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Ternary metal-carbon-hydrogen compounds of some transition metals

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POUNDS OF SOME TRANSITION METALS.

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TERNARY METAL-CARBON-HYDROGEN COMPOUNDS
OF SOME TRANSITION METALS

Joachim Rexer

A Dissertation Submitted to the
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1962

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I. INTRODUCTION

An investigation of the thorium-carbon-hydrogen system (1) resulted in the discovery and characterization of the two new compounds $\text{ThC}\cdot\text{ThH}_2$ and $\text{ThC}\cdot 2\text{ThH}_2$. These compounds have a greater thermal stability than thorium dihydride and have enthalpies of dissociation of 48.4 and 38.3 kcal/mole of hydrogen respectively as compared to 34.2 (2) to 35.2 (3) kcal/mole of hydrogen for thorium dihydride. The metal atoms in $\text{ThC}\cdot\text{ThH}_2$ and $\text{ThC}\cdot 2\text{ThH}_2$ are arranged on a hexagonal closest packed lattice and a monoclinic lattice respectively. The positions of the carbon and hydrogen atoms in these compounds have not been determined and consequently the type of bonding in these compounds cannot be deduced from the bond distances and arrangement. The volume of the $\text{ThC}\cdot\text{ThH}_2$ hexagonal unit cell is very nearly equal to the sum of the volume of a thorium monocarbide primitive unit cell and the volume of a thorium dihydride primitive unit cell. This indicates that the bonding in this compound is probably quite similar to the bonding in thorium monocarbide and thorium dihydride. The metallic luster and electrical conductivity of thorium monocarbide and thorium dihydride are also shown by $\text{ThC}\cdot\text{ThH}_2$.

After thorium was shown to form these ternary compounds,

it was of interest to see if other metals form similar compounds. It was necessary to limit the number of metals to be studied and the metals chosen for study were those metals which form carbides and hydrides with properties and stoichiometry similar to the corresponding compounds of thorium. Table 1 shows the crystal structures for some transition metal carbides and hydrides and the enthalpy of dissociation of the hydrides. Thorium forms a monocarbide with the sodium chloride structure (4) and a dihydride with a distorted fluorite structure (5). Titanium, zirconium and hafnium form a carbide (6 and 7) and a hydride (8 and 9) with the same structures and stoichiometry as those of thorium. To extend the scope of this investigation, some metals that form either a carbide with the sodium chloride structure or a hydride with the fluorite structure were also studied. Yttrium and lanthanum form dihydrides with the fluorite structure (10 and 11) but do not form monocarbides with the sodium chloride structure (12 and 13). Vanadium, niobium and tantalum form monocarbides with the sodium chloride structure (14) but form monohydrides instead of dihydrides (15 and 16). These metals also form lower carbides (6, 17 and 18) in which the metal atoms are arranged in a hexagonal

Table 1. Some transition metal hydrides and carbides

Hydrides			Carbides	
Compound	Structure	ΔH_d kcal/mole	Compound	Structure
ThH ₂	Distorted fluorite	34.7	ThC	Sodium chloride
			ThC ₂	Monoclinic
TiH ₂	Distorted fluorite	39.4	TiC	Sodium chloride
ZrH ₂	Distorted fluorite	49.0	ZrC	Sodium chloride
HfH ₂	Distorted fluorite	33.2	HfC	Sodium chloride
YH ₂	Fluorite		Y ₃ C	Carbon deficient sodium chloride
			Y ₂ C ₃	Existence only suggested
			YC ₂	Calcium dicarbide
LaH ₂	Fluorite	49.7	La ₂ C ₃	Plutonium sesqui- carbide
			LaC ₂	Calcium dicarbide
VH	Metal atoms on a b.c.c. lattice becoming tetrag- onal at higher hydrogen		V ₂ C	Metal atoms on a h.c.p. lattice
			VC	Sodium chloride

Table 1. (Continued)

Hydrides			Carbides	
Compound	Structure	ΔH_d kcal/mole	Compound	Structure
NbH	Metal atoms on a deformed b.c.c. or a f.c. orthorhombic lattice		Nb ₂ C	Metal atoms on a h.c.p. lattice
			NbC	Sodium chloride
TaH	Metal atoms on a b.c. tetragonal lattice becoming orthorhombic at higher hydrogen contents		Ta ₂ C	Metal atoms on a h.c.p. lattice
			TaC	Sodium chloride

closest packed lattice with the carbon atoms occupying one half of the octahedral sites. The formation of ternary compounds of these metals with the stoichiometry $MC \cdot MH_2$ would consist of the solution of hydrogen in the lower carbides rather than the appearance of a new phase.

The investigation of heterogeneous equilibrium reactions requires the determination of the concentration of the components in each phase as a function of temperature. For the systems investigated, the gas phase contained only hydrogen and the concentration of hydrogen in this phase was equal to the pressure. In a binary metal-hydrogen system, the concentration of the components in each condensed phase can be established by determining the variation in the absorbed hydrogen with pressure at a constant temperature. In a metal-carbon-hydrogen ternary system the concentration of the components in each condensed phase can be established by investigating a number of compositions in the ternary phase system. The concentration of the components in each of the condensed phases can sometimes be deduced from the binary phase relationships and the variation of the amount of absorbed hydrogen with pressure at a constant temperature. If the saturation solubility of carbon in the metal

is very low the effect of the carbon solubility on the activity of hydrogen in the metal is insignificant. This was shown to be true for thorium by Peterson and Rexer (1) in their investigation of the ternary thorium-carbon-hydrogen system. They also showed that thorium monocarbide absorbed an insignificant amount of hydrogen. If the quantity of the nonvolatile components, the total quantity of hydrogen, and the volume of the system are known the amount of hydrogen in the condensed phases can be determined by measuring the temperature and pressure at equilibrium. If the binary phase relationships are known as a function of pressure and temperature, the concentration of the components in each of the condensed phases in the ternary system can be determined from equilibrium pressure-composition isotherms. In keeping with the phase rule, the maximum number of phases that can coexist at equilibrium in a ternary system at constant temperature is four. In an equilibrium pressure-composition isotherm for a three component system the equilibrium hydrogen partial pressure is invariant with composition when three condensed phases coexist at equilibrium. If only one or two condensed phases are present at equilibrium the hydrogen content of these phases will

vary with the hydrogen equilibrium partial pressure. The formation of the ternary metal-carbon-hydrogen compounds was detected by observing the variation in composition of the condensed phases with hydrogen equilibrium partial pressure at a constant temperature. Powder x-ray diffraction techniques were used to determine the crystal class and lattice parameters of the ternary compounds, and photomicrographs were used to study the phases present in the hydrogen equilibrated specimens.

II. EXPERIMENTAL

A. Materials

The alloys that were equilibrated with hydrogen were prepared by arc-melting the metal with weighed amounts of carbon in the form of spectroscopic electrode rods. The compositions of the metals are shown in Table 2. Carbon was determined by combustion in oxygen, nitrogen by the Kjehldahl method and oxygen and hydrogen by vacuum fusion. The metallic elements were determined by emission spectroscopy. Hydrogen was obtained by the thermal decomposition of uranium hydride as described by Spedding et al (19).

Arc-melted alloys tend to be inhomogeneous due to the large thermal gradients and non-equilibrium solidification which are characteristic of the arc-melting process. If the components of the specimen are not completely miscible at the arc-melting temperatures, the distribution of the two phases may be quite nonuniform. Microscopic examination of all of the two phase alloys showed zones in which the carbide phase had concentrated. The amount of segregation in the arc-melted alloys depended on the fluidity of the molten pool and the solubility of carbon in the molten metal

at the arc-melting temperatures. The arc-melted alloys of titanium, zirconium and hafnium were very inhomogeneous. The yttrium and lanthanum alloys were more homogeneous because of the higher solubility of carbon in the liquid and greater fluidity of the molten pool. The vanadium specimen was near the composition V_2C and appeared to be quite homogeneous.

