

Metal- Hydrogen Systems

Edited by
T NEJAT VEZIROĞLU
University of Miami,
Florida, USA

Pergamon Press

METAL-HYDROGEN SYSTEMS

Other Titles of Interest

ANDRESEN & MAELAND	Hydrides for Energy Storage
INTERNATIONAL ASSOCIATION FOR HYDROGEN ENERGY	Hydrogen in Metals, 3 Volumes
SILVERMAN	Energy Storage
VEZIROGLU & SEIFRITZ	Hydrogen Energy Systems, 5 Volumes
VEZIROGLU et al.	Hydrogen Energy Progress, 4 Volumes

Pergamon Related Journals *(Free specimen copies available on request)*

Acta Metallurgica
Canadian Metallurgical Quarterly
Energy Conversion and Management
International Journal of Hydrogen Energy
Metals Forum
Scripta Metallurgica
The Physics of Metals and Metallography

METAL-HYDROGEN SYSTEMS

Proceedings of the Miami International Symposium on
Metal-Hydrogen Systems, 13-15 April 1981, Miami Beach,
Florida, U.S.A.

Edited by

T. NEJAT VEZIROĞLU, Director,
Clean Energy Research Institute, School of Engineering and Architecture,
University of Miami, Coral Gables, Florida 33124, U.S.A.



PERGAMON PRESS

OXFORD · NEW YORK · TORONTO · SYDNEY · PARIS · FRANKFURT

U.K.	Pergamon Press Ltd., Headington Hill Hall, Oxford OX3 0BW, England
U.S.A.	Pergamon Press Inc., Maxwell House, Fairview Park, Elmsford, New York 10523, U.S.A.
CANADA	Pergamon Press Canada Ltd., Suite 104, 150 Consumers Rd., Willowdale, Ontario M2J 1P9, Canada
AUSTRALIA	Pergamon Press (Aust.) Pty. Ltd., P.O. Box 544, Potts Point, N.S.W. 2011, Australia
FRANCE	Pergamon Press SARL, 24 rue des Ecoles, 75240 Paris, Cedex 05, France
FEDERAL REPUBLIC OF GERMANY	Pergamon Press GmbH, 6242 Kronberg-Taunus, Hammerweg 6, Federal Republic of Germany

Copyright © 1982 Pergamon Press Ltd.

All Rights Reserved. No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means: electronic, electrostatic, magnetic tape, mechanical, photocopying, recording or otherwise, without permission in writing from the publishers.

First edition 1982

British Library Cataloguing in Publication Data

Miami International Symposium on Metal-Hydrogen
Systems (1981)

Metal-hydrogen systems.

1. Hydrogen as a fuel—Congresses

2. Hydrogen Storage—Congresses

3. Metal hydrides—Industrial applications
—Congresses

I. Title II. Veziroğlu, T. Nejat

665.8'1 TP359.H8

ISBN 0-08-027311-4

In order to make this volume available as economically and as rapidly as possible the authors' typescripts have been reproduced in their original forms. This method unfortunately has its typographical limitations but it is hoped that they in no way distract the reader.

Printed in Great Britain by A. Wheaton & Co. Ltd., Exeter

MIAMI INTERNATIONAL SYMPOSIUM ON METAL-HYDROGEN SYSTEMS

13-15 April 1981
Miami Beach, Florida, U.S.A.

Presented by:

Clean Energy Research Institute
School of Engineering and Architecture
University of Miami
Coral Gables, Florida, U.S.A.

In Cooperation with:

International Association for Hydrogen Energy
International Atomic Energy Agency
International Solar Energy Society
International Association of Housing Science
Florida International University
Florida Solar Energy Center
Department of Mechanical Engineering,
University of Miami

MIAMI INTERNATIONAL CONFERENCE ON METAL-HYDROGEN SYSTEMS

COMMITTEE AND STAFF

Symposium Committee

Arne F. Andresen
Institute for Energy Technology (Norway)

Pierre Azou
Institut Supérieur des Matériaux et de la
Construction Mécanique (France)

Roger E. Billings
Billings Energy Corporation (U.S.A.)

M. R. Louthan, Jr.
Virginia Polytechnic Institute (U.S.A.)

Frank Salzano
Brookhaven National Laboratory (U.S.A.)

Yasuo Sasaki
National Research Institute for Metals (Japan)

John Sheffield (Co-Chairman)
University of Missouri—Rolla (U.S.A.)

Seijirau Suda
Kogakuin University (Japan)

T. Nejat Veziroğlu (Chairman)
University of Miami (U.S.A.)

Staff

Coordinators: Lynn Morris
Lucille Walter
Barbara Berman
Sheila Puryear

Special Assistant: Terri Bolado

Graduate Assistants: S. Bukkapatnam
H. Gürgenci
İ. Gürkan
A. Menteş
R. Samudrala

Undergraduate Assistants: Richard Boorman
Mary Cook
Mark Drews
Cristina Robu

SESSION CHAIRPERSONS AND CO-CHAIRPERSONS

OPENING SESSION

Session Chairperson: J. Catz, University of Miami,
Coral Gables, Florida 33124, U.S.A.

Session Co-Chairperson: J. W. Sheffield, University of
Missouri-Rolla, Rolla, Missouri
65401, U.S.A.

SESSION 1A: GENERAL

Chairperson: M. H. Mendelsohn, Argonne National
Laboratory, Argonne, Illinois
60439, U.S.A.

Co-Chairperson: A. Menteş, University of Miami,
Coral Gables, Florida 33124, U.S.A.

SESSION 1B: HYDRIDE FORMATION

Chairperson: M. R. Louthan, Jr., Virginia Poly-
technic Institute & State University,
Blacksburg, Virginia 24061, U.S.A.

Co-Chairperson: L. N. Blanco, University of Miami,
Coral Gables, Florida 33124, U.S.A.

SESSION 2A: DIFFUSION OF H_2 IN METALS I

Chairperson: S. Talbot-Besnard, C.N.R.S., Ecole
Centrale, 92290 Chatenay, France

Co-Chairperson: L. Poteat, University of Miami,
Coral Gables, Florida 33124, U.S.A.

SESSION 2B: HYDRIDE UTILIZATION

Chairperson: M. Rosso, Brookhaven National Labo-
ratory, Upton, New York 11973, U.S.A.

Co-Chairperson: J. W. Sheffield, University of
Missouri-Rolla, Rolla, Missouri
65401, U.S.A.

SESSION 3A: EMBRITTLEMENT

Chairperson: J. Eckert, Los Alamos Scientific
Laboratory, Los Alamos, New Mexico
87545, U.S.A.

Co-Chairperson: C. de Almeida, University of Miami,
Coral Gables, Florida 33124, U.S.A.

SESSION 3B: HYDRIDE FORMATION II

Chairperson: D. M. Gruen, Argonne National Laboratory, Argonne, Illinois 60439, U.S.A.

Co-Chairperson: İ. Gürkan, University of Miami, Coral Gables, Florida 33124, U.S.A.

SESSION 4A: DIFFUSION OF H₂ IN METALS II

Chairperson: S. Suda, Kogakuin University, Hachioji-shi, Tokyo 192, Japan

Co-Chairperson: B. King, University of Miami, Coral Gables, Florida 33124, U.S.A.

SESSION 4B: STORAGE

Chairperson: M. A. Pick, Brookhaven National Laboratory, Upton, New York 11973, U.S.A.

Co-Chairperson: J. Alexander, University of Miami, Coral Gables, Florida 33124, U.S.A.

SESSION 5A: INTERACTION OF H₂ WITH STRUCTURE

Chairperson: H. S. Cullingford, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87545, U.S.A.

Co-Chairperson: H. Gürgenci, University of Miami, Coral Gables, Florida 33124, U.S.A.

