The Reaction of Hydrogen with Alloys of Magnesium and Copper[1]

BY J. J. REILLY AND R. H. WISWALL

The intermetallic compound Mg_2Cu reacts with H_2 at ~300° to form MgH_2 and $MgCu_2$. Excess Mg in the alloy also reacts to form MgH_2. In the latter case a pressure–composition isotherm exhibits two plateaus. The equilibrium dissociation pressure of H_2 was measured as a function of temperature for both systems from which thermodynamic functions for the reactions concerned were calculated.

Introduction

Hydrogen will react directly and reversibly with a large number of metals and alloys to form metal hydrides. This paper describes the reaction between Mg–Cu alloys and H_2 at elevated temperatures and pressures. The investigation was carried out as part of an energy-storage program in which it was desired to determine the possibility of using reversible metal hydrides as a convenient and cheap means to store hydrogen which is ultimately evolved and used as fuel.

In order to synthesize a reversible hydride, the H_2 pressure must exceed the dissociation pressure, but it is also required that the temperature be high enough so that the reaction takes place at a reasonable rate. Thus, a balance must be struck between temperature and pressure to achieve practical reaction rates. In this particular case H_2 pressures >100 psi and temperatures of several hundred degrees centigrade were required. The Mg–H_2 system has been studied at high pressures and temperatures,[2] but to the authors' knowledge no systematic work has been carried out with those alloy systems which require relatively high pressures to form reversible hydrides. Such high-pressure investigations may be quite fruitful particularly in view of results obtained in low-pressure (1 atm or less) investigations of such reversible alloy systems as ZrNi–H_2 by Libowitz, *et al.*,[3] of several Zr alloys by Pebler and Gulbransen,[4] and of a number of alloys by Beck.[5]

Experimental Section

The materials used in this investigation were hydrogen gas obtained from the Matheson Co., Gold Label grade, having an assay of 99.99% H_2; zone-refined Mg rod, 0.25 in. in diameter and assaying 99.99% Mg with the major impurities being 20 ppm of Fe and 20 ppm of Zn; and Cu foil 10 mils thick which assayed 99.9% Cu and had 300 ppm of Pb and 50 ppm of Fe as the major contaminants.

In order to prepare the alloy, approximately 7 g of the metals was weighed into an Alundum crucible which was introduced into a quartz tube; the latter was then attached to a gas-vacuum manifold. The sample was outgassed and helium was introduced. The metal mixture was then heated to alloying temperature by means of an external induction coil. The melt temperature was monitored by an optical pyrometer. After the alloy formed an apparently homogeneous melt, it was cooled to room temperature and the alloy button was removed from the quartz furnace tube and quickly transferred to a drybox having an argon atmosphere. A portion of the alloy was ground, using a stainless steel mortar and pestle, then passed through a 25-mesh (U. S. standard) screen, after which a 1–4-g sample was introduced into a high-pressure hydriding reactor. A 1-g sample was retained for wet analysis.

The high-pressure reactor (Figure 1) was fabricated from a 0.75-in. stainless steel Conoseal tube fitting manufactured by the Marman Division of the Aeroquip Corp., Los Angeles, Calif. One end of the fitting was plugged and provided with a thermocouple connector. The other end was connected by 0.25-in. stainless steel tubing to a bellows-sealed valve which, in turn, was welded to an O-ring connector through which the entire reactor assembly could be attached to a high-pressure manifold. The manifold consisted of 0.25-in. stainless steel tubing with connections to a pressure transducer, pressure gauges, a vacuum pump, and a high-pressure gas reservoir. A diagram of the manifold and reactor assembly is shown in Figure 2. The reactor was heated by means of an electrical resistance furnace which could be raised and lowered.

The volume of the entire system and each individual subsection was calculated by PVT relationships by admitting a known amount of H_2 from a gas reservoir of known volume. Thus, at room temperature the actual amount of H_2 in all or any isolable portion of the system could be calculated when the pressure was known. In order to calculate the amount of H_2 in the reactor assembly at operating temperature, allowance was made for the transition from operating temperature to room temperature through the use of correction factors obtained in calibration runs at various temperatures using known amounts of H_2.

