CONF-781142--2

BNL-25215

THE METAL HYDRIDE RESEARCH AND DEVELOPMENT PROGRAM AT BROOKHAVEN NATIONAL LABORATORY *

J.R. Johnson and J.J. Reilly
Brookhaven National Laboratory
Upton, New York 11973

NOTICE
This report was prepared as an account of work sponsored by the United States Government Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights

ABSTRACT

This paper is a progress report covering work performed in the hydrogen materials development program at Brookhaven National Laboratory (BNL) for FY78 which encompasses the time period from October 1, 1977 through September 30, 1978. The subjects to be discussed here concern properties of importance in the utilization of metal hydrides as energy storage media. Most of the areas of research were initiated prior to FY78, however all of the results contained in this manuscript were obtained during the aforementioned period of time. The following subjects will be discussed: the properties of ferro-titanium and chrome-titanium alloy hydrides.

I. INTRODUCTION

In the past year our metal hydride development program has been concerned with several areas of research. The areas of emphasis and investigation include the following: [1] properties of manganese substituted ferro-titanium alloys of the general formula $TiFe_xMn_y$; [2] a definition of the low temperature $TiCr_2$-H system; [3] preparation of the high temperature form of $TiCr_2$ and an initiation of studies on this alloy-hydrogen system; [4] properties of manganese and titanium substituted $TiCr_2$ alloys of the general formulas $Ti_xCr_{2-x}Mn$, $TiCr_{2-x}Mn_x$ and $Ti_{1+x}Cr_{1-2x}Mn_{1+x}$; and [5] management responsibilities for several DOE contracts in this area. The first four areas of research were all directed at the identification and characterization of improved alloy-hydrogen storage systems for use with various energy conversion devices.

II. FERRO-TITANIUM ALLOY HYDRIDES

Many metal alloys react directly and reversibly with hydrogen gas at ambient temperatures and reasonable pressures to form solid hydride compounds.(1-5) To date, the metal hydride which has received the most attention and shown the most potential for practical application has been iron titanium hydride. This has resulted principally from its favorable pressure-composition characteristics, production costs and the relative abundance of the starting materials. This metal-hydrogen system was discovered and characterized at BNL.(1)

As has, however, been noted previously, iron titanium hydride is not the ideal storage material for use in all applications and the ability to modify its properties is desirable.(6) Changes in the properties of

---

*Research carried out under the auspices of the United States Department of Energy under Contract No. EY-76-C-02-0016.

8b

MASTER

UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

iron titanium hydride, as well as certain other hydrides, may be affected by the addition of small amounts of other components, by variation in the atom ratio of titanium and iron in the starting alloy or by the partial substitution or addition of another transition metal for iron resulting in a ternary alloy of general composition $TiFe_xM_y$.(1,6-7) The partial substitution of iron by another transition metal makes it possible to "tailor make," to a high degree, an alloy with appropriate properties for particular energy storage and conversion applications.

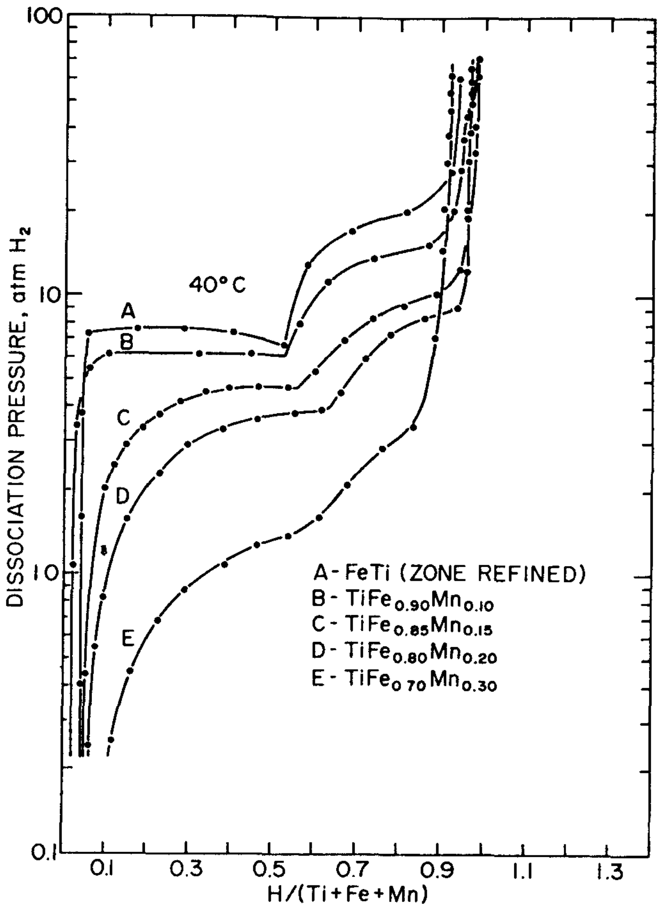
It is the purpose of this section of our paper to discuss certain physio-chemical properties of a specific class of ternary $TiFe_xM_y$ alloys. Namely those ternary alloy-hydrogen systems where M = manganese. The properties to be discussed are of practical importance in the utilization of such solid hydrides as energy storage media and include the following: [1] pressure-composition characteristics; [2] ease of initial activation (hydriding for the first time); and [3] effects of alloy annealing on pressure-composition properties. Previously, results of investigations on particle attrition rate, effects of poisons on activity, effects of long-term cycling on the reversibility of the absorption-desorption reaction, and the development of an optimum alloy for use with an electrochemically regenerative hydrogen chlorine system have been presented for such alloy-hydrogen compounds and therefore they will not be discussed here.(8-10)

