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A SUMMARY OF THE LITERATURE ON RARE EARTH AND TRANSITION METAL HYDRIDES
(Title is Unclassified)

[redacted]

L. C. Beavis, 1413

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ABSTRACT

This report is a summary of the literature readily available through December 1961 on the rare earth and transition metal hydride systems. It is not meant to be all-inclusive. Only reports containing data on properties which are of particular interest to those working in the field of neutron generator design are [illegible]

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March 1962

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A SUMMARY OF THE LITERATURE ON RARE EARTH AND TRANSITION METAL HYDRIDES

Introduction

This report consists of two sections. The first is concerned with hydrides and the second with the interesting pure metals and their nonhydrogenous alloys. The author's original abstract is included when possible along with comments by the author of this memorandum. The titles are compiled in order of publication.

No attempt at making a complete summary of all available literature on the title subject was attempted: first, it would have resulted in a large volume; second, many good surveys are available and are mentioned in this memorandum.

Finally, no attempt at critical comment on the data reported in the abstracted reports is made. There are few expert enough to make such critiques and the author does not consider himself one of the few.

PART I

HYDROGEN IN METALS

Smith, D. P.

University of Chicago Press, 1948

This is the only compilation of hydride data prior to 1950. It is of more historical interest than practical value because little or no information on the transition metals and rare earth hydrides was available at that time.

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DISSOCIATION PRESSURES OF URANIUM HYDRIDE AND URANIUM TRITIDE

Flotow, H., and Abraham, B.

Argonne National Laboratory, AECD-3074, 1951

P-C-T data on various UH_3 and UT_3 mixtures are given. These data should be of interest to those forming beds. However, these may not carry over directly to titanium hydride mixtures.

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AN INTRODUCTION TO THE CHEMISTRY OF THE HYDRIDES

Hurd, Dallas T.

John Wiley and Sons, 1952

Another book of primarily historical interest. Gives a brief explanation of the handling of hydrogen in compounds. References to early work are included.

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THE REACTOR HANDBOOK

AECD 3641, Vol. 3, Sec. 1, 1955

The only data on the rare earth hydrides are some rather old (August 1952) van't Hoff equation coefficients for lanthanum, cerium and praseodymium hydrides and some ΔH of hydride formation values which are in good agreement with modern data.

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PRESSURE-TEMPERATURE-COMPOSITION STUDIES OF SOME RARE EARTH/HYDROGEN SYSTEMS

Mulford, Robert N. R., Holley, Charles E., Jr.

Journal of Physical Chemistry, Vol. 59, pp 1222-1228, December 1955

This is a very complete description of the lighter rare earth hydrides.

Authors' Abstract

Pressure-temperature-composition data are presented for the lanthanum, cerium, praseodymium and neodymium hydrogen systems in the ranges T = 150° to 800°C, p = 0.01 to 400 mm. It is concluded that La, Ce, Pr and Nd all behave similarly with hydrogen exhibiting two solid phases, metal and a hydride phase for compositions between M and MH_2, and a single solid hydride phase for compositions between MH_2 and approximately MH_3. (M = La, Ce, Pr or Nd.) In the latter range, composition is dependent on temperature and pressure. The heats of formation of the MH_2 hydride phases as obtained from the pressure-temperature measurements are: LaH_2 49.7, CeH_2, 33.9, PrH_2 47.8 and NdH_2, 44.8 kcal. per mole of H_2. The equations for the dependence of decomposition pressure on temperature are: for LaH_2: $\log_{10} p = 10.758 - 10858/T$; for CeH_2: $\log_{10} p = 7.708 - 7417/T$; for PrH_2: $\log_{10} p = 10.229 - 10446/T$; for NdH_2 $\log_{10} p = 9.370 - 9796/T$ pressures in mm of mercury, temperatures in degrees Kelvin. The heats and equations are actually for the process $xM(\text{sat. with } H_2) + H_2 = xMH_2$ (sat. with metal). The saturation solubilities vary with temperature.

