**HIGH-PRESSURE HYDROGEN APPARATUS
FOR PCT STUDIES UP TO ~700 MPa AND 200°C:
PRELIMINARY RESULTS ON $\text{LaCo}_5\text{H}_{9.0}$ AT 21°C**

J. F. Lakner
S. A. Steward
F. Uribe

MASTER

February 27, 1976

Prepared for U.S. Energy Research & Development
Administration under contract No. W-7405-Eng-48

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Printed in the United States of America
Available from

National Technical Information Service

U. S. Department of Commerce

5285 Port Royal Road

Springfield, Virginia 22151

Price: Printed Copy \$ ____*; Microfiche \$2.25

<u>* Pages</u>	<u>NTIS Selling Price</u>
1-50	\$4.00
51-150	\$5.45
151-325	\$7.60
326-500	\$10.60
501-1000	\$13.60

LAWRENCE LIVERMORE LABORATORY

University of California Livermore, California 94550

UCRL-52039

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HIGH-PRESSURE HYDROGEN APPARATUS FOR PCT STUDIES AT PRESSURES OF UP TO ~700 MPa AND TEMPERATURES OF UP TO 200°C; PRELIMINARY RESULTS ON LaCo_5H_x AT 21°C

Abstract

An apparatus has been developed to react samples with hydrogen at pressures of up to 689.5 MPa (6865 atm) and temperatures of up to 200°C. It is being used to determine whether RT_5 and RT_3 compounds (where R is a lanthanide element and T is a 3-d transition element, usually cobalt or nickel) "fill up" with hydrogen when subjected to high hydrogen pressures.

Preliminary experiments with LaCo_5 in this apparatus showed a new (third) plateau at 126.7 MPa (1250 atm) in the PCT diagram; only two plateaus have previously been reported. There is an abrupt upturn at an H/LaCo_5 ratio of approximately 8.23. A second run showed an upturn at 2.76. The maximum loading is nine atoms of hydrogen.

Introduction

Several types of intermetallic compounds have an unusual capacity for taking up very large quantities of hydrogen. The most intensively studied type is the RT_5 type, where R is a lanthanide element and T is a 3-d transition element, usually cobalt or nickel.^{1,2} More recently, the RT_3 compounds have begun to be examined as well.³ Both types of intermetallics form hydrides, of the general compositions RT_5H_7 and RT_3H_4 , which may be considered to be interstitial hydrides. Despite the fact that they contain relatively large amounts of hydrogen, many of their possible interstitial sites are vacant. Conceptually, compositions up to RT_5H_9 may be possible.³⁻⁵

Such compositions have never been achieved because previous investigations have been limited to hydrogen pressures of

~10 MPa (~1500 psi). It is possible that at extremely high hydrogen pressures and at low temperatures the RT_5 and RT_3 compounds might "fill up," particularly some of the more stable members (i.e., those containing a low-Z lanthanide).

This report describes an apparatus for use in obtaining hydrogen-absorption isotherms (or desorption isotherms) for the above compounds. We have used this apparatus to obtain a 21°C isotherm for $\text{LaCo}_5\text{H}_{8.3}$ at pressures of up to 137.3 MPa (1354.7 atm). After high-pressure activation, an H/LaCo_5 ratio of 9 was obtained at essentially the same pressure. This isotherm shows a previously unreported new (third) plateau occurring at 126.7 MPa (1250 atm). This discovery is a strong incentive to the investigation of other intermetallics at very high pressures.

Experimental Setup

The hydrogen pressurizing system was designed to be constructed of type 316 and A-286 stainless steels, which are not embrittled by hydrogen. Where a type 316 or A-286 vessel liner requires backup for strength, AISI 4340 steels are used.

ABSORPTION SYSTEM

Figure 1 shows a schematic drawing of the apparatus for hydriding to pressures of 689.5 MPa (6805 atm) and temperatures

to 200°C. The pressure transducers are Teledyne-Taber models 2404, 1205, and 1207.* For pressures above 344.7 MPa (3402 atm) the transducer is an Astra Corporation unit capable of measuring to 689.5 MPa. The use of Manganin coils is

*Reference to a product name does not imply approval or recommendation of the product by the University of California or the U.S. Energy Research and Development Administration to the exclusion of others that may be suitable.

Fig. 1. Schematic drawing of apparatus for hydriding to pressures of up to 689.5 MPa and temperatures of up to 200°C.

also feasible. The pressure transducers are changed by valving during the course of the experiment, in order to obtain the maximum sensitivity. The free-void volumes of both the charge vessel* and the hydriding vessel[†] are kept low to give large pressure differentials when adding hydrogen. The sample is contained within the pressure vessel in a 200-mesh stainless-steel crucible. The porosity of such a crucible permits hydrogen access to the sample in all directions.