Table 2. Composition of the metals in ppm

Element	Ti	Zr	Hf	Y	La	V
Ag		< 50			< 50	
Al		< 100			<100	
Ca		< 50	<100	< 10	< 50	
Cu	< 100	< 50	< 50		<200	
F				105		
Fe	< 100	400	600	209	<500	150
Hf		<1000				
Mg	< 50		<100	13	<100	
N	220	16	97	12	115	60
Ni	< 50		< 50	150	<200	
O	1748	204	162	307	370	150
Si	< 100	<100	<100		< 50	
Sn	< 50					
Ti		<200	<100			
Zr	<200		300			

It is desirable that the specimen that is equilibrated with hydrogen be one single piece. A fragmented specimen has more surface area available for contamination and a

finely divided specimen of a two phase alloy may have individual particles which do not have the same composition as the composition of the total specimen. The yttrium and lanthanum specimens were machined to the desired diameter on a lathe with a cutting tool which had been carefully cleaned with trichloroethylene to avoid oil contamination. These alloys reacted with water and the machined specimens were kept under absolute alcohol prior to weighing and sealing into the equilibrating apparatus. Because the lanthanum specimen was partially molten at the equilibration temperature, it was placed in a tantalum crucible. The machined specimens were approximately six mm in diameter and 15 to 30 mm in length. The titanium, zirconium and hafnium specimens of low carbon content were cut to the desired size with a water cooled abrasive wheel. Those specimens with a higher carbon content and the vanadium specimen were broken into pieces just small enough to fit into the quartz furnace tube. All of these specimens were washed and dried with 95 per cent ethyl alcohol prior to weighing and sealing into the equilibrating apparatus.

B. Apparatus

A schematic diagram of the hydrogen equilibration apparatus is shown in Fig. 1. The quartz furnace tube was 8 mm inside diameter and was attached to the measuring portion of the system by means of a standard ground glass taper joint sealed with Apiezon-W wax. The quartz furnace tube extended into either a solid silver or a stainless steel clad copper block centered in a Multiple Unit, type 70-T, resistance furnace. The temperature was measured by a chromel-alumel thermocouple inserted between the furnace tube and the metal block. The temperature for an axial distance of about six cm within the metal block was uniform to within one centigrade degree. The specimen was centered in this region and, consequently, the existence of an appreciable thermal gradient in the specimen was unlikely. The furnace temperature was controlled by regulating the voltage output of a Raytheon 500 watt voltage stabilizer with an autotransformer and was constant to within two degrees. The apparatus was evacuated with a Duo-Seal type 1405 mechanical pump. The volumes of the various portions of the gas system were determined so that the system could be used to measure the amount of hydrogen added to or taken

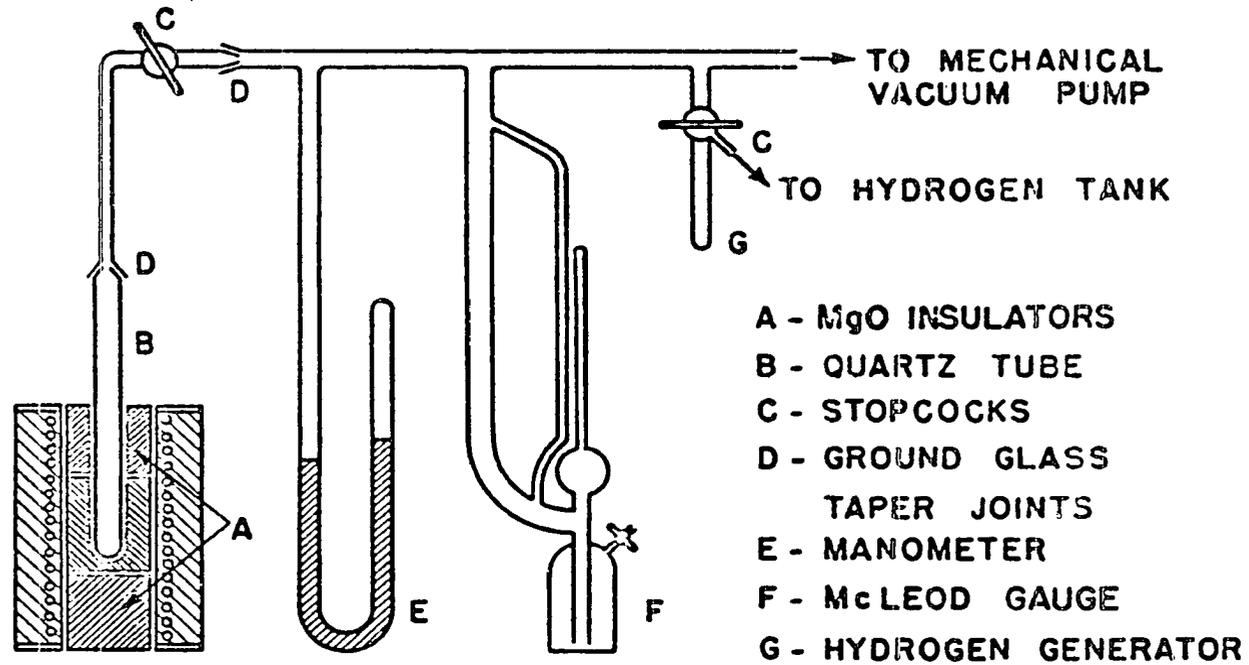


Fig. 1. Schematic diagram of the equilibration apparatus

from the specimen. The amount of gas in the furnace tube at constant pressure decreased with increasing furnace temperature so an effective volume was determined at several furnace temperatures. The mercury manometer could be read to ± 0.3 mm and the McLeod gauge to ± 6 microns up to one cm.

C. Operating Procedure

The amount of hydrogen absorbed by the specimen was determined as a function of the equilibrium hydrogen pressure. After the addition of each successive measured amount of hydrogen, the specimen was allowed to absorb the hydrogen at a constant temperature until equilibrium was reached. Equilibrium was considered to be established after the pressure had been constant within one mm for at least 12 hours. This often requires several days because the attainment of equilibrium required the diffusion of carbon as well as the diffusion of hydrogen. In specimens containing the carbide phase as coarse particles, the rate of attainment of equilibrium was extremely slow. At equilibrium the hydrogen pressure was measured and the amount of hydrogen absorbed by the specimen was determined from

the difference between the total amount of hydrogen present and the amount of hydrogen remaining in the gas phase after equilibrium was established.

III. RESULTS AND DISCUSSION OF RESULTS

A. Pressure-Composition-Temperature Studies

The equilibrium pressure-composition isotherms show that titanium, zirconium, hafnium, yttrium and lanthanum all formed a ternary metal-carbon-hydrogen compound. These ternary compounds have the approximate stoichiometry $MC \cdot MH_x$ with the metal atoms arranged on a hexagonal closest packed lattice. The absorption of hydrogen by V_2C does not produce a new phase but causes an expansion of the hexagonal V_2C lattice.

The interpretation of the pressure-composition isotherms obtained by equilibrating a metal or a metal-carbon alloy with hydrogen requires some knowledge of the phase equilibria in the binary systems. McQuillan (20) showed that at low concentrations hydrogen goes into solution in α -titanium monatomically in keeping with Sievert's law. He also showed that hydrogen lowered the allotropic transformation temperature of titanium from 882°C to a eutectoid reaction at approximately 350°C and 38 atomic per cent hydrogen. The maximum solubility of hydrogen in α -titanium is approximately eight atomic per cent hydrogen

and occurs at the eutectoid temperature. Cadoff and Nielsen (21) showed that carbon raised the transformation temperature to a peritectoid reaction at 920°C . The maximum solubility of carbon in α -titanium is 1.9 atomic per cent at the peritectoid temperature. There is a rapid decrease in the solubility with decreasing temperature to about 0.40 atomic per cent at 550°C . The maximum composition of titanium monocarbide is TiC at all temperatures up to the melting temperature. At the peritectoid horizontal and at 550°C the lower composition limits are approximately $\text{TiC}_{0.58}$ and $\text{TiC}_{0.62}$ respectively.