SESSION 5B: HYDRIDE PROPERTIES

Chairperson: F. Reidinger, Brookhaven National Laboratory, Upton, New York 11973, U.S.A.

Co-Chairperson: E. L. Daly, Jr., University of Miami, Coral Gables, Florida 33124, U.S.A.

FOREWORD

The rapid depletion of the fossil fuel resources constitutes a major challenge to the very same civilization which made possible their ready availability in large quantities and low prices. True, the energy arteries of the corporate body of mankind are still fed mainly by fossil fuels; but they are in danger of running dry soon unless new energy sources are made available. Of the fossil fuels, oil and gas are already endangered species. Coal is still abundant, but it has doubtful prospects because it is less convenient to utilize and creates more environmental problems.

Alternative sources of energy are available, but are relatively undeveloped technologically, or are not yet fully utilized. Common to all of these alternative energy sources, such as solar, hydro, wind, ocean, thermal, salinity gradient, geo-thermal, nuclear, biomass and waste energy, is the need for a medium which can carry the manufactured energy to the consumer in a competitive, convenient and environmentally acceptable way. Of the possible candidates, hydrogen promises to be the ultimate energy carrier — to replace oil and natural gas. One of the several possible ways in which hydrogen may be utilized for this purpose is offered by the metal-hydrogen systems.

Hydriding metals and alloys can store hydrogen safely at relatively low pressures and temperatures. Properties of metal-hydrogen systems can be utilized for many useful applications such as heating and cooling, waste heat storage, pumping, pressurizing, heat-pumping, hydrogen purifying, deuterium separation, electricity production, etc. On the other hand, hydrogen affects, sometimes adversely, the mechanical and physical properties of metals in which it is contained. The Miami International Symposium on Metal-Hydrogen Systems has considered all aspects of such systems, both their utility and the mechanical and physical property changes in metals. There were sessions on hydride formation, hydride properties, energy storage, hydride utilization, interaction and embrittlement. In general, this Symposium provided an international platform for researchers in the new and growing field of Metal-Hydrogen Systems, including Metal Hydrides and Hydrogen in Metals Systems, to present their results and take part in the pertinent discussions at the various sessions of the Symposium.

The papers recommended by the chairpersons and co-chairpersons, together with the Keynote Address and the Banquet Speech, are divided into eight chapters by subject. The reader should be advised that it was difficult to classify specifically some of the papers when there was an overlap in the subject matter. In such cases, we tried to make the best possible choice. It is expected that this work will serve as a reference to the latest developments in the field of Metal-Hydrogen Systems.



T. Nejat Veziroğlu
Editor

ACKNOWLEDGEMENTS

The Symposium Committee gratefully acknowledges the support, help and cooperation of the International Association for Hydrogen Energy, International Atomic Energy Agency, International Solar Energy Society, Florida International University, Florida Solar Energy Center, and the Department of Mechanical Engineering, University of Miami.

We also wish to extend sincere appreciation to the Keynote Speaker, Dieter M. Gruen, Argonne National Laboratory, Argonne, Illinois; and to the Banquet Speaker, W.E. Wallace, University of Pittsburgh, Pittsburgh, Pennsylvania.

Special thanks are due to our authors and lecturers, who provided the substance of the Symposium, as published in the present proceedings under the title Metal-Hydrogen Systems.

And last, but not least, our debt of gratitude is owed to the Session Chairpersons and Session Co-Chairpersons for the organization and execution of the technical sessions. In acknowledgement, we list these persons on the following pages.

Organizing Committee
Miami International Symposium
on Metal-Hydrogen Systems

CONTENTS

Chapter 1: General

<i>Keynote Address: Getting Metal Hydrides to do What You Want Them to</i>	3
<i>D. M. Gruen - Argonne National Laboratory (U.S.A.)</i>	
<i>Banquet Speech: The Quest — From Sir Launfal to Kurt Vonnegut</i>	19
<i>W. E. Wallace - University of Pittsburgh (U.S.A.)</i>	
<i>Some Aspects of Hydrogen Distribution in France</i>	33
<i>H. Barthélémy, M. Calixte and C. Barbe - L'Air Liquide (France)</i>	
<i>Hydrogen Fueled Power Plant System</i>	45
<i>K. C. Chatterjee - Jadavpur University (India)</i>	
<i>Development of Hydrogen-Permeable Metal Membranes for the Li/LiH-Process</i>	55
<i>W. Weirich, F. Behr, B. Biallas, F. Flocke, K. Hunsänger and B. Kügler - Lehrstuhl für Reaktortechnik (F. R. Germany)</i>	
<i>On the Hydrogen Isotope Exchange Between TiMn 1.5Hn and Hydrogen in the Gas Phase by Tritium Tracer Methods - Bulk and Surface Properties</i>	71
<i>G. H. Sicking - Institute für Physikalische Chemie (F. R. Germany)</i>	
<i>E. P. Magomedbekov - MChTI imeni D. I. Medeleeva (U.S.S.R.)</i>	

Chapter 2: Diffusion of Hydrogen in Metals

Diffusion of Hydrogen Through Binary Noble Metal Solid Solutions	91
<i>R. B. McLellan - William Marsh Rice University (U.S.A.)</i>	
Hydrogen Diffusion in Zirconium-Niobium Alloys	109
<i>A. Sawatzky, G. A. Ledoux, R. L. Tough and C. D. Cann - Atomic Energy of Canada Limited (Canada)</i>	
Transport Phenomena of Hydrogen Diluted in Argon at High Temperatures	121
<i>A. E. Nasser and H. I. Sofrata - University of Riyadh (Saudi Arabia)</i>	
Hydrogen and Tritium Permeation through Steels as a Function of Temperature, Up-stream Pressure and Oxygen Potential	129
<i>D. Stöver, H. P. Buchkremer, R. Hecker, H. D. Röhrig and J. Schaefer - Institute für Reaktorentwicklung (F. R. Germany)</i>	
Analysis of a Cooperative Model of Hydrogen Diffusion in a Transition Metal	141
<i>M. H. Lee and S. Bannerjee - University of Georgia (U.S.A.)</i>	
Neutron Scattering Measurements of Low-Temperature Hydrogen Tunneling in Niobium	155
<i>H. Wipf - Technischen Universität München (F. R. Germany)</i>	
<i>A. Magerl - National Bureau of Standards (U.S.A.)</i>	
<i>S. M. Shapiro, S. K. Satija and W. Thomlinson - Brookhaven National Laboratory (U.S.A.)</i>	

Absorption Properties of Mos Stuctures with Transition Metal Gates	165
<i>T. L. Poteat - Bell Laboratories (U.S.A.)</i>	
<i>B. Lalevic - Rutgers University (U.S.A.)</i>	

A CTEM and HVEM Study of Hydride Precipitation in Magnesium	177
<i>T. Schober - Institute für Festkörperforschung (F. R. Germany)</i>	
<i>M. K. Chason - Argonne National Laboratory (U.S.A.)</i>	

Chapter 3: Interaction of Hydrogen with Structure

Mössbauer Study of the Local Hydrogen Distribution Near Substitutional Impurities in β -Pdh _x	187
<i>M. Karger, F. Pröbst, B. Schüttler and F. E. Wagner - Technical University of Munich (F. R. Germany)</i>	

Hydrogen Trapping Behavior in Plain Carbon and Cr-Mo Alloy Steel	197
<i>T. Asaoka - Tokyo Denki University (Japan)</i>	

A Study of Hydrogen Accumulation around Alloying Titanium in Niobium by the Internal Friction Technique	205
<i>G. Cannelli and R. Cantelli - Consiglio Nazionale delle Ricerche (Italy)</i>	

The Phenomenon of Controllable Hydrogen Phase Naklep and the Prospects of its use in Metal Science and Engineering	211
<i>V. A. Goltsov - Donetsk Polytechnical Institute (U.S.S.R.)</i>	