In order to synthesize the hydride, the reactor, containing the alloy sample, was removed from the drybox and connected to the manifold. The sample was outgassed for 1 hr at 300–350°. After outgassing, the sample was then subjected to H_2 pressures up to 350 psia at temperatures up to 350°. The takeup of H_2 by the sample could be followed by the decrease in the H_2 pressure in the manifold and gas reservoir. Blank runs showed the loss of H_2 by diffusion through the wall of the reactor to be negligible at the experimental temperatures and pressures. The sample could be dehydrided by evacuating the reactor and outgassing at 350°. Quantitative measurements were made only on samples that had been through two or more hydriding–dehydriding cycles since such cycling greatly increased reaction rates and substantially reduced the time necessary for equilibration.

Pressure–composition isotherms were obtained by equilibrating the solid hydride phase with H_2, withdrawing H_2 gas from the reactor in small decrements into the reservoir, and measuring each subsequent equilibrium pressure. The change in solid composition was calculated from PVT measurements and by analyzing the solid residues at the end of each run. Occasionally meas-

(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) (a) J. F. Stampfer, Jr., C. E. Holley, and J. F. Suttle, *J. Am. Chem. Soc.*, **82**, 3504 (1960); (b) F. H. Ellinger, *et al., ibid.*, **77**, 2647 (1955).

(3) G. G. Libowitz, H. F. Hayes, and T. R. P. Gibb, Jr., *J. Phys. Chem.*, **62**, 76 (1958).

(4) A. Pebler and E. A. Gulbransen, *Electrochem. Technol.*, **4**, No. 5–6, 211 (1966).

(5) R. L. Beck, "Investigation of Hydriding Characteristics of Intermetallic Compounds," DRI 2059, University of Denver, Denver Research Institute, Denver, Colo., Oct 1962.
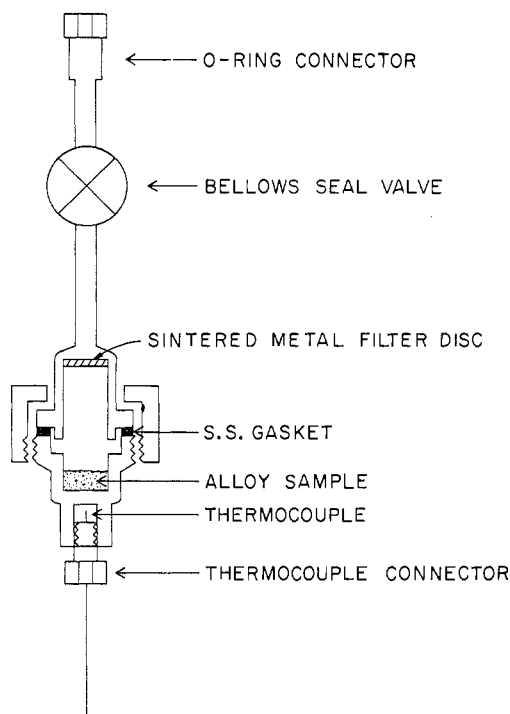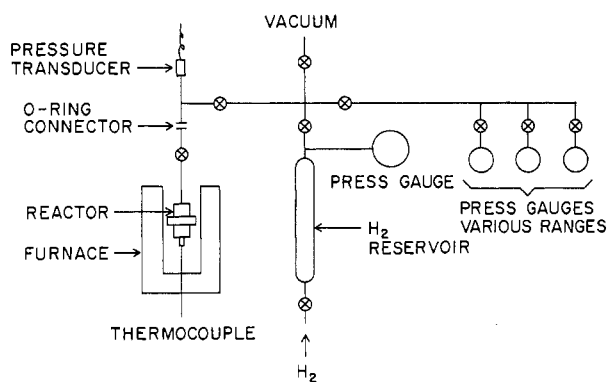
Figure 1.—Stainless steel reactor.