The variation in hydrogen content of titanium metal and the titanium-carbon alloy at 800°C is shown in Fig. 2 as a function of the hydrogen pressure. The amount of hydrogen in solution in the condensed phases was a function of the hydrogen equilibrium pressure until the metal phase, α -titanium, underwent an allotropic transformation. At the pressure at which this transformation occurred, an additional equilibrium phase, β -titanium, appeared and the equilibrium pressure became invariant over the composition range in which this transformation occurred. Above this pressure, the metal phase was β -titanium. In the

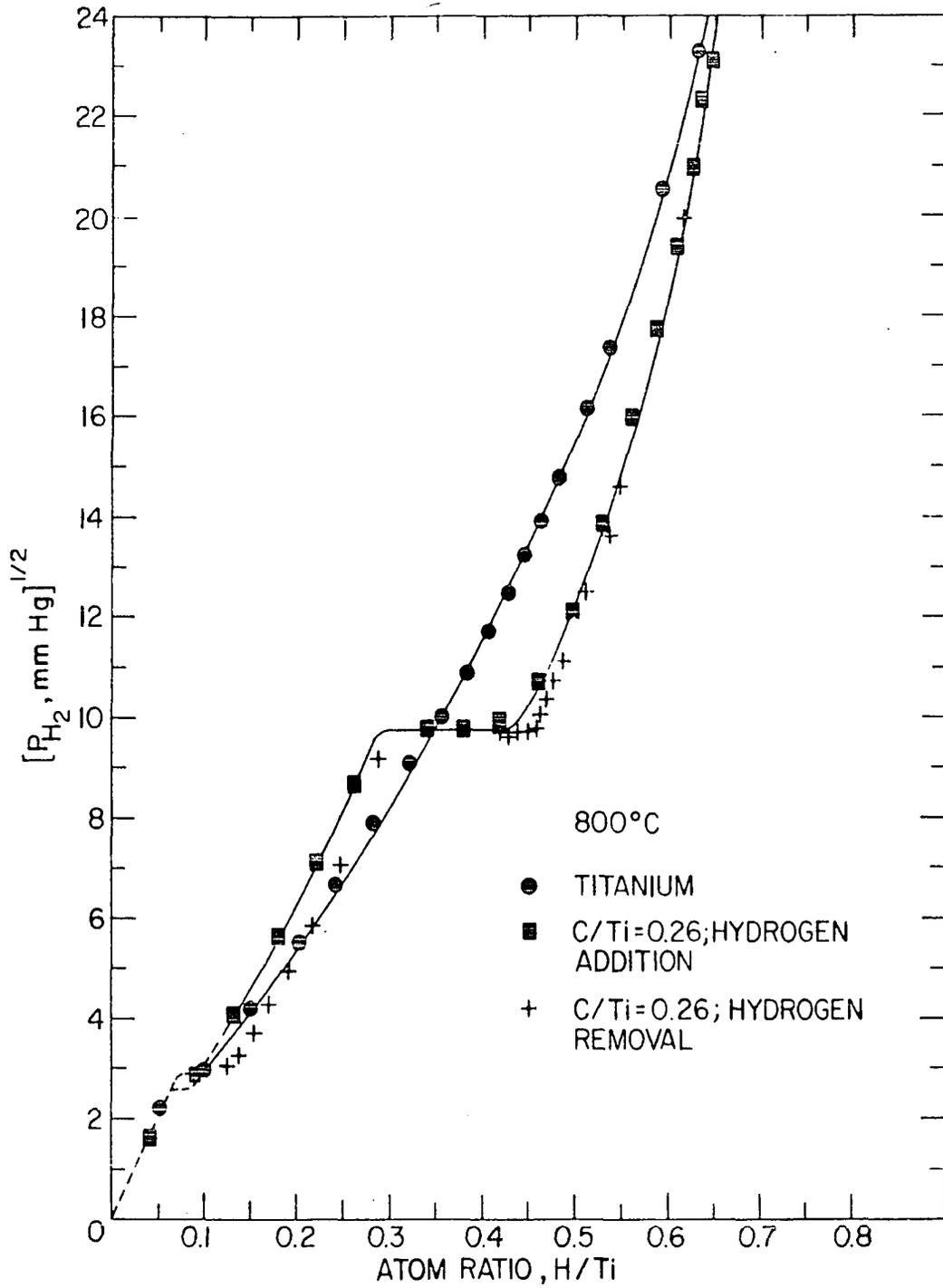


Fig. 2. Pressure-composition isotherm for titanium and a titanium-carbon alloy

pure titanium specimen, the hydrogen content of the β -titanium increased with increasing hydrogen pressure until titanium dihydride started to form. The dissociation pressure of titanium dihydride at 800°C is above one atmosphere and cannot be observed on this equilibrium pressure-composition isotherm. At a pressure of about 95 mm of mercury the hydrogen pressure above the titanium-carbon alloy became invariant over a limited composition range. Three condensed phases must coexist at equilibrium in this pressure invariant region. These phases were β -titanium, titanium monocarbide and a ternary compound of the approximate stoichiometry $\text{TiC}\cdot\text{TiH}_x$. The specimen contained an excess of metal above that needed for the formation of the ternary compound and an increase in the hydrogen pressure above 95 mm of mercury was accompanied by the complete disappearance of the carbide phase.

To show that the reactions that occurred in the ternary system were reversible, the pressure-composition isotherm was established by first adding and then withdrawing known quantities of hydrogen from the specimen. The difference between the two pressure-composition isotherms was expected since the loss of hydrogen through the hot quartz tube was

cumulative and became significant in the latter part of the experiment.

The titanium-carbon alloy was equilibrated with hydrogen at temperatures from 550° to 850°C at 50 degree intervals. The equilibrium pressures are shown in Fig. 3 as a function of the hydrogen content. At 700°C and above the reactions that occurred during the hydrogen equilibration were the same as those described for the equilibration at 800°C. At 650°C and below the ternary compound should form before the metal undergoes its allotropic transformation. At 550°, 600° and 650°C the hydrogen pressure became invariant over a limited composition range at pressures below one cm. It was initially thought that the ternary compound was forming in these pressure invariant regions until a plot of the dissociation pressure against reciprocal degrees Kelvin, shown in Fig. 6, did not give a straight line. An examination of the binary titanium-hydrogen system showed that the constant pressure plateaus at these temperatures were related to the α to β -titanium transformation. The rate at which the ternary compound formed at these temperatures was very slow compared to the rate at which the allotropic transformation occurred. Because of the decreasing rate of

