2}$$

where w is the weight gain and P is the pressure of hydrogen. The significance of this $1/2$ order rate equation is obscure.

e. The Uranium-Hydrogen System (27) and the Thorium-Hydrogen System (28)

The two studies referred to above are excellent; what effect the theoretical aspects of these studies will have on our work is yet to be determined. Suffice it then for now to merely quote the abstracts of these papers, with comments and analyses reserved for subsequent reports.

"The reaction kinetics of $U_3O_8/2H_2 \rightleftharpoons UH_3$ was studied with fine powders on an ultrahigh-vacuum microbalance. The kinetics were found to be first order with respect to uranium for the hydriding reaction and nearly zero order with respect to uranium hydride for dehydriding. A new reaction mechanism is proposed to account for the experimental observations which involves diffusion in the reactant phase by hydrogen before nucleation to form the hydride phase. This reactant phase diffusion and phase transformation reaction with its associated solid state mathematics accounts for all the observations made to date on the kinetics of this system."

"The reaction between thorium and hydrogen, which produced a surface layer of thorium dihydride, was shown to follow the parabolic rate law. At pressures slightly greater than the dissociation pressure of the dihydride, the absorption rate was very dependent on the pressure, but at higher pressures the pressure dependency was less pronounced. Increasing the temperature accentuated the pressure dependency of the absorption rate at the higher pressures. The temperature dependency of the absorption rate satisfied an Arrhenius type equation at temperatures below 550° when the pressure was held constant at 120 mm. The activation energy for diffusion was found to be about 19.6 kcal. The absorption rate was the same for annealed thorium of two purity levels and for cold-swaged thorium."

f. The LaNi_5 - Hydrogen System (29) and the SmCo_5 - Hydrogen System (30)

The LaNi_5 intermetallic compound will absorb hydrogen at room temperature to form a hydride of composition; $\text{LaNi}_5\text{H}_{6.7}$. The hydride retains the hexagonal structure of the parent intermetallic, but the lattice parameters are significantly elongated (25% volume increase) (2).

In the case of the SmCo_5 intermetallic the hydride is of composition SmCo_5H_3 . There is a change in crystal structure from hexagonal to orthorhombic, accompanied by a volume expansion of about 10%.

Experimental Methods

In the van Vucht, et al. (2) experiments, desorption rates were studied by reducing the external pressure to one atmosphere and observing the fraction of hydrogen desorbed as a function of time at various temperatures. Such measurements were carried out for LaNi_5 , and, at one temperature, for $\text{La}_{0.9}\text{Zr}_{0.1}\text{Ni}_5$ intermetallics. It is specifically stated in the paper that no special precautions were taken to measure the rate isothermally.

Reilly and Wiswall (29) measured the rate of decomposition of the LaNi_5 hydride by allowing the hydride to decompose into a vacuum, and measuring the amount of pressure increase in the system. They minimized the self-cooling effect by adding stainless steel balls to serve as a heat reservoir.

Raichlen and Doremus (30), who studied the SmCo_5 hydrogen system, used the same method as did van Vucht, et al. (2), i.e., they measured the fraction of hydrogen desorbed as a function of time against an external pressure of one atmosphere. No mention is made in this paper of the effect of self-cooling during the desorption process.

Observations

The study of van Vucht, et al. (2) showed that after several cycles of hydriding and dehydriding the kinetic data stabilized to the extent that plots of percent hydrogen evolution versus time were realizable. These plots (for LaNi_5) are initially linear for temperatures from 18°C to 49°C ; they then bend off sharply, especially at the higher temperatures, as the percentage of decomposition approaches 100%. The linearity of the plots at short times implies 0'th order kinetics and the authors have estimated an activation energy from these linear plots of about 12 kcal per mole H_2 . Nothing is said in this paper with respect to the curvature of these plots at longer times.