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THE CRYSTAL STRUCTURE OF SOME RARE EARTH HYDRIDES

Holley, C. E., Jr., Mulford, R. N. R., and Ellinger, F. H.

Journal of Physical Chemistry 59, pp 1226-1228, 12 December 1955

This is a companion to the previous abstract.

Authors' Abstract

La, Ce, Pr, Nd and Sm form an isomorphous series of hydrides of composition MH_2 to $MH_{<3}$. X-ray and neutron diffraction data have shown that the MH_2 hydrides have the fluorite-type structure and that the additional hydrogen in the $MH_{>2}$ compositions is statistically distributed in the octahedral interstices of the fluorite structure. The unit cube of the hydride contracts as it takes up hydrogen.

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THE GADOLINIUM-HYDROGEN SYSTEM

Sturdy, Gladys E., and Mulford, Robert N. R.

Journal of American Chem. Society 78 6, pp 1083-1087, 20 March 1956

Describes the work by the authors on gadolinium hydride. This report is undoubtedly the basis for the incorrect assumption of zero differential expansion upon hydriding for gadolinium hydride. The authors, however, do not state that the expansion is zero.

Authors' Abstract

Pressure-temperature-composition data are presented for the gadolinium-hydrogen system. Two hydride phases exist, the first being a cubic structure of ideal composition close to GdH_2, the second being a hexagonal structure of ideal composition close to GdH_3. Both hydrides exist over composition ranges. A partial phase diagram and X-ray data for the Gd-H system are presented. An enthalpy change of -46.9 kcal. per mole of H_2 is obtained from the P-T-C data for the conversion of hydrogen-saturated gadolinium to hydrogen-deficient GdH_2 at temperatures from 600 to 800°.

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SOME PHYSICAL PROPERTIES OF THE HYDRIDES

Elson, R. E., Hornig, H. C., Jolly, W. L., Kury, J. W., Ramsey, W. J., and Zalkin, A.

UCRL-4519, Revised June 1956

LRL - Livermore

This review contains tables of thermodynamic, crystallographic and density data on a wide variety of hydrides. Because of the age of the data some entries are not complete and others may have to be modified to bring this information up to date.

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ZIRCONIUM HYDRIDE

A Compendium on the Systems Zirconium Hydrogen and Hafnium Hydrogen and Related Topics - SRD

Gilbert, P. T., Jr.

NAA-SR-1508

Atomics International, 15 October 1956

A very complete treatment of the hydrides mentioned in the title plus information on other transition element hydrides and binary alloy hydrides.

Some of the work may be getting out of date now, but it is a good place to begin if one is interested in any of the physical and chemical properties of transition metal hydrides.

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THE SYSTEM ZIRCONIUM-NICKEL AND HYDROGEN

Libowitz, G. G., Hayes, Herbert F., and Gibb, Thomas R. P., Jr.

Journal of Phy. Chem. Vol. 62, p. 76, 1958.

This report describes $ZrNiH_3$. It was found that the alloy formed a hydride, approximating the stoichiometric composition of $ZrNiH_{2.93}$. It was less stable than zirconium hydride at elevated temperatures by 10 orders of magnitude in pressure (Diss. pressure = 100 mm at 250°C for $ZrNiH_2$). Noticeable hysteresis in the isotherms is reported.

Authors' Abstract

The interaction of the intermetallic compound ZrNi with hydrogen was studied, and pressure-composition isotherms were obtained at 100°, 200° and 250°. There was no resemblance to the zirconium-hydrogen system. The alloy formed a definite hydride at a limiting composition $ZrNiH_3$, and possibly a second hydride at ZrNiH. X-ray and density measurements on both the alloy and the hydrides indicated a distorted cubic structure for all phases. Hysteresis was observed on the isotherms and a possible explanation for this phenomenon is given on the assumption of lattice defects.