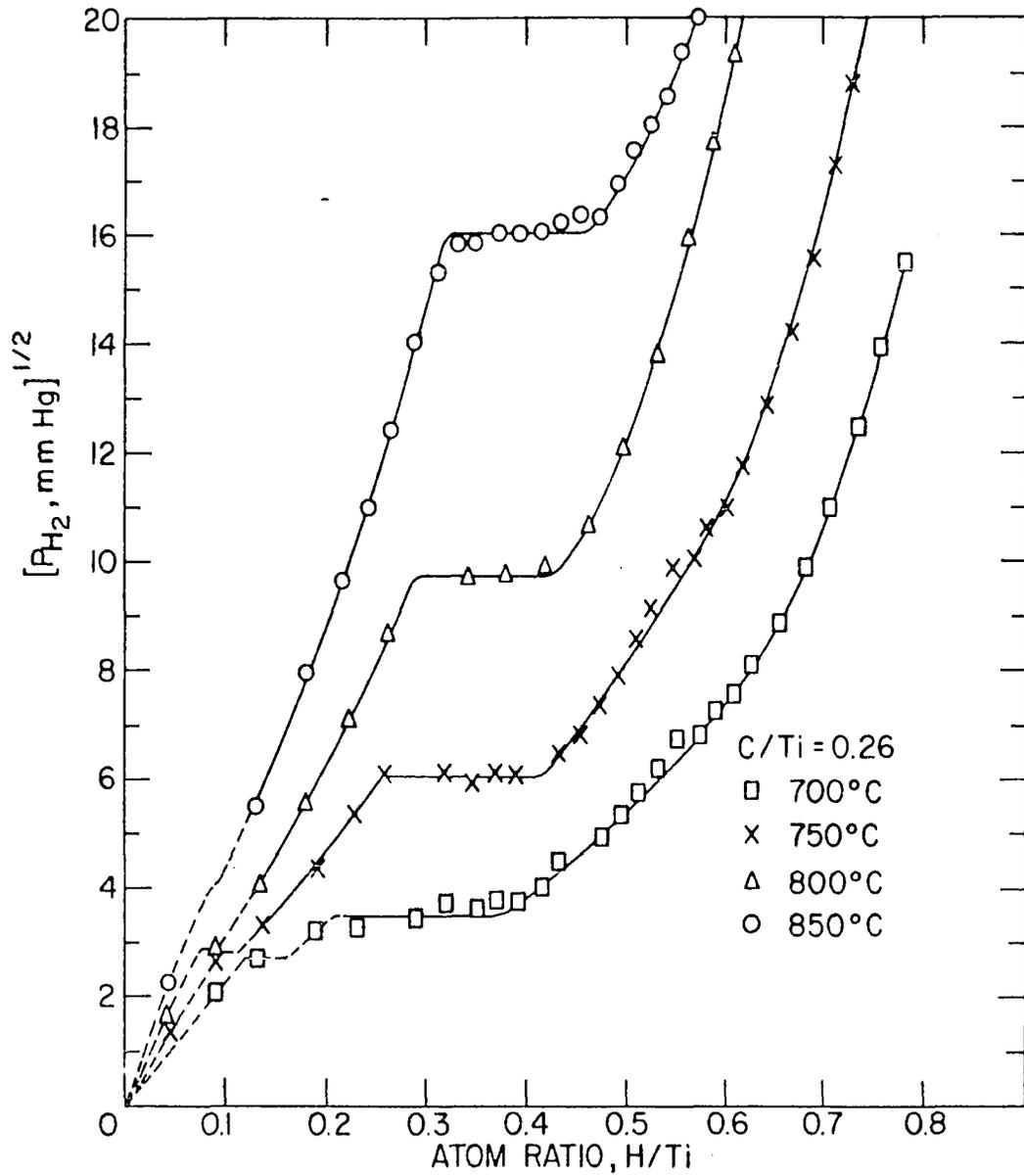


Fig. 3. Pressure-composition isotherms for a titanium-carbon alloy

formation of the ternary compound with decreasing temperature, complete equilibrium was not established at these low pressures and temperatures. At 600°C and a hydrogen equilibrium pressure of about 240 mm of mercury titanium dihydride formed from β -titanium. This reaction did not occur at a constant pressure. A study of the thorium-hydrogen system by Peterson and Rexer (22) showed that the increase in hydrogen dissociation pressure with hydrogen content, in the three phase region, was related to the dissolution of thorium oxide in thorium hydride. It is very likely that the dissolution of an impurity also caused the change in the dissociation pressure of titanium hydride. McQuillan (20) and Haag and Shipko (23) gave different values for the dissociation pressure of titanium dihydride at the same temperature. McQuillan gave an expression for the dissociation pressure of the dihydride as a function of temperature from which a calculated value of 355 mm of mercury was obtained. Haag and Shipko stated that the dissociation pressure shown by McQuillan was about 30 per cent higher than their value. The difference between the dissociation pressure of titanium dihydride found in this investigation and that of other investigators was probably

due to differences in the carbon, oxygen and nitrogen contents of the titanium. Above the dissociation pressure of titanium dihydride, the ternary compound and the dihydride continued to absorb hydrogen with increasing hydrogen pressure. Since the specimen initially consisted of titanium monocarbide and titanium metal and finally consisted of titanium dihydride and the ternary compound, all of the equilibrium phases between titanium carbide and titanium hydride should have formed during the equilibration at 600°C.

The binary zirconium-carbon and hafnium-carbon systems (24) are very similar to the titanium-carbon system. The solubility of carbon in the metal is very low and at temperatures between 850° and 1000°C the composition of the monocarbide in equilibrium with the metal phase is about $MC_{0.5}$. The maximum composition of the monocarbide is MC at all temperatures up to the melting temperature. Carbon raises the allotropic transformation temperature of both metals slightly. In the zirconium-carbon alloy equilibrated with hydrogen β -zirconium was the metal phase at the equilibrating temperatures. With the hafnium-carbon alloy the metal phase was α -hafnium at the equilibrating temperatures.

In the zirconium-hydrogen system, LaGrange et al (25)

showed that hydrogen lowers the transformation temperature to a eutectoid at 547°C and 23 atomic per cent hydrogen. Hafnium undergoes an allotropic transformation at about 1750°C and the effect of hydrogen on this transformation has not been reported. In both the zirconium-hydrogen and hafnium-hydrogen (26) binary systems the first intermediate phase is the dihydride. Edwards, Levesque and Cubicciotti (27) and Martin and Rees (28) showed that the dissociation pressure of zirconium dihydride is above one atmosphere at 900°C. Libowitz (29) gave a relationship expressing the dissociation pressure of hafnium dihydride as a function of temperature from which a calculated value of 158.5 mm of mercury at 850°C was obtained.

The variation in hydrogen content of a zirconium-carbon alloy with a carbon to zirconium atom ratio of 0.12 is shown in Fig. 4 as a function of pressure. The condensed phases absorbed increasing amounts of hydrogen with increasing pressure until the ternary compound started to form. Formation of the ternary compound caused the pressure to become invariant with composition until the carbide phase disappeared. Above the dissociation pressure of the ternary compound, the hydrogen content of the condensed phases,