Hydrogenation/Gas-Release Effects in Austenitic Steels: Quantitative Study	225
--	-----

*H. Mathias and Y. Katz - Nuclear Research
Centre (Israel)
S. Nadiv - Technion (Israel)*

Advancement in Electrochemical Method of Investigation on Hydrogen Penetration into Steel During Metal Electrodeposition	251
--	-----

*V. N. Kudryavtsev, S. P. Bagaev, B. F. Ljachov,
K. S. Pedan - U.S.S.R. Academy of Sciences
(U.S.S.R.)*

Delayed Fracture as a Particular Case of Premature Fracture	259
---	-----

*G. Biggiero and A. Borruto - Rome University
(Italy)*

Chapter 4: Embrittlement

Comparison Between the Behavior of Pure and Commercial Unstable Austenitic Stainless Steels in the Presence of Hydrogen	273
---	-----

*D. Nejem, M. Andriamiharisoa, M. Habashi,
J. Galland, S. Talbot-Besnard and P. Azou
Institut Supérieur des Matériaux et de la
Construction Mécanique (France)*

Effect of Grain Size on Threshold Value K_{ISH} in Ageing Martensitic Fe-Ni-C Alloy Cathodically Hydrogenated at Room Temperature	281
---	-----

*M. Tvrđy - Research Institute of Vitkovice Steel
and Engineering Works (Czechoslovakia)
M. Habashi and J. Galland - Ecole Centrale
des Arts et Manufactures (France)
K. Mazanec - Technical University
(Czechoslovakia)*

*P. Azou - Ecole Centrale des Arts et
Manufactures (France)*

Hydrogen Embrittlement of a Steam Turbine Disc
Alloy in Aqueous Environments 293

*R. Rungta - BATTELLE, Columbus Laboratories
(U.S.A.)*

Hydrogen Embrittlement Inhibition in Rare Earth
Modified P/M 4340 Steel 309

*A. A. Sheinker and B. L. Ferguson -
TRW Incorporated (U.S.A.)*

Some Modes of Failure in C.T.S. Crack
Divider Laminated Steel Composites made from
4340 Steel in the Environments of Hydrogen 327

*M. R. Sabayo - Mehran University of
Engineering and Technology (Pakistan)*

Hydrogen Induced Cracking in Austenitic
Stainless Steel Weld Metals 339

*T. E. Pérez, M. Solari and J. Ovejero García -
Comisión Nacional de Energía Atómica
(Argentina)*

The Effect of Surface Finish on the Deformation
Characteristics of 1015 Steel at 25°C 347

*B. A. Lewis, M. R. Louthan, Jr., J. Wagner,
R. D. Sisson, Jr., R. P. McNitt and
M. R. Louthan, III - Virginia Polytechnic
Institute (U.S.A.)*

Chapter 5: Hydride Properties

Preparation and Properties of $\text{Pd}_{1-y}\text{Ni}_y\text{D}_x$ Alloys 357

*L. Sniadower - Polish Academy of Sciences
(Poland)*

*L. Dumoulin, P. Nedellec and J. P. Burger -
Université Paris-Sud (France)*

Electronic Properties and Equilibrium Lattice
Parameters of Magnesium Hydride 367
*G. Krasko - University of Tübingen
(F. R. Germany)*

Electronic Structure and Non-Occurrence of
Superconductivity in ZrH_2 and NbH_2 381
*M. Gupta - C.M.O.A. and Université Paris-
Sud (France)*

Equilibrium and Susceptibility Measurements
About the Critical Region of the Pd/H_2 System 393
*E. Wicke and J. Blaurock - University of
Münster (F. R. Germany)*

Chapter 6: Hydride Formation

Hydriding Properties of Al-Substituted Misch-
Metall Nickels 407
*S. Suda and Y. Komazaki - Kogakuin University
(Japan)*

*M. Miyamoto and K. Yoshida - Sekisui Chemical
Industry, Ltd. (Japan)*

Non-Metal Absorption by Rare Earth-Silicon
Systems 415
*T. W. Button and I. J. McColm - Bradford
University (England)*

Hydride Formation by Nickel, Palladium and
Platinum 423
*F. A. Lewis and S. G. McKee - The Queen's
University of Belfast (Northern Ireland)*

- Hydrogen Absorption in Aluminium - Magnesium -
Titanium Alloys 437
*D. Lupu, A. Biris, R. V. Bucur, E. Indrea
and M. Bogdan - Institute of Isotopic and
Molecular Technology (Romania)*
- Thermodynamics of $\text{LaNi}_5 + \text{H}_2$ By Differential
Heat Flow Calorimetry: Hysteresis and Entropies 445
*J. J. Murray, M. L. Post and J. B. Taylor -
National Research Council of Canada (Canada)*
- Hydrogen Sorption in Tungsten Trioxide 451
*P. A. Sermon and A. R. Berzins - Brunel
University (United Kingdom)*
- Hydrogen Vanadium Pentoxide Bronze, $(\text{H}_x\text{V}_2\text{O}_5)$ 459
*D. Tinet, H. Estrade-Szwarczkopf and
J. J. Fripiat - Centre de Recherche sur les
Solides à Organisation Cristalline Imparfaite
(France)*
- Reaction Kinetics of the Magnesium Nickel Alloys
and Hydrogen Systems 467
*S. Ono, E. Akiba and K. Imanari - National
Chemical Laboratory for Industry (Japan)*
- Isotopic Effects in Hydrides of Lanthanum-
Nickel Alloys 477
*D. H. W. Carstens and W. R. David -
Los Alamos National Laboratory (U.S.A.)*
- The Influence of Thermal Cycling on the Acoustic
Emission During Hydride Formation in Niobium 485
*G. Cannelli and R. Cantelli - Consiglio
Nazionale delle Ricerche (Italy)*

Stress Induced in Metal Hydrogen Powder Bed by Hydriding Reaction	489
<i>M. Kawamura and S. Ono - National Chemical Laboratory for Industry (Japan)</i>	
<i>Y. Mizuno - Toyobo Co., Ltd. (Japan)</i>	

Chapter 7: Hydrogen Storage

Metal Hydrides for Hydrogen Storage: A Review of Theoretical and Experimental Research, and Critically Compiled Data	503
<i>G. C. Carter - Cabin John, MD 20034 (U.S.A.)</i>	
<i>F. L. Carter - Naval Research Laboratory (U.S.A.)</i>	
An Assessment of Major Factors Affecting the Hydrogen Discharge Rate in Metal Hydride Hydrogen Storage Beds	531
<i>I. A. El Osery - Nuclear Research Center (Egypt)</i>	
<i>V. Mercea - Institute of Molecular and Isotopic Research (Romania)</i>	
Hydrogen Storage Properties of Titanium-Iron- Beryllium and Titanium-Iron-Aluminum Alloys	539
<i>G. Bruzzzone, G. Costa, M. Ferretti and G. L. Olcese - Genoa University (Italy)</i>	
Hydrogen Storage Properties of Fe-Ti-O Alloys	551
<i>Y. Sasaki and M. Amano - National Research Institute for Metals (Japan)</i>	
Magnesium-Alloy Hydrides	557
<i>J. F. Nachman and D. A. Rohy - Solar Turbines International (U.S.A.)</i>	