A. Pressure-Composition-Temperature Characteristics

In a previous article the effects of substitution or addition of another transition metal on the pressure-composition isotherms of iron titanium were presented.(6) All such composition adjustments led to a metal hydride system of increased thermodynamic stability and generally to the introduction of a distortion or sloping effect in the isotherms. The substitution of manganese is no exception to these general observations. This is illustrated in Figure 1. It should be noted that as the content of manganese increases hydride stabilities increase and up to an alloy composition corresponding to $TiFe_{0.8}Mn_{0.2}$ ($\sim$ 11 wt % Mn) no loss of hydrogen capacity occurs. However, upon increasing the manganese concentration of the alloy to $TiFe_{0.7}Mn_{0.3}$ a slight loss in capacity is evident. This undoubtedly results from a significant increase in the amount of a second phase, $Ti(Fe,Mn)_2$, present in the "as cast" alloy. Partial ternary phase diagrams for the Ti-Fe-Mn system for "as cast" and equilibrium compositions have been developed by Sandrock and Murakami and Enjyo.(11-12) They should be consulted by the reader if further information is required.

The increase in stability of the manganese substituted ferro-titanium alloy hydrides may be explained qualitatively in terms of the "Rule of Reversed Stability" formulated by van Mal et al. or by a similar correlation developed by Lundin et al.(4,13) Basically, a smaller metal atom, Fe, is being replaced by a larger one, Mn, in the substituted alloys giving rise to a less stable starting alloy and a more stable hydride.

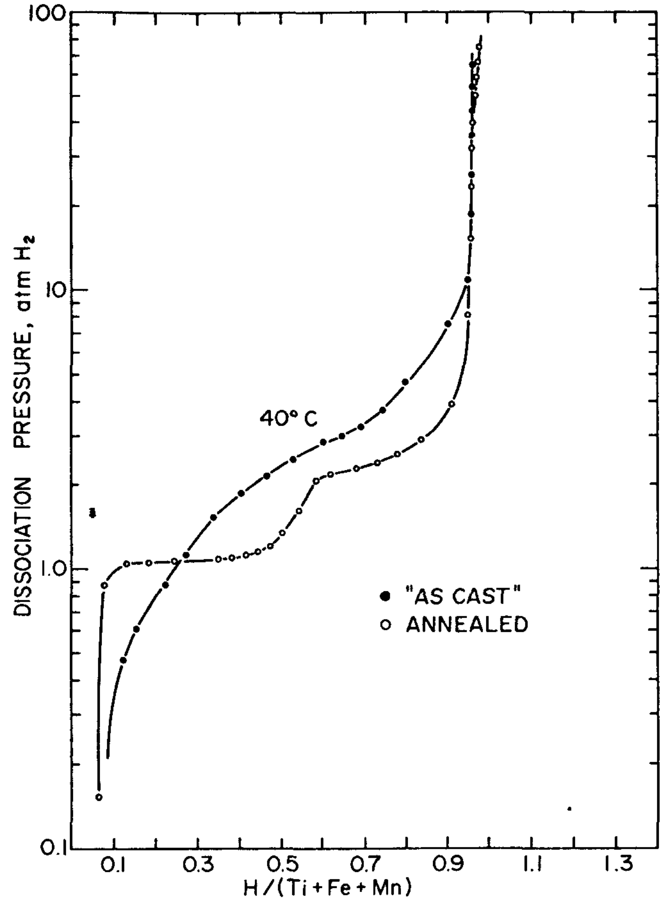
Figure 1. Pressure-Composition Desorption Isotherms for FeTi Alloys of Various Mn Contents at 40°C.