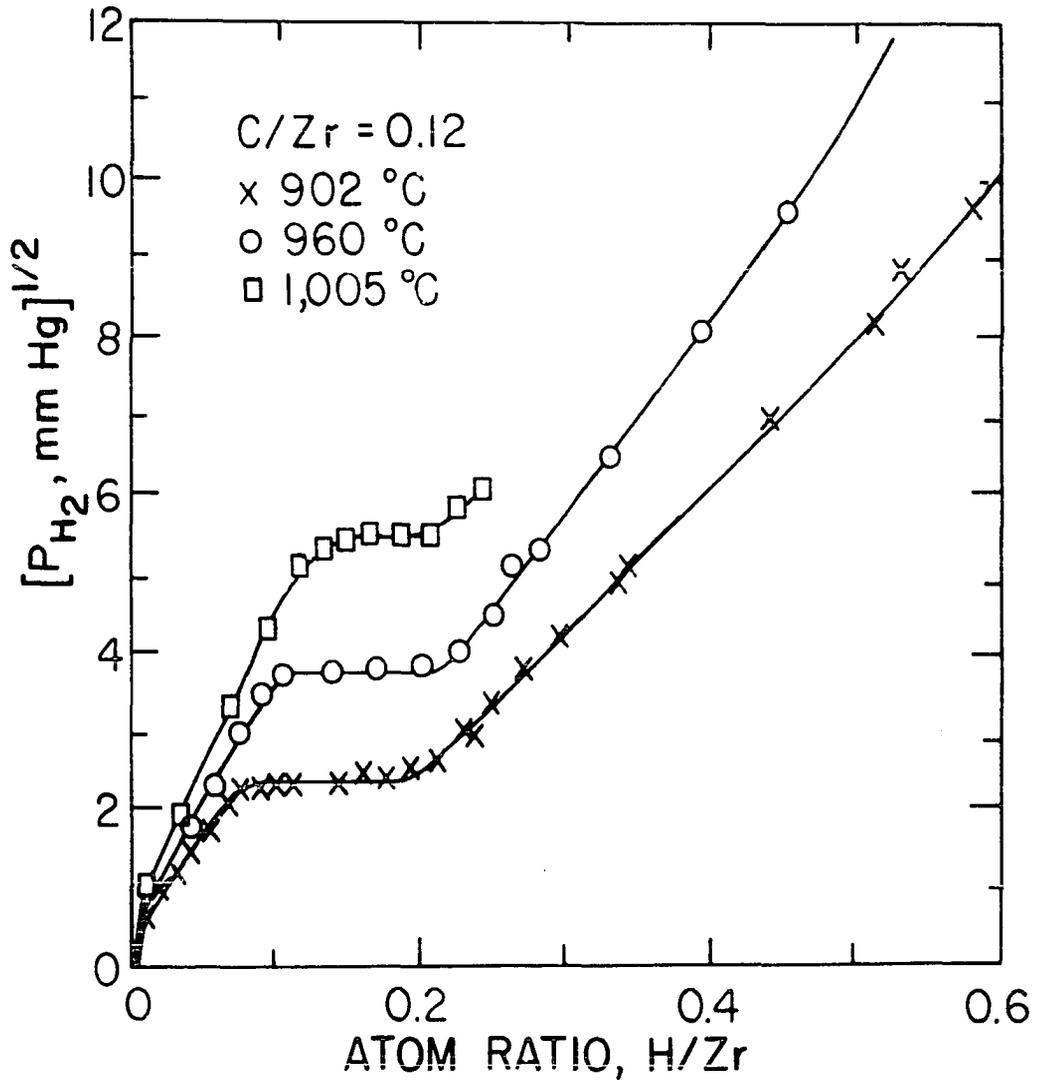


Fig. 4. Pressure-composition isotherms for a zirconium-carbon alloy

β -zirconium and ternary compound, were a function of the hydrogen pressure. Since the dissociation pressure of zirconium dihydride is above one atmosphere at 900°C the formation of this compound was not observed.

The variation in the hydrogen equilibrium pressure with hydrogen content of an alloy of hafnium with a carbon to hafnium atom ratio of 0.055 is shown in Fig. 5. The reactions occurring on absorbing hydrogen are the same as those occurring with the zirconium alloy except that the metal phase was α -hafnium. In addition, at 850°C hafnium dihydride formed from the metal phase and all of the equilibrium phases formed between carbide and hydride should be shown by this isotherm. As in the equilibration of the titanium alloy with hydrogen, the formation of the dihydride did not proceed at a constant pressure. This was most likely caused by the dissolution of an impurity in the hydride phase.

The enthalpies of formation of the ternary compounds of titanium, zirconium and hafnium were calculated from the variation in the equilibrium dissociation pressure with temperature. The logarithm of the dissociation pressure is a linear function of reciprocal degrees Kelvin as can be

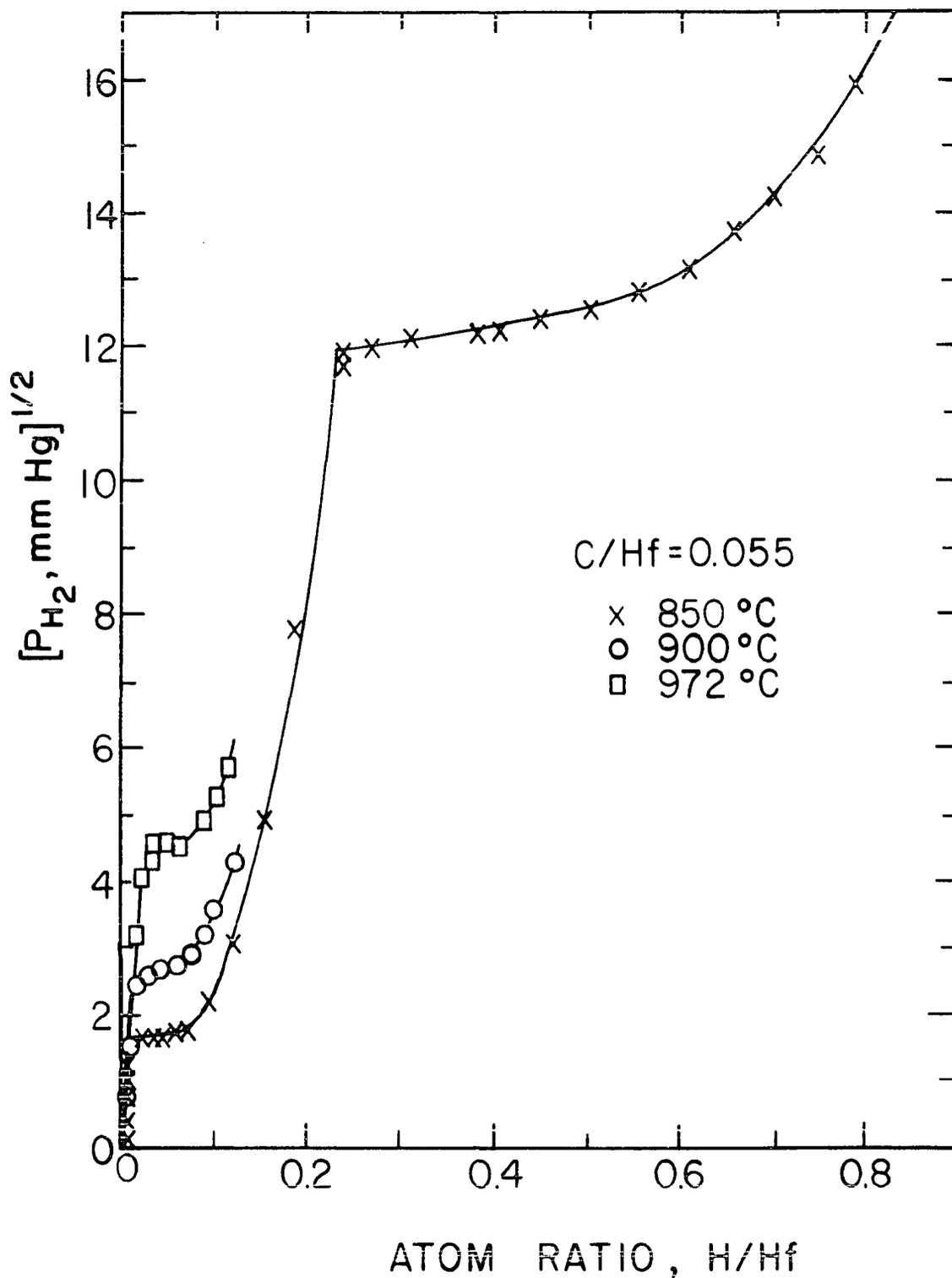


Fig. 5. Pressure-composition isotherms for a hafnium-carbon alloy

seen in Fig. 6. The general reaction for the formation of the ternary compounds is $M(s) + MC(s) + H_2(g) \rightleftharpoons MC \cdot MH_x(s)$ where the composition of the condensed phases is the equilibrium composition and appropriate coefficients should appear in front of the symbol for each phase. The equation relating the dissociation pressures to temperature is

$$\log_{10}P(\text{mm Hg}) = A - B/T.$$

The constants of this equation were obtained by a method of least squares and are given in Table 3 together with the enthalpy changes per mole of hydrogen accompanying the formation of the ternary compounds.