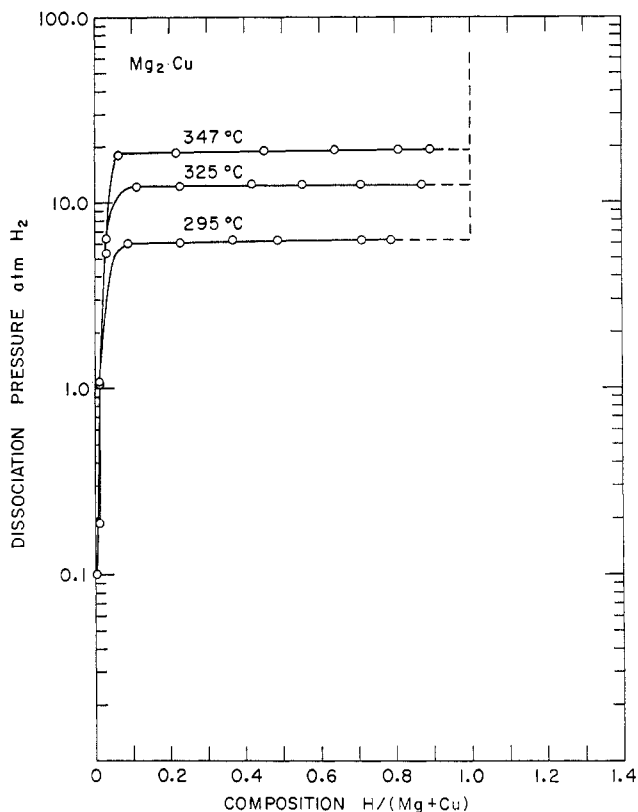Figure 2.—Schematic of experimental apparatus.

Figure 3.—Pressure–composition isotherms for the Mg_2Cu–H_2 system.

urements were made in the opposite direction by the addition of measured increments of H_2 to the reactor; however, equilibrations were extremely slow in this direction as stoichiometric values were approached.

Results and Discussion

Mg forms two intermetallic compounds with Cu, Mg_2Cu and $MgCu_2$.[6] The latter did not react with H_2 at temperatures up to 350° and H_2 pressures of 330 psia; however, Mg_2Cu reacted fairly rapidly at 300° and H_2 pressures of ≈ 300 psia.

In Figure 3 are shown several pressure–composition isotherms for the Mg_2Cu–H_2 system. The initial alloy composition was 44 wt % Mg and 56 wt % Cu (theoretical composition of Mg_2Cu is 43.4 wt % Mg and 56.6 wt % Cu). The only phase present, as determined by an X-ray diffraction pattern of the alloy, was Mg_2Cu. As usual with such isotherms, there is an ascending curve on the left where a solid solution of hydrogen in the metal phase (Mg_2Cu in this case)

(6) M. Hansen, "Constitution of Binary Alloys," McGraw-Hill Book Co., Inc., New York, N. Y., 1958.

exists. This is followed by a pressure plateau. It is believed that its appearance corresponds to the initiation of the reaction

$$2Mg_2Cu + 3H_2 \rightleftharpoons 3MgH_2 + MgCu_2 \qquad (1.$$

all the solid phases being understood to be saturated with hydrogen. X-Ray diffraction patterns of the solid in the region where the atomic ratio H/(Mg + Cu) = 0.4 showed lines for all three solid compounds taking part in reaction 1. There were no unidentified lines. Similar analysis of the product material (H/(Mg + Cu) $\cong$ 1.0) showed only the presence of the MgH_2 and $MgCu_2$. Since, as noted above, $MgCu_2$ did not react with H_2 and the only other phase present in the product is MgH_2, it is almost certain that no ternary hydride formed. When the hydride was decomposed by removing H_2, the diffraction pattern of the residue showed only the phase Mg_2Cu to be present which was the initial starting material; thus reaction 1 is reversible.