A Hydrogen Storage Bed Design for Tritium Systems Test Assembly	601
<i>H. S. Cullingford, M. G. Wheeler and J. W. McMullen - Los Alamos National Laboratory (U.S.A.)</i>	
Storage of Tritium in Metal Hydrides	619
<i>J. M. Yaraskavitch and W. J. Holtslander - Atomic Energy of Canada Limited-Research Company (Canada)</i>	
Chapter 8: Hydride Utilization	
Evaluation of the Argonne Multi-Tube Hydride Heat Exchanger	633
<i>I. Sheft and G. Lamich - Argonne National Laboratory (U.S.A.)</i>	
Evaluating Metal Hydride Energy Conversion Systems	649
<i>S. Suda and N. Kobayashi - Kogakuin University (Japan)</i>	
Chemical Heat Pump/Heat Transformer Based on Metal-Hydrogen Reactions	657
<i>A. Nonnenmacher and M. Groll - Universität Stuttgart (F. R. Germany)</i>	
Use of Vanadium Dihydride for Production of High-Pressure Hydrogen Gas	667
<i>D. H. W. Carstens and W. R. David - Los Alamos National Laboratory (U.S.A.)</i>	
A Chemical Compressor Based on Compacted Metal Hydrides	675
<i>E. Tuscher - Universität Wien (Austria)</i>	
<i>O. J. Eder - Österreichisches Forschungszentrum Seibersdorf (Austria)</i>	
<i>P. Weinzierl - Universität Wien (Austria)</i>	

Studies on High Temperature Reactor Cooling Gas Purification by Means of Getters	681
<i>K. D. Fischmann - INTERATOM GmbH (F. R. Germany)</i>	
<i>H. D. Röhrig - Kernforschungsanlage Jülich (F. R. Germany)</i>	
Hydrogen Absorption and Temperature Programmed Desorption (TPD) Studies of Iron and Chromium Substituted ZrV_2	691
<i>M. H. Mendelsohn and D. M. Gruen - Argonne National Laboratory (U.S.A.)</i>	
Cooling and Heating Power of a Modular Heat- Exchanger Filled with PMH	701
<i>M. Ron, U. Navon and I. Levitas - Israel Institute of Technology (Israel)</i>	
Author Index	713
Subject Index	715

Chapter 1

GENERAL

This page intentionally left blank

Keynote Address

GETTING METAL HYDRIDES TO DO WHAT YOU WANT THEM TO*

D. M. Gruen

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439, USA

Metal hydride research is becoming a rapidly growing branch of materials science, due in part to the challenges presented by this field for modifying metal hydrides in such a way as to make them truly useful. Binary metal hydrides have of course been known for a very long time, but it was not until about ten years ago, with the discovery of the AB₅ compounds at the Phillips Laboratories in Eindhoven, that intermetallic hydrides with truly unusual properties began to be developed. These properties are now very familiar to us: (1) the hydrogen dissociation pressures are one to several atmospheres near ambient temperatures; (2) the kinetics of absorption and desorption are extremely rapid, in many cases being limited by the heat transfer characteristics of the materials; (3) the reactions are thermally reversible; (4) the amount of hydrogen stored in these materials is very large, approaching in many cases the volumetric density of liquid hydrogen itself. The intermetallic hydrides are therefore essentially unique in all of chemistry, particularly in displaying thermally reversible reactions with good kinetics. Their ability to store very large amounts of hydrogen is an added bonus.

All these facts were known, in the early 1970's, and it was natural to ask, "What can be done with these materials? They are certainly interesting from a scientific point of view; they have fascinating physicochemical properties; but will they remain laboratory curiosities?" In part, the burden of this paper is to review those factors one must learn to control in order to modify the materials to make them useful. We want to be able to do a kind of materials engineering that will enable one to tailor the properties of the materials for specific tasks. Essentially, that is the problem we faced when we began to work in this field. We had to ask ourselves the question: "What modifications of metal hydrides are required to make these materials optimally useful in particular applications such as chemical heat pumps?" The solution to this problem has turned out to be more generally applicable to other types of metal hydrides than originally anticipated. By gaining an un-

*Work performed under the auspices of the Office of Basic Energy Sciences, Division of Materials Sciences, U.S. Department of Energy.

derstanding of the factors controlling the free energies of formation of the hydrides, one can, in fact, modify the alloys in such a way as to impart certain desired properties.

The familiar phase diagram of the $\text{LaNi}_5\text{-H}_2$ system is shown in Fig. 1. The diagram is characterized by so-called alpha and beta regions, with a rather flat plateau in the region where the alpha phase is being converted to beta. Another characteristic is the increasing hydrogen pressure with increasing temperature. Hysteresis loops are associated with the adsorption and desorption of hydrogen. The compound LaNi_5 has created so much interest, in part, because the hydrogen dissociation pressures are in the range of from one to ten atmospheres at temperatures between 15°C and 75°C .

It occurred to us sometime ago that the AB_5 hydrides could be useful for chemical heat pump systems. A chemical heat pump is essentially a thermally activated engine. With a pair of hydrides having different dissociation pressures at some given temperature, one can, by applying a thermal gradient, cause hydrogen to be transferred from one to the other, and therefore construct a "chemical" heat pump which functions in the same way as an absorption refrigerator whose essential components are a generator, a condenser, an absorber and an evaporator (Fig. 2). To make such a system work, it is essential to have a pair of metal hydrides possessing very specific properties.

How do we obtain the right pair of metal hydrides? If we examine a series of van't Hoff plots (Fig. 3) displaying the logarithm of the hydrogen dissociation pressure plotted against the inverse of the absolute temperature, one has a series of straight lines with different slopes. The different slopes, of course, reflect different enthalpies of hydriding, each one characteristic of a particular metal hydride. We wish to construct a chemical heat pump operating in a temperature regime convenient, for example, for solar energy applications, having a high temperature input of about 100°C and a low temperature input of perhaps 4 to 10°C . In that temperature regime, it is easy to see that the enthalpies of the hydrides for such a device are limited to a very narrow range of values. In order not to be burdened with thick walled vessels, one does not want to operate at pressures that are excessively high, but prefers to be in about the one atmosphere to ten atmosphere pressure range, thus again narrowing the choice of the range of enthalpies of hydriding, to between 7 and 10 kcal/mole of hydrogen absorbed.

Surveying the periodic table of elements, we find that the binary hydrides fall essentially into two classes: those too stable for our purposes, such as CaH_2 or TiH_2 on the one hand, and the unstable hydrides such as FeH and NiH on the other. The intermetallic hydrides, because they are composed of elements forming stable and unstable hydrides, bring the enthalpies into a very convenient range for our purposes. If we examine the thermodynamics for the operation of a chemical heat pump in more detail, we find essentially three types of situations (Fig. 3). First, the pair of metal hydrides can have different slopes, that is, different enthalpies, but the same entropy. Second, they could have different slopes and different intercepts; that is, different enthalpies and different entropies. Third, they could have the same slope and different intercepts, or the same enthalpies but different entropies. One could operate with materials having any of these different enthalpy-entropy characteristics, but the optimal heat pump action would occur for the situation in which the enthalpies of the two hydrides are different, and the entropies are the same. Furthermore, if we examine the