In the Reilly and Wiswall (29) report on the dehydriding of LaNi_5 hydride, a correlation was made between the logarithm of the amount of undecomposed hydride and the time. That is, a linear plot was obtained between $\log(\text{hydride})$ versus time. This corresponds to 1st order kinetics, and 1st order rate constant at 30°C is given as 0.10 sec.^{-1} . The activation energy is not given in this report.

The percent hydrogen desorbed versus time curves obtained by Raichlen and Doremus (30) for the SmCo_5 -hydrogen system are similar to those obtained by van Vucht, et al. (2) for the LaNi_5 -hydrogen system. However, Raichlen and Doremus have attempted to interpret their data in terms of a rate determining step. While their analysis is quite complex, in short it can be summarized by stating that they conclude that it is not diffusion of hydrogen out of the hydride that controls the rate, but rather, the transformation of orthorhombic hydride to hexagonal intermetallic. The activation energy reported in this study is, again, 12 kcal per mole.

g. Conclusions from the Literature Survey

It is quite apparent that no simple picture appears with respect to the kinetics of hydriding or dehydriding of metals and intermetallic compounds. There are cases of 0'th order, 1'st order, (-1)'th order and complex order kinetics, depending on the particular system under investigation. It is certainly obvious that diffusion controlled rates are not dominant in these systems. There are so many variables: surface area, condition of the surface, purity of the gas, volume changes upon hydriding, etc., that every potentially practical hydride system must be investigated properly and systematically to determine its own idiosyncrasies. One problem peculiar to these systems is that of local or bulk temperature changes due to exothermic or endothermic absorption or desorption reactions in short periods of time.

2. Equipment

Attempts to use the initially constructed hydriding apparatus for kinetics of desorption measurements were found to be awkward because of heavy use for the determination of PTC data for the $\text{LaNi}_5 - \text{H}$ system and because of lack of specific flexibility for the kinetics measurements.

Therefore, another apparatus was constructed and is now currently being employed for these measurements. The reaction chamber is copper and the sample is mixed with a preponderance of -150 mesh copper powder. The copper acts in two ways: to increase the thermal conductivity to maintain isothermal conditions as closely as possible, and to provide a large thermal sink. The copper powder is lightly pressed with the LaNi_5 hydride powder to increase the contact area. The copper reaction chamber has been machined with heat transfer fins on the exterior surface. Thus, the surface area is greatly increased which will aid in maintaining as close to isothermal conditions as possible. Additionally, the entire reaction chamber is placed in a stirred water bath controlled to the reaction temperature.

The remainder of the system is similar in all respects to the hydriding system described in Section VII, A, 1, with one exception. The system is compact enough to bake-out at elevated temperatures (up to 150°C) and has a liquid nitrogen trap interposed between the fore pump and the system to prevent back streaming of oil vapor. Also, the fore pump will be provided on the downstream side with a gas collection and measurement system. Thus, one can obtain desorption data in the reaction system against a vacuum.

3. Approach

Studies have been initiated to measure the absorption and desorption data in the range of 25 to 65°C . Principally, data will be taken in the desorption mode, since this is the information of most practical use for applications. Theoretically, it is of interest to compare absorption and desorption to shed some insight on the two mechanisms and how they relate to the observed hysteresis, if this is the case.

Preliminary data have been taken at 25, 45, and 65°C both in the absorption and desorption modes. Investigations are continuing in shake-down experiments to optimize the experimental conditions.

VIII. ENHANCEMENT STUDIES OF NEW SYSTEMS

A. Introduction

This phase of the overall program is designed to predict, to search, and to screen for alloys that appear to have promise as potential unstable hydrides. The ultimate objective is to develop hydrides that demonstrate excellent storage and retrieval of hydrogen capabilities for subsequent power or energy applications. Generally, the properties sought for the ideal storage material are as follows:

1. High saturation capacity for hydrogen
2. Low density of metal or hydride
3. Low heat of reaction
4. Surface passivity to contaminants
5. Rapid kinetics of absorption and desorption
6. Near ambient pressure-temperature relationships
7. High thermal conductivity
8. Low heat capacity
9. Ability for indefinite recycling
10. Safe materials to handle and use
11. Low cost materials

The achievement of all these properties in one hydride is obviously not possible. However, many of them can be attained or improved over those of the hydrides currently known. The compromise that one can achieve, then, must suit efficient use, practical operation, and reasonable cost criteria. Certainly the currently known unstable hydrides are far from ideal. Intuitively, one feels that enhancement will come with the appropriate research and development.