B. Heat Treatment (Annealing) Effects

Many of the manganese systems exhibit sloping plateaus in their pressure-composition isotherms. In general, this phenomena is composition dependent and results from non-equilibrium solidification effects. Such solidification processes arise from large differences in liquidus-solidus temperatures in the phase equilibria and may give rise to segregation within a single phase region or more generally coring. This may be eliminated, in many cases, by homogenization-annealing of the starting intermetallic and such a case is shown for the $TiFe_{0.76}Mn_{0.13}$-H_x system in Figure 2. The annealed sample was heat treated in a resistance furnace under an inert atmosphere for 3 days at 1000°C prior to hydriding. Of course, temperature and hold times must be optimized individually for alloys of differing compositions.

Figure 2. A Comparison of Pressure-Composition Desorption Isotherms for Annealed and "As Cast" $TiFe_{0.76}Mn_{0.13}$ at 40°C.



C. Ease of Initial Activation

The activation (first complete hydriding) of pure iron titanium is time consuming, requires pressures on the order of 65 atm and outgassing temperatures $\geq$ 300°C. These conditions require the use of materials for hydride bed reservoirs which are expensive and involve stringent design constraints. Further, the alternative of activating the alloy in a separate vessel and subsequently transferring it to the reservoir is not attractive. Any simplifications in the activation procedure which would moderate the conditions necessary and reduce the time required are important since substantial reductions in cost could be obtained. Such simplifications can be realized by the use of ternary manganese substituted ferro-titanium alloys as all these materials studied, to date, activate much more easily than iron titanium as shown in Table I.

Table I

LOW TEMPERATURE ACTIVATION EXPERIMENTS FOR $TiFe_xMn_y$ ALLOYS

Alloy Composition	Maximum Outgassing Temperature (°C)	Time at 500 PSIA(hr)	Final H/Ti	% Reaction
TiFe	200	72	0.0	0
$TiFe_{0.9}Mn_{0.1}$	25	27	0.48	25
$TiFe_{0.9}Mn_{0.096}$ (INCO #4)	25	19	1.72	96
$TiFe_{0.85}Mn_{0.15}$	25	6	1.94	100
$TiFe_{0.8}Mn_{0.2}$	25	45	1.16	60
$TiFe_{0.7}Mn_{0.2}$	50	3.5	1.79	94
$TiFe_{0.77}Mn_{0.09}$	25	27.5	1.79	100
$TiFe_{0.73}Mn_{0.13}$	25	19	1.82	100

The percent reaction is a measure of hydrogen content actually attained versus the maximum possible under the conditions specified. It is likely that the same properties which result in an increased rate of particle attrition, as discussed previously, are also responsible for the ease with which such alloys can be activated.(10-11) Basically, this is related to the presence of other phases which may be hydridable or simply provide pathways or nucleation sites for hydrogen.