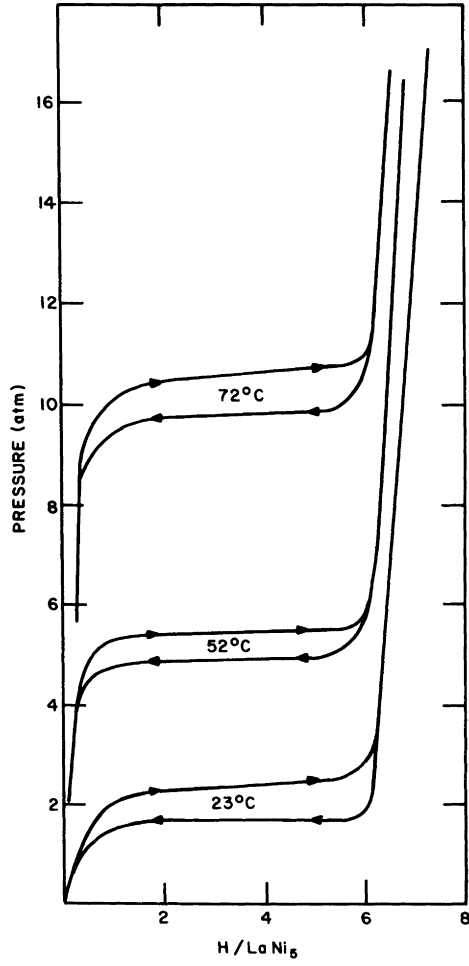


Fig. 1. Absorption-desorption isotherm for $\text{LaNi}_5 + \text{H}_2$

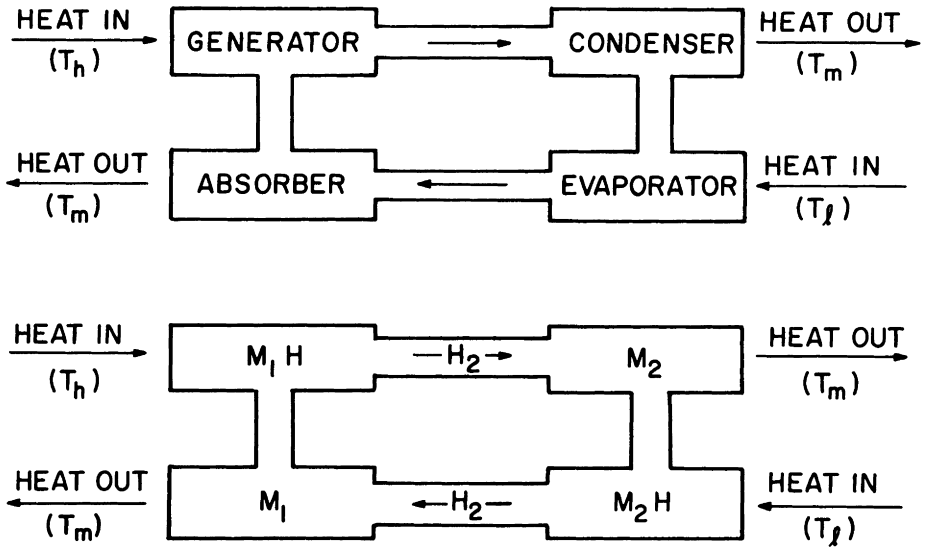


Fig. 2. Two metal-hydride refrigerator cycle.

Fig. 3. Three examples of chemical heat pump thermodynamic relationships.

relationships between the enthalpies and the temperatures, we find that the ratio of the enthalpies of the pair of hydrides $\Delta H_{m1}/\Delta H_{m2}$ is equal to the ratio of the (absolute) high and intermediate temperatures, T_h/T_m , over which one wishes to operate the heat pump. Once a temperature regime has been chosen, the ratio of the enthalpies of the two hydrides is fixed by the laws of thermodynamics.

These relationships are universally applicable to all chemical heat pump systems, whether based on hydrides or ammoniates or alcoholates. Another relationship that can be derived is that the square of the intermediate temperature is equal to the product of the high and low temperatures,

$$T_m^2 = T_h \times T_l .$$

We can use these equations to determine the values which the enthalpies of the pair of hydrides have to have. If one wants to operate at a rejection temperature of 50°C, and have a high temperature input of 109°C, then the low temperature is fixed at 0°C. The second hydride has to have an enthalpy of 8.3 kcal/mole if the first hydride has an enthalpy of 7 kcal/mole. In other words, if ΔH_{m2} is chosen to be that of LaNi_5H_6 , then the other hydride has to have an enthalpy of 8.3 kcal/mole in order to operate the heat pump with an optimum C.O.P. in a temperature regime with $T_m = 50^\circ\text{C}$, $T_l = 0^\circ\text{C}$, and $T_h = 109^\circ\text{C}$. And so it goes: the lower the temperature from which one wishes to pump heat, the higher the input temperature and the higher the enthalpy of the second hydride has to be. For pumping from -10°C , the enthalpy would have to be 8.6 kcal/mole, while for pumping from -20°C , it would have to be 8.9 kcal/mole of H_2 absorbed. These examples illustrate how closely one needs to control the thermodynamic properties of the pair of hydrides in order to use them in an optimal fashion in a chemical heat pump. The first problem one faces in trying to put this idea into practice is to be able to "manufacture" hydrides having appropriate enthalpies and entropies.

How can this be done? When we first began work on this question about five years ago, the answer was unknown. We did know that there were a number of properties that influence to some degree the free energy of hydride formation, and therefore the hydrogen dissociation pressures. Among these are, in the case of LaNi_5 , the lanthanum-to-nickel ratio, as determined by the Eindhoven group. In surveying the literature, one found studies of the thermodynamic properties of quite a few of the AB_5 series of compounds. Plotting the logarithm of their dissociation pressures against the crystallographic cell volume, one obtained a reasonably good correlation, reminiscent of the interstitial-hole volume relationship found by Lundin, for example, at the Denver Research Institute a number of years ago. This correlation was observed not only in the AB_5 system, but in other intermetallic hydride systems as well.

The crystal structure of LaNi_5 may be described in terms of two different layers: one layer contains both La and Ni atoms; the other layer is composed entirely of Ni atoms, and so on.

When one substitutes Group IIIA or IV metals--aluminum, gallium, indium, silicon, germanium and tin--for Ni in the AB_5 structure, the atoms of these elements go into the second layer, the one which, in LaNi_5 , is composed only of Ni atoms.

Austin Dwight, working at the Argonne Laboratory, found a number of years ago, that the element Al substitutes for Ni in LaNi_5 and is particularly

effective in increasing the cell volume of LaNi_5 because aluminum is a larger atom than nickel. The cell volume for the composition LaNi_4Al relative to LaNi_5 has increased some 4 to 5 percent (Fig. 4).

The result of such substitutions on hydride properties is shown in Figs. 5 and 6. The composition $\text{LaNi}_{4.6}\text{Al}_4$, for example, has a substantially lower hydrogen decomposition pressure than LaNi_5 : ~ 1 atm at 48°C , compared to ~ 5 atm for LaNi_5 .

A systematic study substituting Al for Ni was carried out. It turned out that the enthalpy of hydriding is a linear function of the Al content (Fig. 7). Since there is also a linear relationship between the Al content and the cell volume, the enthalpy changes linearly with either the Al content or the cell volume. Furthermore, the entropy changes in these reactions are virtually identical across the series of Al-substituted intermetallics; and therefore the logarithm of the hydrogen dissociation pressure, which is proportional to the free energy change, is a linear function of the Al content as well. It is possible, then, to change the hydrogen dissociation pressure at some given temperature by almost three orders of magnitude by going from LaNi_5 to $\text{LaNi}_{3.5}\text{Al}_{1.5}$ in a continuous fashion. One therefore has a sensitive means of control over a parameter which is so important for heat pump applications. Analogous work has been done by us with all of the Group IIIA and IVA elements. All behave similarly in a qualitative sense, but differ in some details associated with specific chemical bonding and electronic factors. The salient result of this work is that we now know, by changing the chemical composition of the hydrides, how to "tailor" the thermodynamic properties, and therefore the hydrogen dissociation pressures, to an extent that enables us, in fact, to build a chemical heat pump.

The HYCSOS Metal Hydride Chemical Heat Pump System is shown in Fig. 8. There are four vessels containing 10 pounds each of the appropriate hydride filling the interstices between four nesting coils of tubular heat exchangers. The four vessels constitute the four elements of an absorption refrigerator referred to earlier. The status of this system has progressed to an engineering development effort which is being carried out industrially.

Another and totally different application of hydrides is in a very low pressure regime, as low as 10^{-11} or 10^{-12} atm. Of course, the more stable the hydride in a thermodynamic sense, the lower the dissociation pressure. In the case of the heat pump systems, we were working with materials with enthalpies of 7 to 10 kcal; but for materials like zirconium hydride, the enthalpies are ~ 40 kcal, making the hydrogen dissociation pressure so low that the substances are, in fact, hydrogen getters.