To the right of the plateau, the isotherm probably ascends very steeply owing to the fact that MgH_2 is almost a stoichiometric compound[2a] ($MgH_{1.99\pm0.01}$) and the dissolution of hydrogen in $MgCu_2$ is negligible. This portion of the isotherm is represented as a dashed line and could not be definitely established because a small amount of solid hydride had to be decomposed before the first equilibrium point on the right could be defined. Several attempts were made to approach equilibrium from the opposite direction by adding H_2, but as the stoichiometric concentration was approached

$(H/(Mg + Cu) = 1.0)$ the reaction rate in this direction was extremely slow, and practical measurements could not be made.

The dissociation pressures (plateau region) for reaction 1 found at each of a series of temperatures were (given as T (°C), P (atm)): 274, 3.05; 300, 6.02; 324, 11.97; 347, 18.98; and 350, 21.50.

A plot of these dissociation pressures *vs.* the reciprocal of the absolute temperature gives a straight line for log $P_{atm} = -(A/T) + B$, where $A = 3809$ and $B = 7.437$. Thermodynamic functions per mole of H_2 for reaction 1 calculated from these data are given below. The standard states taken for the solids are the pure materials under a pressure of 1 atm and for H_2 as an ideal gas at 1 atm pressure.

$$\Delta H°_{298} = -17.4 \pm 1.0 \text{ kcal/mole of } H_2$$

$$\Delta G°_{298} = -7.3 \pm 1.0 \text{ kcal/mole of } H_2$$

$$\Delta S° = -34.0 \pm 0.7 \text{ cal/mole of } H_2 °K$$

The $\Delta H°_{298}$/mole of H_2 for reaction 1 noted above is consistent with known heats of formation of the solid compounds taking part in the reaction. The heats of formation at 298° for $MgCu_2$ and Mg_2Cu are, respectively, 5.4 $\pm$ 1.1 and 4.0 $\pm$ 1.8 kcal/mole as reported by Smith and Christian[7] and, for MgH_2, 17.8 kcal/mole as reported by Stampfer, *et al.*[2a]

If Mg is present in the alloy in excess of the composition corresponding to Mg_2Cu, the pressure–composition isotherm exhibits two plateaus as shown in Figure 4. In this case it is believed that the lower pressure plateau is due to the known reaction of Mg with H_2

$$Mg + H_2 \rightleftharpoons MgH_2 \qquad (2)$$
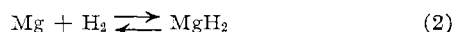
When all of the free Mg is exhausted, the second and higher plateau appears, which is due to reaction 1 of the intermetallic compound, Mg_2Cu, with H_2. An X-ray diffraction pattern taken of material whose composition corresponded to that of the lower plateau region $(H/(Mg + Cu) = 0.5, 330°$ isotherm, Figure 4) has shown MgH_2, Mg_2Cu, and Mg to be present.

In these alloys the lengths of each pressure plateau are proportional to the relative amounts of free Mg and Mg_2Cu initially present. The arrows shown in Figure 4 mark where the boundary between the upper and lower plateaus should occur as predicted by reactions 1 and 2. The calculations did not take into account the formation of solid solutions which occurs to some extent as indicated by slope of the line connecting the two plateaus. In Figure 5 are shown pressure–composition isotherms with alloys containing a large excess of Mg. The short upper plateau is depicted as a dashed line since it was too far to the right to be accurately determined. In systems where a smaller ratio of gas volume to sample weight obtains, *i.e.*, where the generation of a substantial amount of H_2 does not greatly change the solid composition, the upper plateau will appear.