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FABRICATION AND PROPERTIES OF HYDRIDED YTTRIUM - CRD

McCurty, J. A., Funston, E. S., Bohlander, K. M.

APE529

General Electric Aircraft Nuclear Propulsion Department, February 1959

Gives data on yttrium hydride and alloys of yttrium. Also some data on hydrogen diffusion through an iron-chromium-aluminum alloy.

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PROCEEDINGS SECOND METAL HYDRIDE CONFERENCE October 14, 15, 16, 1959

LAB-6 - SRD

A number of presentations on metal hydrides and how they can be applied to reactors. The experimental techniques described are of more interest than the actual information on properties.

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THE HYDRIDES OF THE RARE EARTH METALS

Mirheeva, V. L., and Fost, M. E.

Russian Chemical Review, Vol. [illegible]

This is a very good review article which summarizes [illegible] available information on the rare earth hydrides. It, of course, contains a comprehensive bibliography.

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THE NATURE AND PROPERTIES OF TRANSITION METAL HYDRIDES

Libowitz, G. G.

Journal of Nuclear Materials Vol. 2, #1 (1960) pp 1-22

This report is a very good summary of the work on the transition and rare earth hydrides, with the conspicuous exception of yttrium hydride, from about 1947 to 1959. An excellent bibliography is included with the article.

Author's Abstract

The basic chemical and physical properties of transition metal hydrides are reviewed with particular emphasis on the hydride phases rather than dilute solutions of hydrogen in metals. The review includes discussions of the phases present in metal-hydrogen systems, their crystal structures, pressure-composition-temperature relations, thermodynamic properties, and electrical and magnetic properties.

The nature of transition metal hydrides is considered. Evidence is given to show that they are definite chemical compounds (rather than solid solutions) having some degree of ionic character. The large deviations from stoichiometry exhibited by these compounds can be explained on the basis of lattice defects.

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BONDING MECHANISMS IN THE TRANSITION METAL HYDRIDES

Beck, Richard L.

TID-12507

Denver Research Institute, April 1960

This report is an attempt at explaining the observed properties of transition metal hydrides in terms of the type of chemical bond with which the metal and hydrogen are connected.

Author's Abstract

The effective hydrogen radii in the transition metal hydrides were calculated on the basis of crystal geometry and verified by calculations based on Pauling's values for metallic radii. These data showed that the M-H bonds are predominantly metallic, with no more than the predicted 25% ionic character based on electronegativity. Arguments are presented which indicate that uranium does not exhibit its maximum metallic valence in the UH_3 compound. Evidence is also presented which shows that the metal atoms in the rare earth trihydrides are bonded metallically to the first two hydrogen atoms but are bonded ionically to the third hydrogen.

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A REVIEW OF THE RARE EARTH HYDRIDES

Mulford, R. N. R.

AECU-3813

Los Alamos Scientific Laboratory, April 1960

A good review of the rare earth hydrides. Included are data on crystal structures of the different hydride phases, densities of the hydrides, van't Hoff plots, heats of formation and generalized phase diagrams.

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EQUILIBRIA IN THE TITANIUM HYDROGEN AND ZIRCONIUM HYDROGEN SYSTEMS AT LOW PRESSURES

[illegible], V. [illegible], and Prolovskaya, N. G.

Russian Journal of Physical Chemistry, Vol. 34 #5, May 1960, pp 1104-1109

[illegible] only complete set of data of these two systems in the pressure, concentration, temperature [illegible] interest to us.

[illegible] data vary from 0 - 1.77 atomic ratio for Ti and 0-1.81 atomic ratio for Zr. Pressure data [illegible] 10^{-1} to 10^{-7} torr and temperature data are from 100°C to 450°C.

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INVESTIGATION OF DESORPTION OF HYDROGEN AND DEUTERIUM FROM PALLADIUM WITH A PULSED MASS SPECTROMETER

[illegible], Yu. N., and Ionov, N. I.