B. Approach

The outline of the most appropriate program for the alloys is difficult because so many possibilities exist. The field is wide open because the area of unstable hydride technology is relatively new. Stable hydrides have been in existence for many decades, but only a few unstable types have been identified since their discovery in 1969. One must narrow down the possible approaches in an optimum manner and attempt to be selective by applying general principles deduced from hydride theory. However, a fundamental understanding of the elemental properties that are prerequisites for

an optimum unstable hydride is poorly developed because of the lack of previous experimentation. It is one of the objectives in this study to develop these insights in the process of searching and screening for alloys.

The selection of materials has now been completed after careful analysis. Binary, ternary, and quaternary systems were selected. The characteristics that were taken into account in this analysis were as follows:

1. For intermetallic compounds, the selection of structure-types that are compatible with hydriding were chosen.
2. For ternary compositions, a rationale for selection was followed, such as the search for possible pseudo-binary systems for solid solutions of binary intermetallic compounds.
3. Considerations of the valence, the atomic diameter, electron concentration, size of interstices, and electronic structure were taken into account as one would with the stable hydrides.
4. A liberal use of transition metals in Groups III, IV, and V transition metals was sought because of their known propensity to hydrogen occlusion.
5. The avoidance of the surface-active elements because of the possible poisoning activity was stressed.
6. The selection of predominantly brittle materials was made, since microfracture is felt to be a criterion of optimum kinetics of desorption.
7. Attention was closely paid to the ternary and quaternary phase equilibria in the rationale of selection.
8. Selection was made of elements of the system which are reasonable in cost, although this was not always followed if some fundamental insights could be divulged.
9. The use of elements in the alloy systems with a density of less than about 8.5 grams/cc, was generally followed for the practicality of application.
10. Quaternary addition elements were selected in some cases for possible passivation of the surface to poisons.

The screening of these alloy systems will be done primarily by activation experiments and by cursory pressure-temperature composition studies. The key factors are total absorptivity and rapid kinetics. Once a promising alloy has been singled out, a more thorough property analysis will be undertaken.

C. Experimental

1. Studies of the V-Cr and Nb-Mo Systems

The V-Cr and Nb-Mo systems were selected because of earlier cursory studies (31) by this author that indicated they may have potential as unstable hydrides. They were found to spontaneously absorb hydrogen at room temperature and relatively lower pressures. The specific alloys that will be screened are:

V - 30% Cr
 V - 40% Cr
 V - 50% Cr
 Nb - 30% Mo
 Nb - 40% Mo
 Nb - 50% Mo

Many of these have already been melted. Studies have been commenced on the V-40% Cr alloy. It was found that it would activate readily at room temperature without raising the temperature as is the case with pure vanadium. A pressure of 600 psi was employed for activation. Some of the sample was transferred to the Sieverts apparatus for analysis below one atmosphere pressure. It was found that absorption would occur at very low pressures at room temperature. A saturation value of H/V-Cr was found at 25°C, and currently, the pressure-temperature-composition relationships are being outlined more fully. The chromium is of interest because of the potential of obtaining a "stainless" surface which will absorb and desorb readily and which will not easily poison.

D. Design and Construction of Ultra High Pressure Hydriding Apparatus

It is a matter of history in the study of metal hydrides that many interesting reactions have gone unnoticed by investigators who have failed to achieve an activation of the material, e.g., Fe Ti, LaNi₅, and the dihydride states of V and Nb.