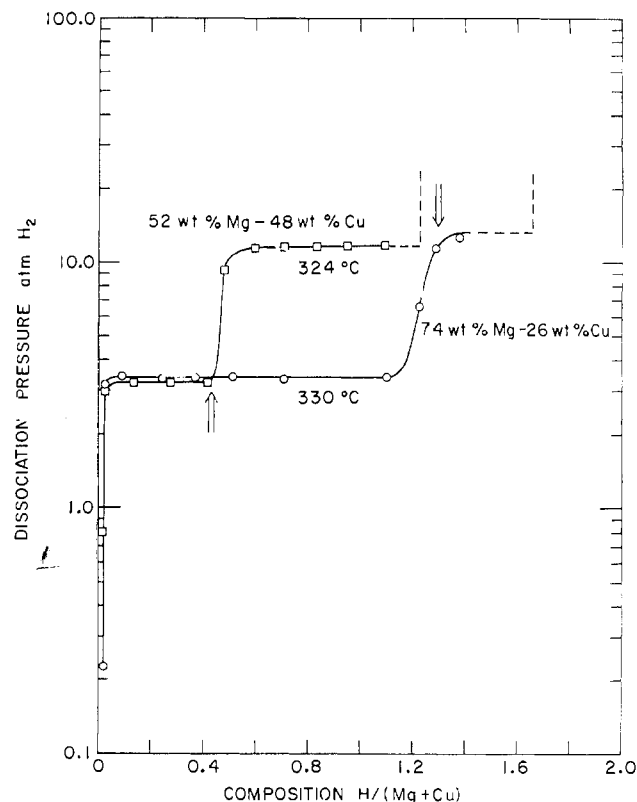(7) J. F. Smith and J. L. Christian, *Acta Met.*, **8**, 249 (1960).

Figure 4.—Pressure–composition isotherms for the system Mg_2Cu–Mg–H_2. Arrows indicate predicted appearance of upper plateau as calculated from initial alloy composition.

It is interesting to note that the presence of Mg_2Cu apparently has a catalytic effect for reaction 2 since substantially higher H_2 pressures and temperatures are necessary to form MgH_2 from Mg alone.[2] In addition, the decomposition of MgH_2 with Mg_2Cu present was quite rapid, particularly at the higher H/Mg ratios where equilibrium dissociation pressures could be reached in about 1 hr even at 275°.

The dissociation pressures (plateau region) for MgH_2 in the presence of Mg_2Cu at various temperatures are (given as T (°C), P (atm)): 273, 0.63; 300, 1.42; 330, 3.20; 350, 5.41; and 375, 9.59.

A plot of these dissociation pressures *vs.* the reciprocal of the absolute temperature yields a straight line for log $P_{atm} = -(4094/T) + 7.299$. The thermodynamic functions for the formation of MgH_2 calculated from these data, assuming Mg_2Cu acts purely as a catalyst, are

$$\Delta H_f°_{298} = -18.7 \pm 1.0 \text{ kcal/mole}$$

$$\Delta G_f°_{298} = -8.7 \pm 1.0 \text{ kcal/mole}$$

$$\Delta S_f°_{298} = -33.4 \pm 0.7 \text{ cal/mole °K}$$

These values are in good agreement with previous values obtained by Stampfer, *et al.*,[2b] which are

$$\Delta H_f°_{298} = -17.790 \text{ kcal/mole}$$

$$\Delta G_f°_{298} = -8.170 \text{ kcal/mole}$$

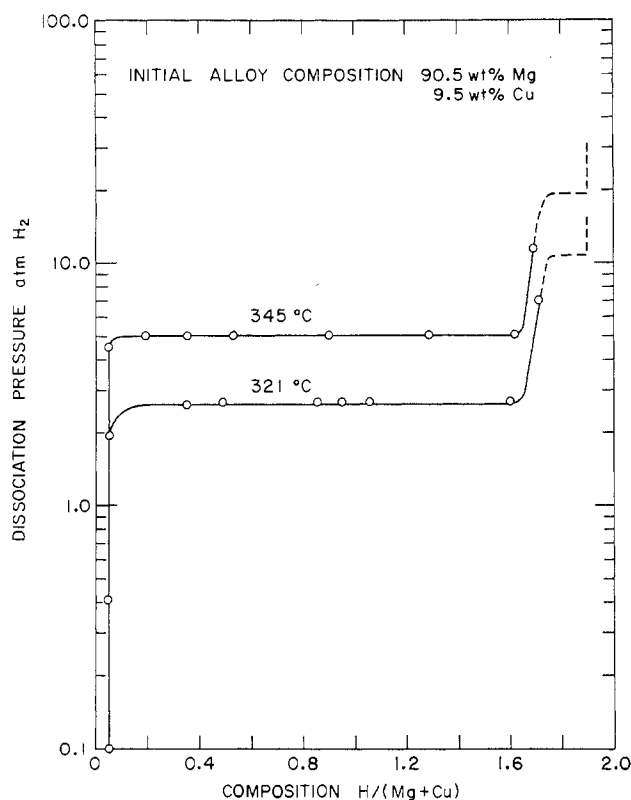$$\Delta S_f°_{298} = -32.3 \text{ cal/mole °K}$$