One often needs to pump hydrogen down to very low partial pressures in vacuum systems, and one may employ a hydrogen getter for this purpose. The materials suitable for such an application must have very special characteristics. As stated earlier, many elements and compounds form stable hydrides, but very few of them perform the functions of "bulk" getters, which implies an ability to absorb hydrogen at ambient temperatures with good kinetics. Sublimed titanium, for example, can be an active hydrogen getter; however, once the surface of that film has been saturated with hydrogen, the bulk of the titanium will react with hydrogen only very slowly. A material that has been available commercially as a bulk hydrogen getter is ST-101, an alloy of Zr and Al made

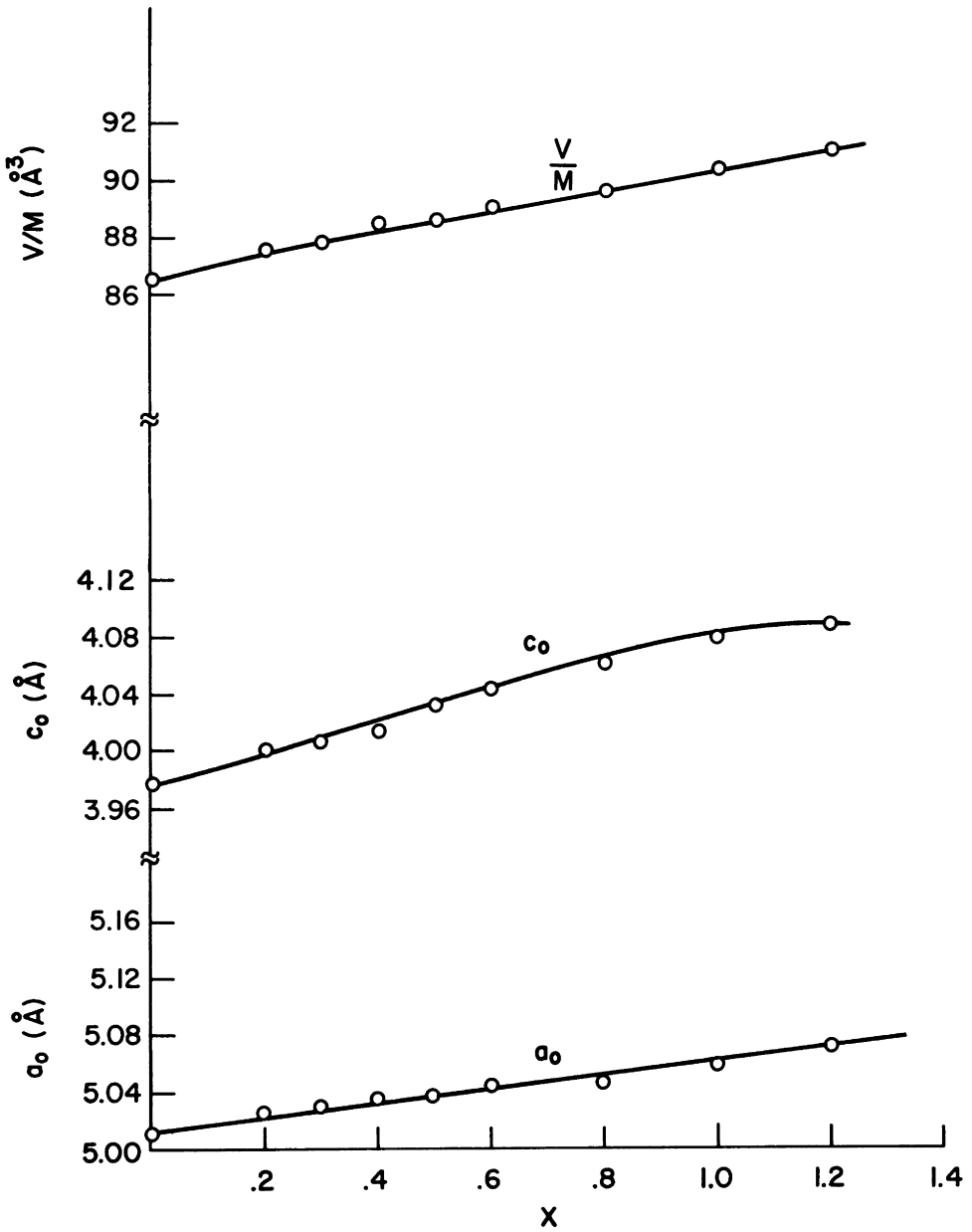


Fig. 4. Cell volume vs. Al content in $\text{LaNi}_{5-x}\text{Al}_x$.

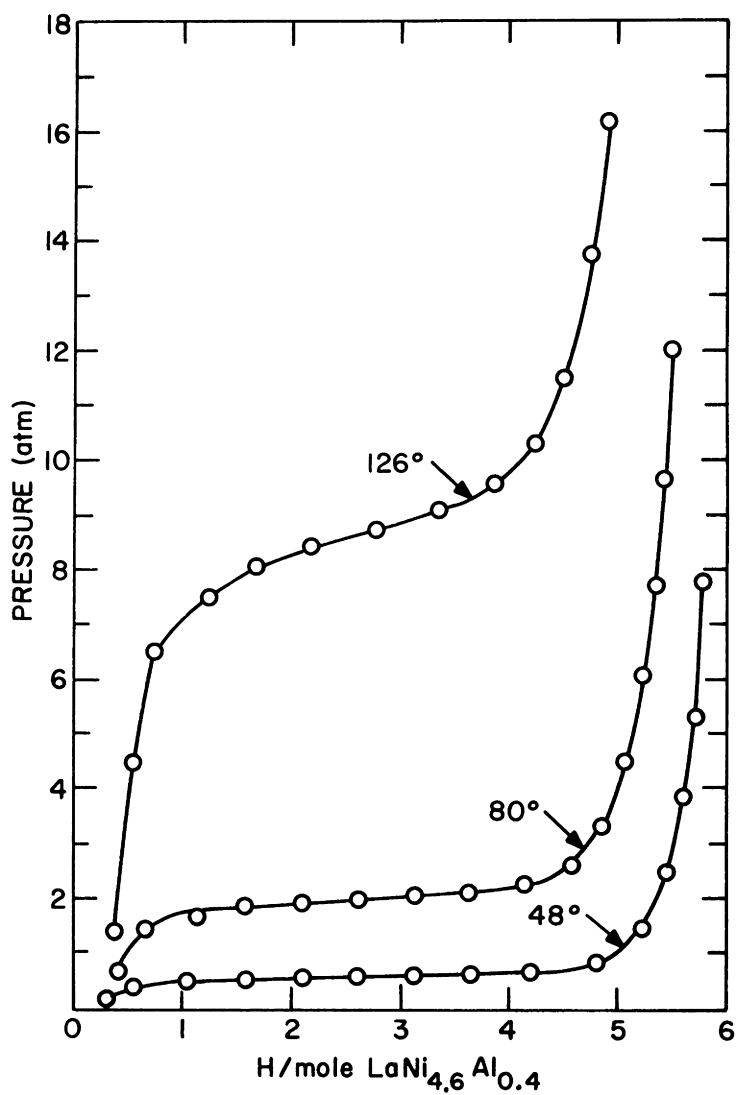


Fig. 5. Desorption isotherms for $\text{LaNi}_{4.6}\text{Al}_{0.4}$.