In this survey of unstable hydrides which are potentially serviceable as fuel storage media, we wish to make certain that all commercially practicable activation conditions are applied to candidate hydride materials before they are rejected as "inactive".

There is also some curiosity in the minds of the authors about the existence of higher hydrides of materials such as the AB₅-alloys or Fe Ti. In both cases more potential hydrogen sites are available in the metal lattice than are filled during normal hydriding reactions carried out at 100 atm or less.

Additionally, many of the known hydride reactions involve a process called "activated chemisorption" which requires that a certain level of kinetic energy be attained by the hydrogen adatom before it can be absorbed past the surface of the metal.

Because of these items of interest to the present study, an ultra-high pressure hydriding apparatus is being constructed which will provide pressures up to 2000 atm (30,000 psi). Little information is available on the reactions of hydrogen in this pressure regime presumably because it is very difficult to produce and handle hydrogen at this pressure by conventional techniques.

Known metal hydrides such as mischmetal-nickel hydride can provide phenomenal pressure merely by heating them in a closed system to moderately high temperatures. This means of attaining high pressures also avoids traditional contamination problems which arise from the pump oil vapor in multistage high pressure pumps.

The system will be assembled from commercially available components designed for use at the pressure and temperature conditions desired for this testing program.

The apparatus is extremely simple and rugged. Two reaction chambers and all necessary valves and fittings were obtained from High Pressure Equipment Company of Erie, Pa. One chamber, termed the pump, will contain an unstable hydride such as mischmetal nickel hydride and will be fitted with a pressure transducer, an output valve and an input valve. The system will be saturated with hydrogen at room temperature by adding gas through the input valve. It will then be closed and heated until the desired pressure is attained. The output valve is then opened to deliver the hydrogen at ultra-high pressure to the second chamber which contains material to be hydrided. The second chamber also has a pressure transducer and a valve for evacuation.

The entire apparatus will be housed in a suitable explosion shield to protect against failure of any component.

IX. POTENTIAL APPLICATIONS FOR DOD

One of the objectives of the overall program is to assess the potential of applications within DOD. This objective was to be initiated in the third year after the development studies of unstable hydrides was well along towards completion. However, the study of the safety aspects of LaNi_5 recently stimulated interest on the part of several groups in the U.S. Army. This was manifest some months ago by several requests for copies of the paper "Safety Characteristics of LaNi_5 Hydrides" that was presented by Lundin at the THEME Conference in Miami Beach, Florida. Messrs. Larry Miasco of the Propulsion Systems Laboratory, and Edward Rambie of the Fuels and Power Systems group, both of TACOM, were sent papers, and discussions with both by telephone took place in regard to further interest at TACOM. Miasco said there had been earlier studies made of the potential of hydrogen as a fuel for armored vehicles and hydrides as storage media. The conclusions were that although the combustion kinetics of hydrogen were good, the energy density of the hydride was considered too low. Thus the interest was limited, and the idea was relegated to a lower priority. Miasco recommended that contacts be made with Mr. R. D. Quillian, Director of the U.S. Army Fuels and Lubricants Research Laboratory in San Antonio, since he had the responsibility for advanced fuels, and the earlier studies were principally centered there. A telephone call to Mr. Quillian confirmed his former interest and the fact that studies had been made.

After discussing some of the safety work at DRI with him, he expressed renewed interest. The study at DRI had demonstrated that LaNi_5 hydride is relatively "fireproof". The test in which a 30-caliber round was fired into a quantity of the material without explosion or fire, was put forth as evidence, along with other tests which showed the relatively safe properties. Mr. Quillian was intrigued by the possibility of a "fireproof" fuel. Also, he admitted that the subject of fire safety on board armored vehicles hit on a sensitive nerve. It was elicited that energy density could be sacrificed at the expense of such a profound increase in fire safety. He inquired further about Army interest. He later recommended that Dr. John O'Sullivan of the U.S. Army Mobility Equipment Research and Development Center at Fort Belvoir would be interested in learning of this development. A telephone call was placed to Dr. O'Sullivan. He said he was funding some Brookhaven National Laboratory studies. His feeling was that it was premature yet to consider applications until more studies have been conducted. He felt properties could be improved, and hoped that new hydrides could be found. Then, based on a greater selection of hydrides, one might develop more appropriate applications. The use of hydrides as a source for auxiliary power was proposed by Dr. O'Sullivan as a more immediate application.