Table 3. Some constants and enthalpies of formation for carbohydrides

Compound	A	B	ΔH_f kcal/mole
TiC·TiH _x	10.91	9,560	-43.7
ZrC·ZrH _x	9.82	10,670	-48.8
HfC·HfH _x	9.24	9,870	-45.2

The complete equilibrium phase relationships between yttrium and carbon have not been reported and no pressure-composition-temperature studies have been reported for the

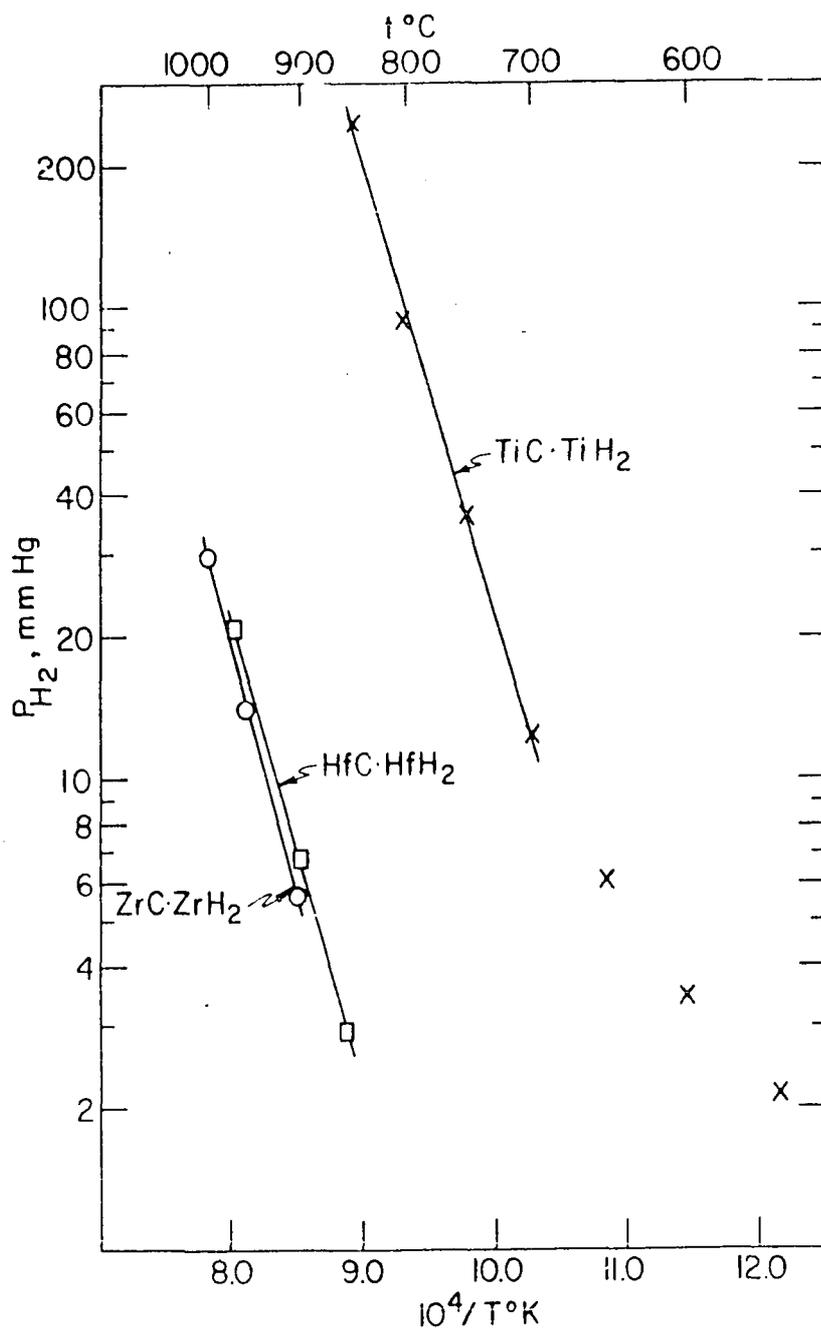


Fig. 6. Logarithm of equilibrium hydrogen pressure vs reciprocal temperature

yttrium-hydrogen binary system. Spedding, Gschneidner and Daane (12) investigated the crystal structures of some of the rare earth carbides and showed that the carbide in equilibrium with yttrium metal is Y_3C . This compound appears to exist over the range of composition from $YC_{0.25}$ to $YC_{0.40}$. Yttrium also forms a dicarbide and possibly forms a sesquicarbide. Lundin and Klodt (10) reported that the first intermediate phase formed in the binary yttrium-hydrogen system is yttrium dihydride which is isomorphous with lanthanum dihydride.

An alloy of yttrium with a carbon to yttrium atom ratio of 0.17 was equilibrated with hydrogen at $951^{\circ}C$. The equilibrium hydrogen pressure is shown as a function of the hydrogen content in Fig. 7. Constant pressure plateaus were observed at one mm and at 10 mm. At a pressure of one mm of mercury, the ternary compound of approximate stoichiometry $YC \cdot YH_x$ formed and at 10 mm yttrium dihydride formed. Above the dissociation pressure of the dihydride, the hydrogen content of the condensed phases, ternary compound and dihydride, increased with pressure.

The binary lanthanum-carbon system was investigated by Spedding et al (13) who found two intermediate compounds.