Three band heaters (each 1125 W, 208 V, and 5 A) heat the central section of the vessel for the determination of isotherms above room temperature. A Leeds & Northrup No. 60 control unit coupled to a Fincor saturable-core reactor controls the temperature. A maximum temperature of 200°C is possible at maximum pressure.

PRESSURE VESSEL

Autoclave Engineers and LLL designed a double-walled pressure vessel (Fig. 2) consisting of a liner of A-286 ACQ steel (supplied by the McInnes Steel Company), 2.54 cm in diameter, shrunk into a supporting body of AISI 4340 steel (9.53 cm o.d.). The bore is 0.794 cm, and the liner has a 60° cone seat at each end. The short length, ~50 cm, permits handling the vessel in a glove box for sample loadings under argon. "Phonograph grooves" on the exterior surface of the liner permit any diffused gas to reach either weep hole. The inside of the liner may be gold plated if

Fig. 2. Pressure vessel for operating conditions of 689.5 MPa and 200°C. Liner is necessary to prevent hydrogen attack of supporting body. Autoclave/LLL design.

it is found that hydrogen losses are significant at temperatures above ambient. The properties of the steels are given in Table 1.

Hydraulic proof testing of the vessel was conducted at 120,000 psi because tests

Table 1. Properties of the steels used to construct the pressure vessel.

Steel	Ultimate tensile strength (psi)	Yield strength at 0.2% offset (psi)	Elongation ^a (%)
A-286	179,000	154,000	14.5
AISI-4340	154,000	142,000	18

^aElongation in 2 in.

*24.87 cm³.

[†]13.48 cm³ with 200-psi pressure transducer; 11.05 cm³ excluding the 200-psi pressure transducer.

at the normal 1.5 times design pressure would cause yielding and closure of the "phonograph grooves" of the liner. The use of a 21-6-9 stainless steel permits a higher safety factor.

GAS COMPRESSION

Figure 3 shows the schematic diagram for the compression of hydrogen, which occurs in two stages. First the hydrogen is compressed in a 1-liter cylinder to about 344.7 MPa (3402 atm) and then is released to a 10:1 intensifier for further compression by means of a hand pump.*

*An air-driven pump can be substituted for the hand pump.

A floating beryllium-copper piston within the A-286 liner of the 1:1 compressor separates Dow-Corning 200 fluid and the hydrogen gas. An Autoclave Engineers 413.7-MPa (4082-atm) pump⁶ pressurized the DC 200 fluid. This application of DC 200 fluid is relatively new. Its advantages over conventional hydraulic liquids are as follows:

1. It is an ideal lubricant for elastomeric O-rings.
2. Its vapor pressure is low.
3. It is inert to hydrogen.

The alternative system used at LLL consists of compressing hydrogen gas in a diaphragm compressor and feeding this compressed gas to the 10:1 intensifier. The

Fig. 3. Schematic diagram of 689.5 MPa apparatus for the compression of hydrogen gas.

hydrogen for the compressors is purified by passing it through a molecular sieve and a liquid-nitrogen trap.

The compressed gas is then admitted to the hydriding gas bottle, as shown in Figs. 1 and 3.

INTENSIFIER

The 10:1 hydrogen intensifier is shown in Fig. 4. The design is such that there is no oil contamination of the hydrogen gas. In other words, the compression fluid does not wet the high-pressure piston. The packing on the moving piston (1.9-cm diam) is a Bridgman design. Increasing the internal pressure increases the effectiveness of the seal. Like the pressure vessel, the intensifier has a liner of A-286 stainless steel to protect the AISI 4340 body from hydrogen embrittlement. The A-286 steel can be replaced by 21-6-9 stainless steel.

The method of releasing any gas trapped under the cap (center of Fig. 4) is significant. The axial hole in the plug connects to X grooves machined into the bottom of the piston rod. Gas escapes by this path. A hole drilled into the side of either plug or rod would result in unequal stress distribution and subsequent buckling of the part.

PRESSURE MEASUREMENT, COMPRESSION SYSTEM

Helical coil gauges indicate gas pressure. The Astra Corporation fabricates these coils by hard-working type 316 stainless-steel tubing to 135,000-psi yield* and 150,000-psi tensile strength.

* Designated as quarter-hard.

Fig. 4. Intensifier for the compression of hydrogen to 689.5 MPa. Autoclave Engineers, Inc., plug-and-rod design slightly modified by LLL.

Elongation is 15% in 2 in. The coils are then seasoned at 130,000 psi before calibration.

It should be noted that tubes made of austenitic 300-series stainless steel may rupture under hydrogen exposure. Under conditions of high pressure and localized plastic deformation they are susceptible

to hydrogen-induced cracking. One particular Astra coil failed because laps and folds formed on the inside of the coil during fabrication resulted in severe stress risers and subsequent rupture.

VALVES

The valves have a nominal rating of 100,000 psi (689.5 MPa) and are fabricated from austenitic type 316 stainless steel. The stems are of Haynes Stellite 25 for strength. The packing is of leather between Teflon washers, which are in turn sandwiched between beryllium-copper washers.