The matter was not dropped yet at DRI. Further considerations were developed, and an idea proposed for a combined application for armored vehicles, possibly including tanks. Several more cursory experiments were conducted with encapsulated FeTi hydride in a 2 in. diam. malleable cast iron pipe. The three types of 30-caliber ammunition were fired into it at 15 yards range; one standard, the second armor-piercing, and the third a tracer. Again, no fire or explosion occurred. The armor-piercing did penetrate both sides, but the other two were stopped within the pipe.

The idea that developed was to employ encapsulated hydride as a combination fuel and composite armor. In discussions with the personnel in the Mechanics Division at DRI, the concept of the composite armor was not found unreasonable. The hydride granules are rather high density and act as an excellent absorber of high-velocity fragment or ballistic impact energy. One obtains a "sandbag" effect from the high-density hydride granules. Containing the granules in high hardness armor plate modules would present a rather formidable composite armor. The incoming ballistic item would have to penetrate a front wall of hardened plate, a predetermined thickness of high-density hydride granules and another thickness of armor plate which comprises the back wall of this "fireproof" fuel tank - composite armor module. There should be reasonable justification to use these modules as sidewalls and backwalls on an armored vehicle. This is rather a revolutionary concept when one has normally thought of placing the fuel tanks in the rear out of the way.

Cursory calculations were made as far as weight and fuel considerations. If one considers the specifications and how one might modify an M-59, armored personnel carrier for this application, some interesting facts are revealed. It was calculated that 6,800 lbs. of FeTi hydride, replacing 400 lbs. of gasoline, would fuel the 22 ton vehicle for a range of 200 miles. Modules of 2 in. inner-thickness and 90 sq. ft. on each of two sides of the vehicle would be fitted with FeTi hydride fuel. The replacement of the 400 lbs. of gas, an armored gas tank, and some of the bulk of 180 sq. ft. of side armor plate would be more than offset. One gains a relatively fireproof fuel that would stop small arms fire. These calculations were not meant to be definitive, only indicative. Further refinements would have to be made to prove feasibility for the U.S. Army

Based on these considerations discussions by telephone were carried on again with Mr. Edward Ramble of TACOM. He suggested that the idea be presented by formal letter to TACOM, since it now contained elements of interest to various groups there. A letter, suggesting additional TACOM studies on this concept, will be sent to the Commanding General.