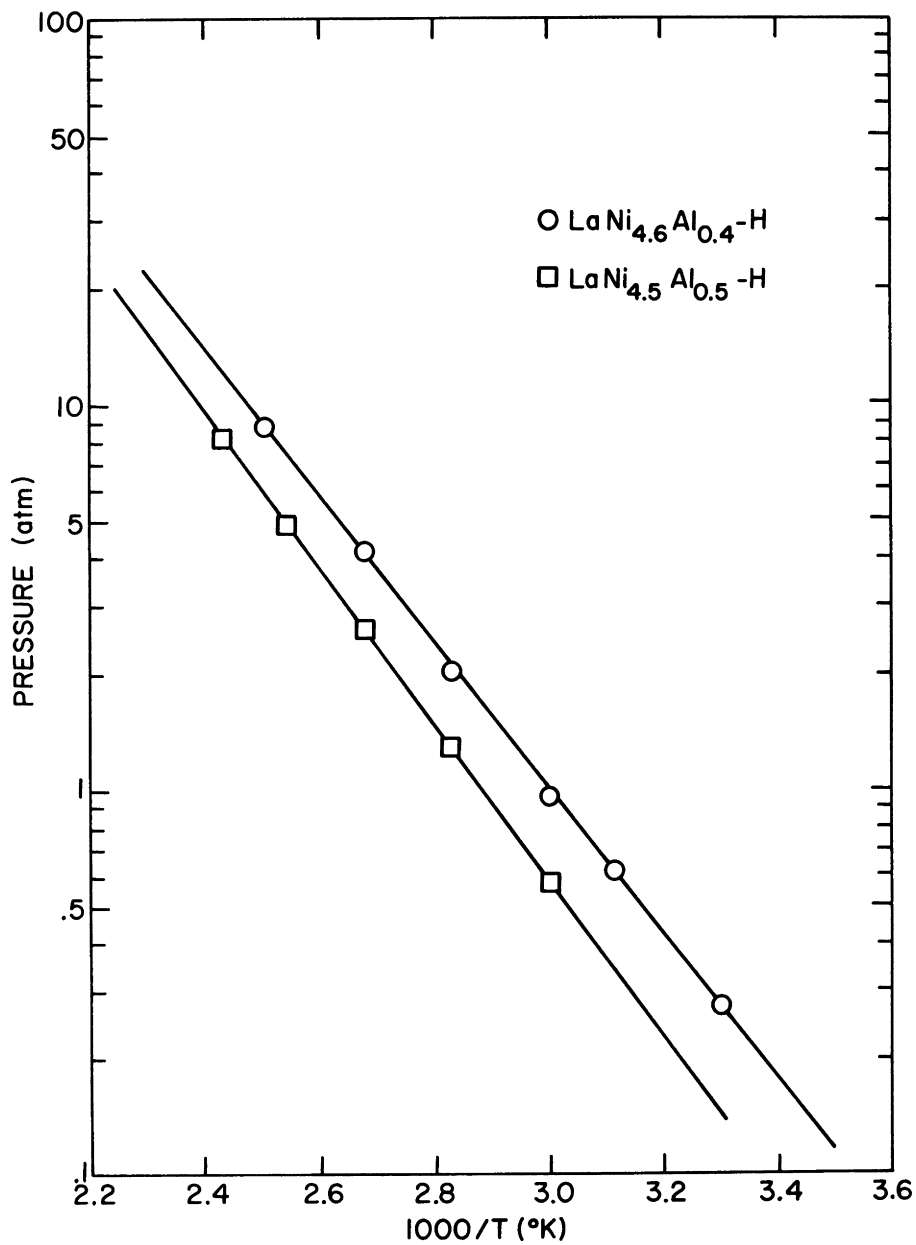


Fig. 6. $\text{Log } P_{\text{plateaus}}$ vs. $1000/\text{temperature}$.

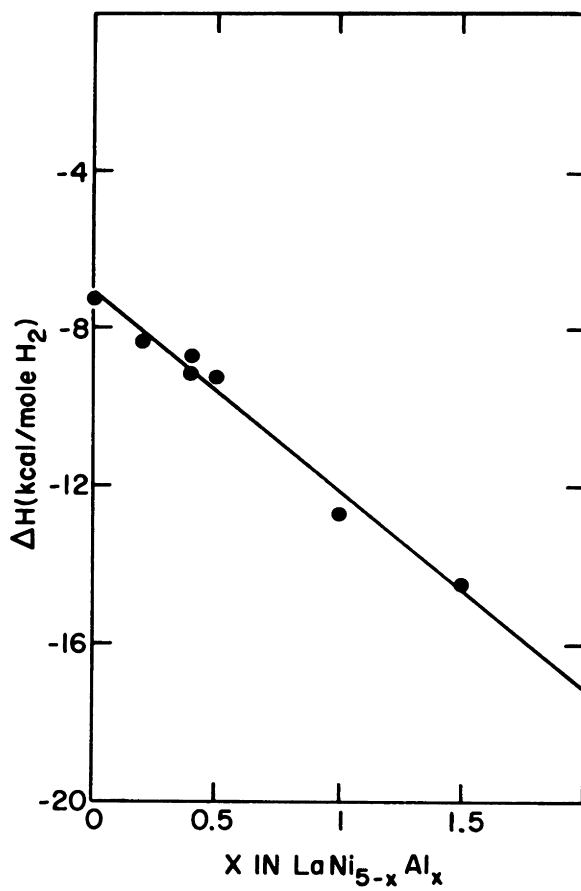


Fig. 7. ΔH vs. X in $LaNi_{5-x}Al_x$.