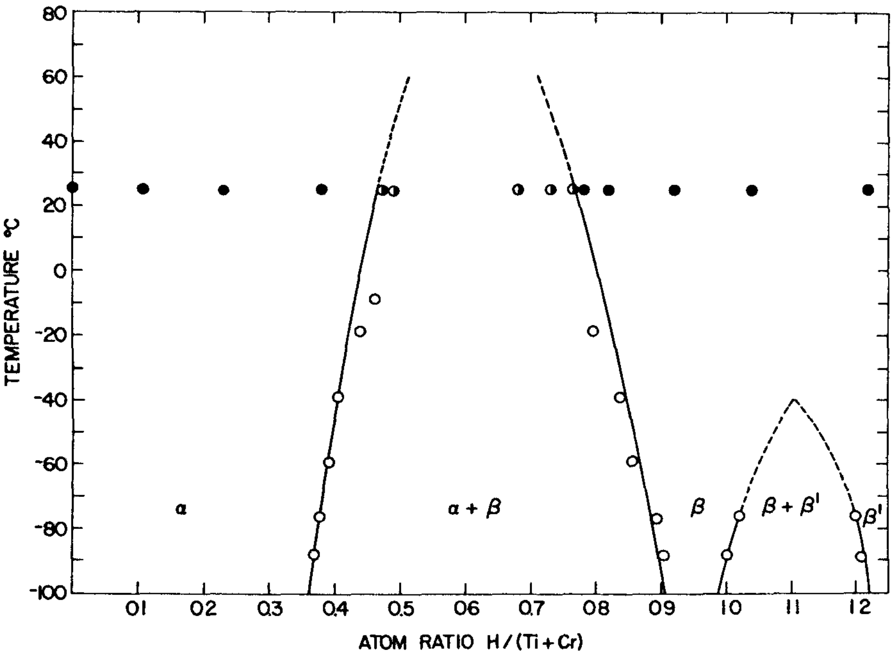
III. NONSUBSTITUTED TITANIUM-CHROMIUM ALLOY HYDRIDES

The binary Ti-Cr alloy system exhibits one intermetallic compound, $TiCr_2$, of which there are two temperature dependent allotropes.(14) Both are Laves phases, the low temperature form having the cubic $MgCu_2$ (C15) structure while the high temperature form has the hexagonal $MgZn_2$ (C14) structure. Both forms will react with hydrogen to form hydride phases which contain an appreciable amount of hydrogen.(15) The maximum hydrogen capacity measured for the cubic phase, to date, has been 2.5 wt% whereas that for the high temperature hexagonal phase is 2.4 wt%. We were particularly interested in these alloy-hydrogen systems because of their high storage capacities.

A. The Low-Temperature (C15) TiCr$_2$-H System

Previously, we reported some of the properties of the cubic (C15) TiCr$_2$-H system in which we discussed pressure-composition characteristics including hysteresis effects, thermodynamic considerations and the method of preparation of the starting intermetallic.(9) Briefly, the most important points were that two hydride phases exist in the system at -78°C (195°K), hysteresis is virtually absent and the hydrides are very unstable. In order to more fully characterize this system, we have carried out extensive X-ray diffraction investigations at room temperature on hydrides of varying composition which complement and confirm our pressure-composition data and allow us to construct a phase diagram for the alloy-hydrogen system. The resulting diagram is presented in Figure 3.

Figure 3. Phase Diagram for the TiCr$_{1.8}$-H System Derived from P-C-T and X-ray Diffraction Data. The Latter Were Collected at the Compositions Indicated: o one solid phase; ◐ two solid phases.



It should be noted here that this is not a complete phase diagram for this system but one which can be constructed from the data presently available (temperature dependent pressure-composition measurements and room temperature X-ray data). The salient features are as follows: [1] the terminal solubility of hydrogen in the α phase increases with temperature and corresponds to a composition of $TiCr_{1.8}H_{1.3}$ at 25°C (the lattice parameter of the fcc α phase increases correspondingly with hydrogen content); and [2] only one hydride phase exists at room temperature and it has a composition range extending from $TiCr_{1.8}H_{2.1}$ to $TiCr_{1.8}H_{3.6}$. This phase is orthorhombic with lattic parameters varying slightly with hydrogen content. It should also be noted that the α phase region is a region of solid solution of hydrogen in the starting intermetallic and has the same fcc (C15) structure.

To our knowledge, this is the first example of a structural transformation of a Laves phase due to hydrogen absorption. Previous investigators have noted that a number of ZrM_2 (where M is a transition metal) Laves phases, which absorb large quantities of hydrogen, do not undergo phase transformations but merely lattice expansions.(16-18).

B. The High Temperature (C14) $TiCr_2$-H System

The limits of homogeneity of the hexagonal (C14) $TiCr_2$ phase are both temperature and composition dependent. The (C14) phase however exists within the composition limits from ∿ $TiCr_{1.75}$ to $TiCr_{1.95}$. All such compositions are metastable below the temperature range 850 to 1150°C. The high temperature intermetallics may however be prepared and studied since the rate of transformation to low temperature $TiCr_2$ is negligibly slow at the temperatures of interest.