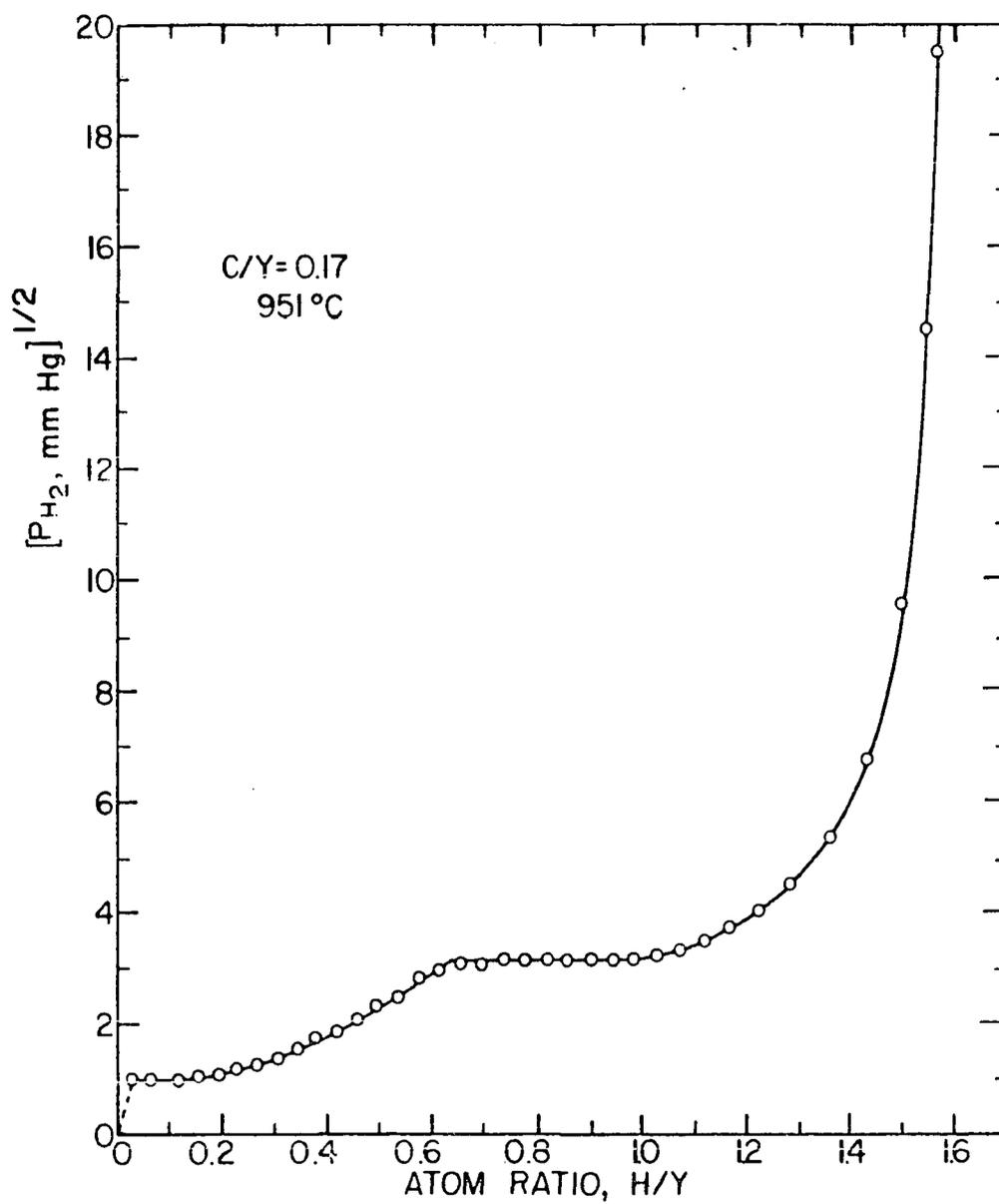


Fig. 7. Pressure-composition isotherm for a yttrium-carbon alloy

These compounds are lanthanum sesquicarbide and lanthanum dicarbide. They also found that carbon lowers the melting point of lanthanum from 920°C to a eutectic occurring at 806°C and 20.6 atomic per cent carbon. The effect of hydrogen on the melting point of lanthanum is not known. Mulford and Holley (30) studied the binary lanthanum-hydrogen system and derived an equation relating the dissociation pressure of the dihydride to temperature. According to their equation the dissociation pressure of the dihydride should be 32 mm of mercury at 901°C .

At 901°C a lanthanum-carbon alloy, with a carbon to lanthanum atom ratio of 0.38, consisted of liquid lanthanum in equilibrium with a very small amount of solid lanthanum sesquicarbide. The variation in the hydrogen content of this specimen is shown in Fig. 8 as a function of pressure. Hydrogen went into solution in the condensed phases until there was an abrupt change of slope in the equilibrium pressure-composition isotherm. This abrupt change occurred at a pressure of 11 mm of mercury and was caused by the formation of a new condensed phase, the ternary compound. Because initially the specimen contained only a very small amount of the solid sesquicarbide phase, the pressure

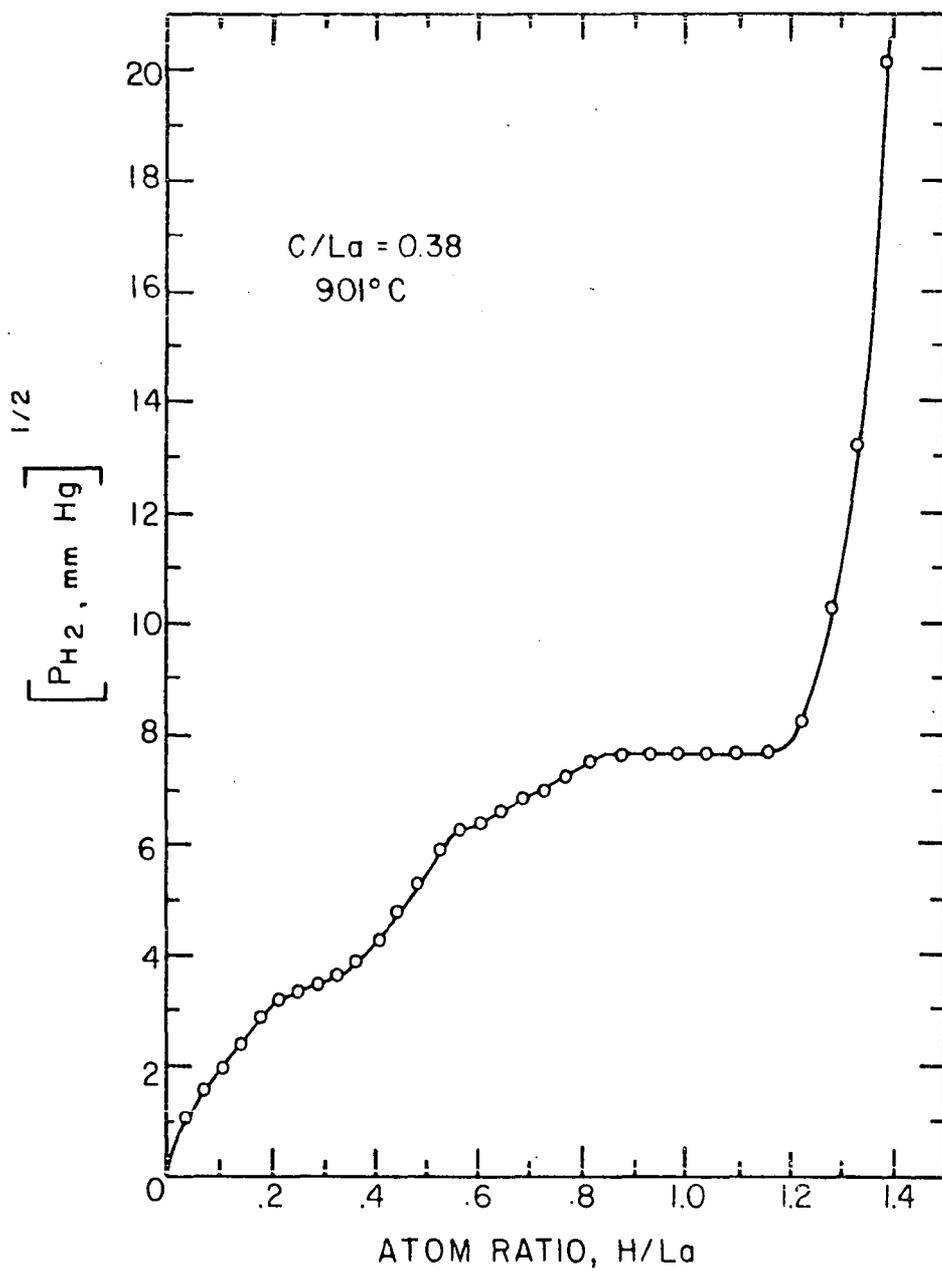


Fig. 8. Pressure-composition isotherms for a lanthanum-carbon alloy

invariance in this three condensed phase region was not observed. After the carbide phase disappeared further formation of ternary compound resulted in a decrease in the carbon content of the liquid phase below its saturation value. The ternary compound continued to form but at increasingly higher hydrogen equilibrium pressures. In the lanthanum-carbon system at 901°C a two phase region comprised of γ -lanthanum and liquid exists between the composition limits of 1.7 and 2.8 atomic per cent carbon. As the carbon content of the liquid phase decreased through the formation of the ternary compound, a very small composition region should have been encountered in which γ -lanthanum, liquid and ternary compound coexist. Since this composition region was very narrow, a pressure invariant region was not observed. At a pressure of 39 mm of mercury an abrupt change in slope in the pressure-composition can be seen which corresponded to the appearance of γ -lanthanum. At a pressure of 58 mm, lanthanum dihydride formed and the pressure became invariant over a limited composition range. The dissociation pressure of the dihydride observed in the investigation is higher than the value reported by Mulford and Holley (30). Above the dissociation pressure of the

dihydride the condensed phases, lanthanum dihydride and the ternary compound, absorbed increasing amounts of hydrogen with increasing pressure.