SAMPLE PREPARATION AND PROCEDURE

The LaCo_5 intermetallic was prepared from 99.9% pure lanthanum metal obtained from the Research Chemicals Corporation and 99.5% pure cobalt obtained from the Ventron Corporation. The analyses for both elements are shown in Table 2.

Table 2. Analysis of lanthanum and cobalt metals used in obtaining the PCT isotherm (Fig. 5).

Impurity	Lanthanum ^a (ppm)	Cobalt (ppm)
Aluminum	0.05	--
Carbon	--	150
Calcium	0.02	
Iron	0.02	20
Magnesium	0.01	--
Nickel	--	2500
Silicon	0.03	--
Tantalum	n.d.	---
Yttrium	<10	---
Other rare earths	n.d.	---
Other elements	--	<10

^a Lot 3-197.

The lanthanum and cobalt were arc-melted in a cooled copper crucible under an atmosphere of purified argon gas. A tungsten electrode with direct polarity was used. This means that the flow of current was from the tungsten electrode (positive) to the copper crucible (negative). The LaCo_5 button was then homogenized under vacuum at 900°C for 96 hr to obtain the single-phase compound. X-ray diffraction patterns were obtained to confirm the formation of the compounds and to establish the absence of other phases. The lattice constants agreed with the literature reference values and showed the structure to be hexagonal.

An alloy button was crushed under argon to particles of about 100 Tyler mesh with a mortar and pestle and introduced into a 200-mesh wire-screen crucible (triple wall), which was then placed in the pressure vessel. An iron-constantan thermocouple in a 316 stainless-steel sheath was also inserted into the crushed sample. The assembled pressure vessel with its charge was connected to the hydriding system, and the whole system was pumped out with a mechanical pump and a liquid-nitrogen trap to 0.01 Torr. Then hydrogen was introduced into the system at about 35 MPa (340 atm) and left for several hours until the pressure became constant; the system was then evacuated. This process of activation was repeated five times before actual PVT readings were taken.

The number of moles of hydrogen delivered in increments to the sample was determined by the use of an LLL computer code that took into account the compressibility factor Z for each condition. A plot was then made of atoms of hydrogen absorbed per mole of LaCo_5 as a function of pressure in atmospheres.

Discussion and Results

Figure 5 shows a pressure-composition absorption isotherm for 21°C that was obtained in a preliminary experiment with LaCo_5 in the 689-MPa apparatus. The isotherm shows three distinct plateaus, at 0.00554 MPa (0.0547 atm), 0.16 MPa (1.6 atm), and 126.7 MPa (1250 atm). Previous work⁷ at Philips Research Laboratories shows two plateaus (Fig. 6); these investigators were limited in their pressure capability. The highest plateau has a

Fig. 5. Absorption isotherm for the pseudo-binary LaCo_5 system at 21°C.

Fig. 6. Desorption isotherms for LaCo_5 at various temperatures (taken from Ref. 7).

limiting composition of $\text{LaCo}_5\text{H}_{8.23}$, with a gradually ascending portion ending at a ratio of 8.3 and approaching a composition of LaCo_5H_9 . It has been predicted that a composition corresponding to LaCo_5H_9 is possible.^{3,5} Further aspects of this work are discussed in a separate paper.⁸

A subsequent experiment showed that a loading of nine atoms of hydrogen per mole of LaCo_5 actually occurred. The plateau region extended to an H/LaCo_5 ratio of 8.76. We believe that this greater loading was the result of activation at the high pressure on the first run.

For work above about 2100 atm and 25°C we are fortunate to have available the works of Michels et al.,⁹ which present

PVT data to 2950 atm and 423°K. For pressures above 2950 atm it would be necessary to run a calibration curve using a dummy sample of the same volume. A known amount of gas, measured at a low pressure and temperature, would be compressed to a pressure above the sample-vessel pressure and then released to the sample vessel.

The actual sample would then be run, and a new curve of pressure as a function of moles of hydrogen added (measured at a low pressure and temperature) would be established. The difference between the two curves at a particular pressure would represent the moles of gas absorbed by the sample.

Summary

An apparatus was developed in which measured amounts of hydrogen can be delivered to samples at pressures of up to 689.5 MPa (6805 atm) and temperatures of up to 200°C. With this apparatus, pressure-composition isotherms can be extended to hitherto inaccessible regions.

A preliminary experiment was performed on the intermetallic compound LaCo_5 . Three plateau regions were found: at

0.00554, 0.16, and 126.7 MPa. An upturn occurs on the 126.7-MPa plateau at an H/LaCo_5 ratio of 8.23. On a second run, the upturn occurred at a ratio of 8.76. The maximum loading for the second run was nine atoms of hydrogen per mole of LaCo_5 .

This discovery suggests that additional plateaus may exist in other intermetallic compounds at pressures not previously investigated.

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