IX. REFERENCES

1. J. Zijlstra and F. Westerdorp, *Solid State Communications*, Vol. 7, p. 857, 1969, Pergamon Press.
2. J. H. N. van Vucht, F. A. Kuijpers, and H. C. A. M. Bruning, *Philips Res. Reports*, 25, (1970) 133-140
3. F. A. Kuijpers, *J. Less-Common Metals*, 27 (1971) 27.
4. F. A. Kuijpers and N. H. Van Mal, *J. Less-Common Metals*, 23 (1971) 395.
5. K. H. J. Buschow and N. H. van Mal, *J. Less-Common Metals*, 29 (1972) 203.
6. H. H. van Mal, K. H. J. Buschow and F. A. Kuijpers, *J. Less-Common Metals*, 32(1973) 289-296.
7. N. H. van Mal, K. H. J. Buschow and A. R. Miedema, *J. Less-Common Metals*, 35 (1974) 65-76.
8. J. J. Reilly and R. H. Wiswall, *Inorg Chem* 6 (1967) 2220.
9. J. J. Reilly and R. H. Wiswall, *Inorg Chem* 9 (1970) 2252.
10. J. J. Reilly and R. H. Wiswall, *Inorg Chem* 9 (1970) 1678.
11. R. H. Wiswall and J. J. Reilly, *Inorg Chem* 11 (1972) 1691.
12. J. J. Reilly and R. H. Wiswall, "Metal Hydrides for Energy Storage", BNL-16889, 7th Intersociety Energy Conversion Engineering Conf. San Diego, Sept. 1972.
13. J. J. Reilly and R. H. Wiswall, "The Effects of Minor Constituents on the Properties of Vanadium and Niobium Hydrides", BNL-16546, International Meeting on Hydrogen in Metals", Julich, Germany, March 1972.
14. D. H. W. Carstns and J. D. Farr, "The formation of Niobium Dihydride from Niobium Catalyzed by LaNi_5 ", LA-UR-73-415, Los Alamos Scientific Laboratories, N. Mexico, January, 1973.
15. J. J. Reilly and R. H. Wiswall, "The Formation and Properties of FeTi Hydride", BNL - 177711, Aug. 1973.
16. D. P. Gregory, "A Hydrogen-Energy System", Institute of Gas Technology, American Gas Assn., Chicago, Ill. (1972).
17. J. Jaffee, Report NOLTR 65-67, April 1965, U. S. Naval Ordnance Laboratory, Maryland.

18. S. Stein, Technical Report 2636, Sept. 1956, Picatinny Arsenal, Dover, N. J.
19. H. G. Dorsett, M. Jacobson, J. Nagy, R. Williams, RI 5624, 1960, U. S. Bureau of Mines.
20. M. Jacobson, A. Cooper, and J. Nagy, RI 6516, 1964, U. S. Bureau of Mines.
21. C. E. Lundin, F. Perkins, R. Sullivan, Final Report DRI No. 2446, Contract No. 57-1971, "Development of Alloys for Envelope Materials", Sandia Laboratories, Albuquerque, N. Mex., Feb. 1968.
22. J. Anderson, T. Wallace, A. Bowman, C. Radosevich, M. Courtney, "Hydrogen Absorption by AB₅-Compounds", LA-5320-MS, Los Alamos Scientific Laboratory, July 1973.
23. Edwin E. Swain, Jr. and Frederick K. Heumann, "The Reaction Between Lithium and Hydrogen at Temperatures between 29°C-250°C, Knolls Atomic Power Laboratory, Schenectady, New York, KAPL-1067, March, 1954.
24. W. M. Albrecht, W. P. Goode, and M. W. Mallett, Journal of the Electrochemical Society, 106, No. 11, 981-986 (1959).
25. W. M. Albrecht and M. W. Mallett, Transactions of the Metallurgical Society of A.I.M.E., 204-210, April 1958.
26. E. A. Gulbransen and K. F. Andrew, Metals Transactions, 185, 741-748 (1949)
27. J. B. Condon and E. A. Larsen, The Journal of Chemical Physics, 59, 855-865 (1973).
28. D. T. Peterson and D. G. Westlake, Phys. Chem, 63, 1514-1516 (1959).
29. J. J. Reilly and R. H. Wiswall, Jr., "Hydrogen Storage and Purification Systems", Brookhaven National Laboratory, BNL 17136, August 1972.
30. J. S. Raichlen and R. H. Doremus, Journal of Applied Physics, 24, No. 8, 3166-3170 (1971).
31. R. D. McCarty and Lloyd A. Weber, "Thermophysical Properties of Parahydrogen from the Freezing Liquid Line to 5000 R for Pressures to 10,000 Psia", Technical Note 617, U. S. Dept. of Commerce, National Bureau of Standards, April 1972.

ACKNOWLEDGMENTS

The authors are grateful to the Advanced Research Projects Agency for their support of this research. The contract is No. F44620-74-0020 and is being monitored under the auspices of AFOSR.

CEL