Journal of Technical Physics - Soviet Physics, Vol. 5 #2, August 1960, pp 195-200

A report which gives conclusive evidence that absorbed hydrogen is atomic but that the surface acts as a catalyst on desorption for recombination to molecular species.

Authors' Abstract

A pulsed mass spectrometer has been used to investigate the possible formation of positive and negative hydrogen ions in the penetration of hydrogen (at pressures from 0 - 120 mm Hg) through a palladium membrane at temperatures of 80 - 750°C. With a mass spectrometer sensitivity of 10^{-12} amp/cm^2, neither positive nor negative hydrogen ions have been observed. In the interaction between the heated palladium membrane and the hydrogen, the number of hydrogen atoms which are formed in the desorption of atoms is less than 1% of the number of hydrogen molecules. In the diffusion through the membrane of an equimolecular mixture of H_2 and D_2 there are effects due to HD molecules; these are produced in amounts corresponding to what one would expect for random formation from H and D atoms.

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SUMMARY REPORT
October 1, 1958 to September 30, 1960
Bapt, Richard L.
Research and Development of Metal Hydrides - SRD
LAB-10

Describes work on zirconium hydride primarily. In addition, however, are P-C-T data on scandium, erbium, dysprosium, gadolinium and titanium in the high pressure > .1 torr and high temperature, > 900°C, region.

Author's Abstract

A detailed study of the fundamental relations in the zirconium-hydrogen system was made in order to clarify the many points of dispute and to evolve a complete picture describing all phases of this system. These data provided the necessary foundation from which an intelligent evaluation of the engineering properties of pure and alloyed zirconium could be made.

Another phase of this work was directed toward an engineering evaluation of means for utilizing the various high cross-section metal hydrides in shielding or control applications. These materials would combine the processes of thermalization and absorption. Consequently, they are of considerable interest for use in shielding or controlling epithermal reactors.

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HYDRIDES OF RARE EARTH METALS AND THEIR PRACTICAL APPLICATIONS
Mitchayeva and Kost
GE - XDC - 60-10-63

This is an article of little value because it gives only incomplete P-C-T data on cerium hydrides.

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PREPARATION AND PROPERTIES OF SCANDIUM DIHYDRIDE
McGuire, J. C., and Kempter, C. P.
Journal of Chemical Physics, Vol. 33 #5, 11/60, pp. 1584-1585

The only generally available report on scandium hydride. It reports that scandium forms a dihydride but no trihydride as do yttrium and lanthanum. The calculated ΔH is 16.62 k cal/mol. It is pointed out that this value of ΔH may be low.

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CHEMICAL THERMODYNAMICS OF MATERIALS AT HIGH TEMPERATURES
Edwards, Russell K.
IIT-246-FR, June 30, 1961
Illinois Institute of Technology

Rather complete P-C-T data on the yttrium and scandium hydrogen systems at high temperature > 850°C is given.

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[illegible] EARTH HYDROGEN SYSTEMS

[illegible] and Hardcastle, Kenneth

[illegible] August 1961

[illegible] California

Data on the high pressure hydrogen systems of scandium, lanthanum, cerium, europium, ytterbium and [illegible] are presented. It was found that lanthanum and cerium trihydrides have heats of dissociation of [illegible] cal/mol of H_2. A hydride of ytterbium $YbH_{2.5}$ was formed under 20 atmosphere pressure. [illegible] No hydrides higher than the dihydride were formed for scandium and europium. [illegible] measurements on the hydrides were made and reported. Nuclear magnetic resonance [illegible] on $LuH_{2.8}$ were made.

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OTHER REPORTS WHICH ARE NOT REFERENCED ELSEWHERE

BIBLIOGRAPHY ON HYDRIDES

Lindsay,

AFCRC-TR-58-561

This bibliography gives primarily hydride data for the elements which are not transition or rare earth.