Figure 5.—Pressure–composition isotherm for the system 90.5 wt % Mg–9.5 wt % Cu–H$_2$.

In order to obtain a further check on the validity of eq 1 and 2, several alloys of various compositions were hydrided and dehydrided several times and then finally contacted with H$_2$ for several days. The H$_2$ pressure over the alloy was held 200 psi above the hydride dissociation pressure. These samples were analyzed for hydrogen content, and, as shown in Table I, the actual hydrogen contents are in good agreement with predicted values.

TABLE I

MAXIMUM HYDROGEN CONTENT OF Mg–Cu ALLOYS

Alloy composition,[a] wt %	Predicted value			Actual value		
	H/(Mg + Cu)	H/Mg	Wt % H	H/(Mg + Cu)	H/Mg	Wt % H
44.1 Mg 56.1 Cu	1.02	1.51	2.69	1.03	1.53	2.72
44.1 Mg 56.2 Cu	1.02	1.51	2.69	0.96	1.42	2.53
55.0 Mg 45.0 Cu	1.28	1.69	3.71	1.28	1.69	3.71
52.0 Mg 48.1 Cu	1.22	1.65	3.43	1.15	1.56	3.25
90.5 Mg 9.5 Cu	1.88	1.96	6.85	1.82	1.88	6.62

[a] By wet analysis.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK, NEW YORK 10027

Transition Metal Borohydride Complexes. I. The Solid-State Structure of Borohydridobis(triphenylphosphine)copper(I)

By STEPHEN J. LIPPARD AND KENNETH M. MELMED

The crystal and molecular structure of borohydridobis(triphenylphosphine)copper(I) has been determined by a three-dimensional X-ray crystallographic analysis. The compound crystallizes as colorless needles in space group C2/c with unit cell dimensions $a = 24.64$, $b = 9.058$, $c = 15.43$ A, $\beta = 116.2°$, $Z = 4$. From 1750 independent observable reflections collected on a full-circle automated diffractometer, the structure was solved by use of conventional Patterson, Fourier, and least-squares refinement techniques. All atoms including hydrogen were located and refined to final values of the discrepancy indices of $R_1 = 0.059$ and $R_2 = 0.044$. The coordination geometry of the copper atom is quasi-tetrahedral, with two hydrogen atoms of the borohydride group bridging the copper and boron atoms. The resultant distances—Cu–P $= 2.276 \pm 0.001$, Cu–B $= 2.184 \pm 0.009$, Cu–H $= 2.02 \pm 0.05$, (B–H)$_{av}$ $= 1.31 \pm 0.05$ A—and angles—P–Cu–P' $= 123.26 \pm 0.06$, P–Cu–B $= 118.4 \pm 0.1°$—suggest delocalized bonding between the copper atom and the borohydride group in which direct Cu–B overlap might be significant.

Introduction

In 1949, Hoekstra and Katz prepared the first transition metal borohydride complexes by allowing metal (Ti, Hf, Th) halides to react with lithium borohydride or aluminum borohydride.[1] Since that time, a number of workers have succeeded in isolating compounds containing BH$_4^-$ bonded to a transition metal.[2–13] Char-

acteristically, these complexes are nondissociative in solution, decompose at various temperatures to form the free metal and numerous other products both in

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