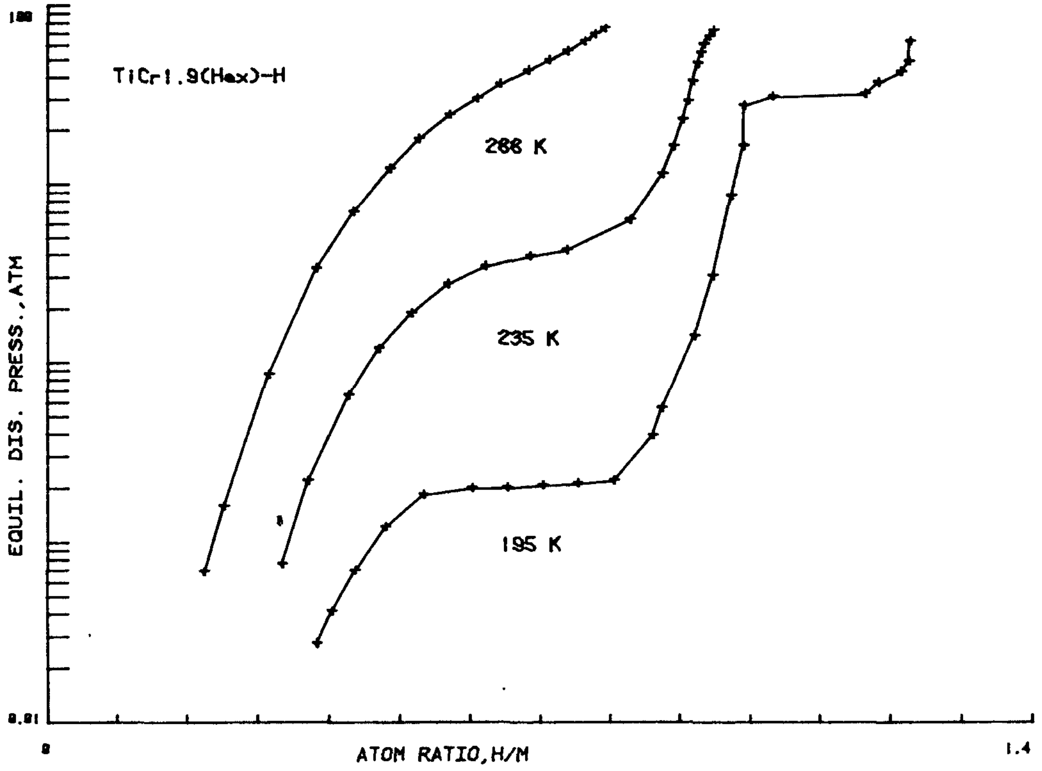
We have prepared single phase hexagonal $TiCr_{1.9}$ and have obtained p-c-t data at temperatures ranging from -78 to 30°C. This alloy also reacts with hydrogen sequentially at -78°C to form two hydride phases. Starting with the hydrogen saturated solid, the reactions taking place at -78°C may be written as follows:

$$2.5TiCr_{1.9}H_{1.6} + H_2 \rightleftarrows 2.5TiCr_{1.9}H_{2.4} \quad (1)$$

$$1.67TiCr_{1.9}H_{2.4} + H_2 \rightleftarrows 1.67TiCr_{1.9}H_{3.6} \quad (2)$$

Figure 4 illustrates p-c-t isotherms for the hexagonal $TiCr_{1.9}$-hydrogen system. The thermodynamic stability of the hydride phases is considerably higher than those formed in the corresponding cubic $TiCr_2$-hydrogen system. This is apparent from the plateau dissociation pressures for the hydrides, which are ∿ 2 and 50 atm in the (C15) cubic system and 0.2 and 30 atm for the (C14) hexagonal system. Additionally, it appears as though there is no hydride phase present at room temperature for the high temperature hexagonal (C14) alloy-hydrogen system (see Figure 4); merely a continuous lattice expansion as the hydrogen content increases.