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MAGNESIUM HYDROGEN SYSTEM

Journal of American Chemical Society, 82, 3504 (1960)

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NIOBIUM HYDROGEN SYSTEM

Kamiatky, S.

Journal of Less Common Metals, 2 (1960) 466-480

Some references on yttrium hydride furnished by Richard L. Beck of DRI in a private communication which are not included elsewhere.

GE ANPD	Apex 308	5/6/1957
	Apex 334	8/1/1957
	Apex 349	11/15/1957
	Apex 360	2/20/1958
	Apex 449	5/20/1958
	Apex 424	8/20/1958

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PART II

CONSTITUTION OF BINARY ALLOYS - 2nd Edition

Hansen, M.

McGraw Hill Book Co., New York, N. Y., 1958

A general survey of binary alloy phase data, with some data on the rare earth alloys included.

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DYSPROSIUM-LITERATURE SURVEY

Wasielewski, G. E.

KAPL-M-GEW-1, 11/10/58

Knolls Atomic Power Laboratory

The title of this report is a trifle misleading as it contains much information on many of the other rare earths in comparative tables. This report contains information on the chemical and physical properties of dysprosium primarily. In addition some information on alloys and compounds is included. The bibliography included is of value.

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THE PROPERTIES OF THE RARE EARTH METALS AND COMPOUNDS

Gibson, J. A., Miller, J. F., Kennedy, P. S., and Rengstoff, G. W. P.

Battelle Memorial Institute, May 1, 1950

This is a very good compilation in tabular form of the physical and chemical properties of the pure rare earths, and yttrium, and their alloys and compounds. Included are a large number of phase diagrams. Little information on the hydrides is included.

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TECHNICAL DATA

Lindsay Chemical Division, American Potash and Chemical Corporation, West Chicago, Illinois

R-7-1059 and R-6-859

Gives a summary and physical and chemical properties of rare earth metals and yttrium.

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RARE EARTH MINERALS AND METALS

Parker, J. G.

Bureau of Mines Mineral Yearbook 1960 (Supt. of Documents, U. S. Government Printing Office, Washington, D. C.)

Lists domestic suppliers of rare earths, the general purification techniques and some potential uses.

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ELECTRICAL RESISTIVITY OF THE HEAVY RARE-EARTH METALS

Colvin, R. V., Legvold, S., and Spedding, F. H.

Phy. Rev. Vol. 120 63, November 1, 1960, pp 741-745

Authors' Abstract

The electrical resistivities of polycrystalline Gd, Tb, Dy, Ho, Er, Tm and Lu have been measured between 1.3°K and room temperature. The slope of the resistivity curve for Gd changes near the Curie point. The curve for Tb is very much like that for Gd but there is some evidence that two ordering temperatures exist for this metal. Dy, Ho, and Tm all show peaks in resistivity near their Neel points, while Er shows only a change in slope at its Neel point. The change from ferromagnetism to antiferromagnetism in Dy is seen as a sharp rise in the resistivity.

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RARE EARTH ALLOYS

Gschneider, K.

Van Nostrand, Princeton, N. J., 1961

The most complete and best treatment of the rare earths and their alloys available with theoretical treatment of alloying. Some hydride data is also included.

Physical and chemical properties are compiled as well as a great number of phase diagrams.

Gschneider is familiar enough with the field to make estimates of the value of the data he has collected and has attempted to resolve disparities where they exist.

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THE RARE EARTHS

Edited by Spedding and Daane

John Wiley & Son, Inc., New York, N. Y., 1961

The compilation of the papers presented at the first Rare Earth Symposium, November 1959. Covers the entire broad subject of the rare earths and therefore it isn't of as much value as Gschneider's book, which only treats properties of the materials.

The papers in the book are grouped into the following four main topics

I. Occurrence and extraction of rare earths.

II. Preparation of rare earth metals.

III. Properties of rare earth metals and alloys.

IV. Applications of rare earth metals and compounds.

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