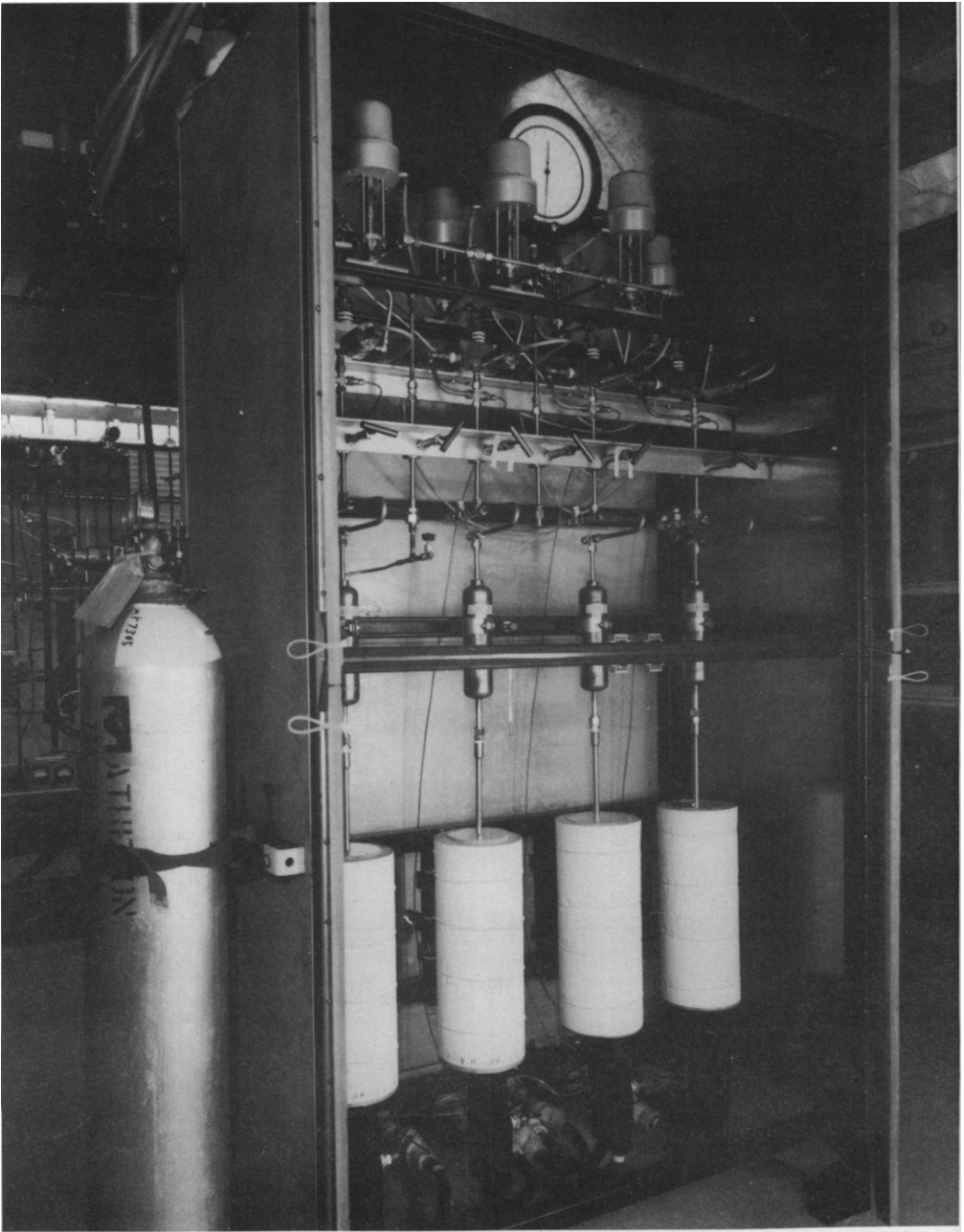


Fig. 8. HYCSOS Metal Hydride Chemical Heat Pump.

by SAES Getters, in Milan, Italy.

We have developed a new family of hydrogen getters that give one a similar kind of flexibility in terms of hydrogen pumping in vacuum systems that one now has in chemical heat pump applications. ZrV_2 forms a well-known Laves phase hydride. Replacing some of the V in ZrV_2 with Cr, just as substituting some of the Ni with Al in the AB_5 compounds, changes the hydrogen dissociation pressures and thus modifies the thermodynamics of the hydrogen reaction in a very well-defined way. If one plots the cell volume versus the enthalpy, one observes linear behavior. Since the Cr additions decrease the cell volume, increases in the hydrogen decomposition pressure are induced analogous to the situation in the $LaNi_{5-x}Al_x$ system. This effect is shown in Fig. 9, which represents three different ternary Cr substitutions in ZrV_2 . Very similar observations were made with Fe substitutions. Substituting Cr for V in the ZrV_2 phase increases the hydrogen dissociation pressure in a predictable way. In another sense, the situation found in the Laves phase hydrides is quite different than in the case of the AB_5 's. Because one does not have an alpha-beta transformation, there is a continuous range of solid solutions as hydrogen is added to ZrV_2 , preserving the alpha phase over the entire composition range. Consequently, there is no plateau region and the pressure continuously increases with increasing H/M ratio.

But the pressures are in a very convenient and interesting range for getter applications. In Fig. 10, we have compared ST-101, the material that I mentioned as the only commercially available hydrogen getter, with these two Fe- and Cr-substituted Laves phase alloys.

There are certain applications for hydrogen getters which require one to operate in a particular temperature regime, both for pumping and for regenerating the getter; for example, for in-torus pumping in a Tokamak fusion device. The Tokamak Fusion Test Reactor (TFTR) now under construction at the Princeton Plasma Physics Laboratory near Princeton, New Jersey, is designed to demonstrate break-even fusion. In this machine one needs to getter hydrogen isotopes to minimize hydrogen recycling. Both deuterium and, in the later stages of operation of this machine, tritium as well, need to be pumped. Since the gettering is being done in the torus of the Tokamak, one would like the temperature at which the regeneration takes place to be, say 400°C . One therefore searches for a material that can getter hydrogen at 200°C and which could be regenerated at 400°C . Comparing the pressure composition characteristics of ST-101 (the straight line) with the points representing the situation for the Cr and Fe substitutions in Laves phase alloys (Fig. 10), it is seen that the latter may have pressure-temperature characteristics desirable for Tokamak applications. Again, we have achieved a degree of flexibility in tailoring hydride materials, this time for getter applications.

The present situation in the field of metal hydrides is rich in potential applications. There are storage applications; there are the thermal energy applications, such as heat pumps, thermal-to-electric converters and compressors. Other possible uses involve getters, selective hydrogen absorbers, hydrogen purifiers, and various applications in nuclear reactors as moderators and hydrogen scavengers. Targets in roasting neutron sources and storage materials for tritium are applications already in use. Other possibilities include uses for deuterium isotope separation. The power of the intermetallic hydrides to act as hydrogenation catalysts has already been demonstrated, and

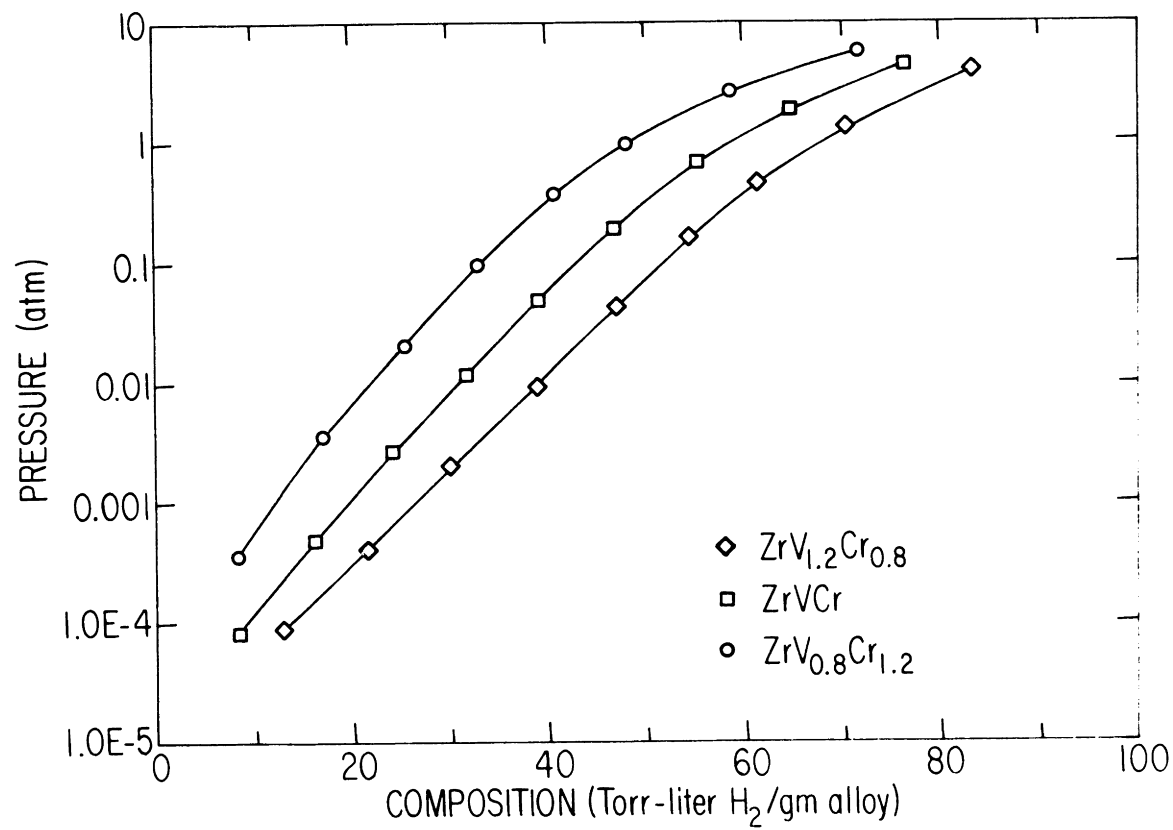


Fig. 9. Composition (Torr-liter H_2 /gm alloy) vs. Pressure (atm).