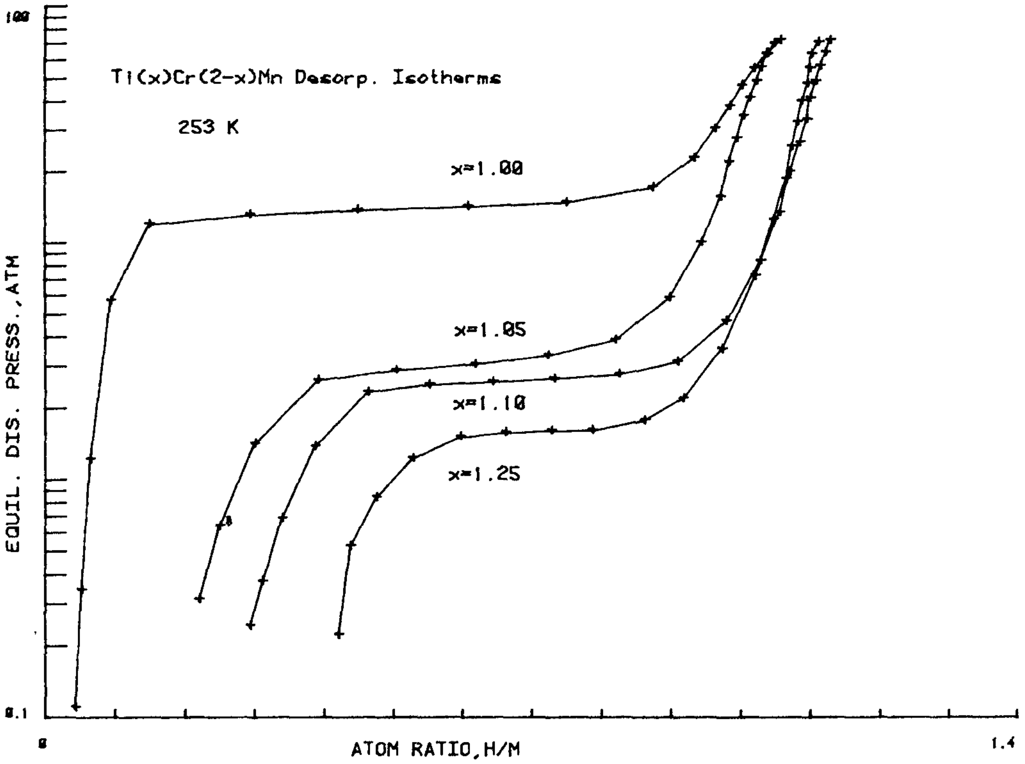
Figure 4. Pressure-Composition Desorption Isotherms for the High Temperature (C14) $TiCr_{1.9}$-H System at Various Temperatures.



IV. TITANIUM AND MANGANESE SUBSTITUTED $TiCr_2$ HYDRIDES

Whereas the "Rule of Reversed Stability" would predict the formation of stable hydrides from the low temperature form of $TiCr_2$ they are, in fact, very unstable, even to the point of limited utility for practical applications. However, as we have seen for substituted ferro-titanium hydrides it should be possible to modify their properties by composition changes. To this end, investigations of manganese and titanium substituted $TiCr_2$ hydrides have been undertaken. The alloy systems which have been investigated are of the general formulas $Ti_xCr_{2-x}Mn$, $TiCr_{2-x}Mn_x$ and $Ti_{1+x}Cr_{1-2x}Mn_{1+x}$. Most emphasis, to date, has been directed toward the alloy-hydrogen systems of composition $Ti_xCr_{2-x}Mn$-H_y. Figure 5 demonstrates the variation in pressure-composition properties of these hydrides as a function of titanium content at -20°C. The notable features are an increase in stability and decrease in usable hydrogen with increasing titanium content. Additionally, we have investigated hysteresis for a few such systems and found it to be small as in the parent system.

Figure 5. Pressure-Composition Desorption Isotherms for Various $Ti_xCr_{2-x}Mn$ Alloys at -20°C.



Alloy systems of general composition $TiCr_{2-x}Mn_x$, however, may be more promising. We have obtained pressure-composition data on the hydride system $TiCr_{0.75}Mn_{1.25}$-H_x and find that its hydrogen storage capacity is significantly greater than the corresponding $Ti_{1.25}Cr_{0.75}Mn$ hydrogen system while its thermal stability is only slightly less. The plateau pressure of the annealed $TiCr_{0.75}Mn_{1.25}$-H_x system is ∿ 3 atm at -20°C whereas that for the $Ti_{1.25}Cr_{0.75}Mn$-H_x system is ∿ 1.5 atm at the same temperature.

REFERENCES

1. J.J. Reilly and R.H. Wiswall, Jr., "Formation and Properties of Iron Titanium Hydride," Inorg. Chem., Vol. 13, 218 (1974).

2. G.D. Sandrock, "A New Family of Hydrogen Storage Alloys Based on the System Nickel-Mischmetal-Calcium," Proc. 12th IECEC, Vol. 1, 951 (1977).

3. K.H.J. Buschow and H.H. van Mal, "Phase Relations and Hydrogen Absorption in the Lanthanum-Nickel System," J. Less-Common Metals, Vol. 29, 203 (1972).

4. H.H. van Mal, K.H.J. Buschow and A.R. Miedema, "Hydrogen Absorption in $LaNi_5$ and Related Compounds: Experimental Observations and Their Explanation," J. Less-Common Metals, Vol. 35, 65 (1974).

5. J.H.N. van Vucht, F.A. Kuijpers and H.C.A.M. Bruning, "Reversible Room Temperature Absorption of Large Quantities of Hydrogen by Intermetallic Compounds," Philips Res. Rept. 25, 133 (1970).

6. J.J. Reilly and J.R. Johnson, "Titanium Alloy Hydrides, Their Properties and Applications," Proc. 1st World Hydrogen Energy Conference, Miami Beach, Florida, March 1976.

7. J.J. Reilly and R.H. Wiswall, Jr., "The Effect of Minor Constituents on the Properties of Vanadium and Niobium Hydrides," Proc. of International Meeting on Hydrogen in Metals, Jülich, Germany, March 1972.

8. J.J. Reilly and J.R. Johnson, "Metal Hydride Materials Program at BNL-Current Status and Future Plans," Proc. of the ERDA Contractors' Review Meeting on Chemical Energy Storage and Hydrogen Energy Systems, CONF-761134, Airlie, Virginia, November 1976.

9. J.R. Johnson and J.J. Reilly, "The Metal Hydride Development Program at Brookhaven National Laboratory," Proc. of the DOE Chemical Energy Storage and Hydrogen Energy Systems Contracts Review, JPL 78-1, Hunt Valley, Maryland, February 1977.

10. J.R. Johnson and J.J. Reilly, "The Use of Manganese Substituted Ferro-Titanium Alloys for Energy Storage," Proc. of the International Conference on Alternative Energy Sources, Miami Beach, Florida, December 1977.

11. G.D. Sandrock, "The Interrelations Among Composition, Microstructure and Hydriding Behavior for Alloys Based on the Intermetallic Compound FeTi," Final Report, Contract BNL-352410S, June 1976.

12. Y. Murakami and T. Enjyo, "Investigation of Ti Rich Ti-Fe-Mn Alloy System on the Solid Equilibrium Relation in the Ti-Fe-Mn System," Nippon Kinzoku Gakkaishi, Vol. 22, 329 (1958).

13. C.E. Lundin, F.E. Lynch and C.B. Magee, "A Correlation Between the Interstitial Hole Sizes in Intermetallic Compounds and the Thermodynamic Properties of the Hydrides Formed from Those Compounds," J. Less-Common Metals, Vol. 56, 19 (1977).

14. P.A. Farrar and H. Margolin, "A Reinvestigation of the Chromium-Rich Region of the Titanium-Chromium System," Trans. Met. Soc. AIME, Vol. 227, 1342 (1963).

15. J.R. Johnson and J.J. Reilly, "The Reaction of Hydrogen with the Low Temperature Form (C15) of $TiCr_2$," Inorg. Chem., accepted for publication in November 1978 volume.

16. A. Pebler and E.A. Gulbransen, "Thermochemical and Structural Aspects of the Reaction of Hydrogen with Alloys and Intermetallic Compounds of Zirconium," J. Electrochem. Tech., Vol. 4, Nos. 5-6, 211 (1966).

17. A. Pebler and E.A. Gulbransen, "Equilibrium Studies on the Systems $ZrCr_2$-H_2, ZrV_2-H_2, and $ZrMo_2$-H_2 between 0° and 900°C," Trans. Met. Soc. AIME, Vol. 239, 1593 (1967).

18. D. Shaltiel, I. Jacob and D. Davidov, "Hydrogen Absorption and Desorption Properties of AB_2 Laves-Phase Pseudobinary Compounds," J. Less-Common Metals, Vol. 53, 117 (1977).