B. X-ray Analysis

Powder x-ray diffraction methods were used to characterize the ternary compounds. The specimens were prepared by equilibrating alloys, with the proper carbon to metal atom ratio, with hydrogen above the dissociation pressure of the compound at elevated temperatures. The equilibrated specimens were found to be very brittle and were crushed to a fine powder with a diamond mortar. This powder was sifted through a 250 mesh screen. The diffraction patterns were recorded with an 11.46 cm diameter Debye-Scherrer camera and nickel filtered copper radiation. Although the positions of the carbon and hydrogen atoms could not be established by x-ray methods, it was found that the metal atoms were arranged on a hexagonal closest packed lattice in all of these ternary compounds. The lattice parameters, shown in Table 4, were corrected for systematic errors by using Cohen's (31) method of least squares. This table also shows the lattice parameters of $VC_{0.48}$ and the same specimen

equilibrated with hydrogen. Equilibrating $VC_{0.48}$ with hydrogen caused an expansion of the lattice and did not result in the appearance of a new phase.

Table 4. Lattice parameters of the ternary compounds

Compound	$a_0(\text{\AA})$	$c_0(\text{\AA})$	c/a
$TiC \cdot TiH_x$	3.083	5.042	1.635
$ZrC \cdot ZrH_x$	3.347	5.469	1.634
$HfC \cdot HfH_x$	3.427	5.476	1.598
$YC \cdot YH_x$	3.732	5.960	1.597
$LaC \cdot LaH_x$	4.041	6.554	1.622
$VC_{0.48}$	2.889	4.579	1.585
$VC_{0.96} \cdot VH_{0.46}$	2.899	4.600	1.587

C. The Composition of the Ternary Compounds

The stoichiometry of the ternary compounds could not be determined by an analysis of a specimen containing only the ternary compound. This was due to the difficulty in preparing the compounds and because the phases present in the equilibrated specimens could not be separated. The stoichiometry of the compounds, therefore, had to be

determined from the amount of carbon, hydrogen and metal present in the equilibrated specimens and the volume per cent of the phases present.

Microscopic examination showed that all of the hydrogen equilibrated specimens, except $VC_{0.96} \cdot VH_{0.46}$, contained more than one phase. In calculating the amount of hydrogen present in the ternary compounds, it was assumed that the carbide phase left in the specimen after the equilibration did not absorb any hydrogen. The hydrogen content of the metal phase left in the specimen was determined from the binary pressure-composition-temperature studies reported by other investigators.

The hydrogen equilibrated $VC_{0.48}$ specimen was a single phase and an analysis of the amount of each of the components present was all that was necessary to establish the stoichiometry as $VC_{0.96} \cdot VH_{0.46}$. The hydrogen equilibrated yttrium-carbon and lanthanum-carbon specimens contained hydride plus ternary compound. Yttrium dihydride was identified by its characteristic blue color and comprised 71 volume per cent of the specimen. The major constituent in the lanthanum specimen was the ternary compound which was optically active under polarized light. A determination

of the amount of this phase present showed it to vary from 67 volume per cent near one end of the specimen to 51 volume per cent near the other end. Since the hydrogen content of the hydrides of these metals is not known as a function of pressure and temperature, the hydrogen content of the ternary compounds could not be determined. By assuming that the phases in a specimen had equal densities, a stoichiometry of $MC \cdot MH_x$ was calculated for both the yttrium and lanthanum ternary compounds.

Hydrogen was added to specimens of titanium, zirconium and hafnium having a carbon to metal atom ratio of 0.50, 0.48 and 0.42 respectively at temperatures ranging from 925° to 1000°C. The hydrogen pressure was always kept above the dissociation pressure of the ternary compounds and below that of the dihydrides. The rate at which the specimens absorbed hydrogen was extremely slow. The titanium and hafnium specimens were equilibrated for two months and the zirconium specimen for four months. Microscopic examination of the equilibrated specimens showed that the titanium and hafnium specimens contained two phases and the zirconium specimen three phases. The minor constituent in the titanium specimen comprised 6 volume per cent of the total

specimen and was titanium monocarbide. In the hafnium specimen there was 27 volume per cent of the minor phase present and this phase was hafnium metal. The zirconium specimen contained 10 volume per cent of each of the minor phases which were zirconium monocarbide and zirconium metal. The hydrogen content of the equilibrated specimens was determined and the calculated stoichiometry of these preparations of the ternary compounds was as follows, $\text{TiC} \cdot \text{TiH}_{0.45}$, $\text{ZrC} \cdot \text{ZrH}_{1.46}$ and $\text{HfC} \cdot \text{HfH}_{0.88}$. The stoichiometry of the ternary compounds shows that they exist over a wide range of hydrogen composition in much the same manner as a dihydride of these metals. The carbon to metal stoichiometry could be determined with considerable accuracy and was always one carbon atom to two metal atoms. It is quite likely that at high enough pressure and low enough temperatures the stoichiometry of these ternary compounds would approach $\text{MC} \cdot \text{MH}_2$.

IV. CONCLUSIONS

This investigation showed that a new type of ternary compound containing carbon, hydrogen and a metal was formed by several metals. The metals that formed these ternary compounds did not all form carbides and hydrides with similar properties and stoichiometry and it is possible that other metals also form similar ternary compounds. Titanium, zirconium, hafnium, yttrium, lanthanum and vanadium all form ternary compounds with the approximate stoichiometry $MC \cdot MH_x$. The compounds have a wide range of hydrogen content, and are more stable thermally than the hydride of the same metal. The metal atoms in the $MC \cdot MH_x$ compounds are arranged on a hexagonal closest packed lattice. The reaction of hydrogen with V_2C resulted in an expansion of the hexagonal V_2C lattice rather than the appearance of a new phase. The enthalpies of formation for the ternary compounds of titanium, zirconium and hafnium are -43.7, -48.8 and -45.2 kcal/mole of hydrogen respectively.

The positions of the carbon and hydrogen atoms in the $MC \cdot MH_x$ structure have not been determined and consequently the bonding in these compounds can not be deduced from the

bond distances and arrangement. It was suggested by Peterson and Rexer (1) that the bonding in $\text{ThC}\cdot\text{ThH}_2$ is probably quite similar to the bonding in thorium monocarbide and thorium dihydride. Table 5 shows the volumes of the $\text{MC}\cdot\text{MH}_x$ hexagonal unit cells calculated from the lattice constants and compares them to the sum of the volume of the monocarbide primitive unit cell and the volume of the dihydride primitive unit cell. The small difference between these two volumes indicates that the bonding in the ternary compounds is probably quite similar to the bonding in the carbides and hydrides. The metallic luster and electrical conductivity of the monocarbides and dihydrides of these metals were also shown by the ternary compounds.

Table 5. Comparison of calculated and observed volumes of ternary compounds

Ternary Compound	Observed Volume	Calculated Volume
$\text{ThC}\cdot\text{ThH}_x$	79.5\AA^3	79.3\AA^3
$\text{TiC}\cdot\text{TiH}_x$	41.5\AA^3	42.4\AA^3
$\text{ZrC}\cdot\text{ZrH}_x$	53.1\AA^3	53.5\AA^3
$\text{HfC}\cdot\text{HfH}_x$	55.7\AA^3	51.4\AA^3

Hägg (32) examined the zirconium-hydrogen binary system at room temperature by x-ray methods and reported two intermediate phases between zirconium and zirconium dihydride. Most subsequent investigations of this system did not confirm the existence of these two phases. The first intermediate phase was reported to be cubic with $a_0 = 4.669\text{\AA}$. Peterson and Rexer (1) showed that the lattice parameter of this phase is very nearly equal to the lattice parameter of zirconium monocarbide. In Hägg's gamma phase the metal atoms were reported to be arranged on a hexagonal closest packed lattice with a_0 varying from 3.342\AA to 3.346\AA and c_0 from 5.464\AA to 5.466\AA . The lattice parameters of this intermediate phase agree very well with those of the zirconium ternary compound. It thus appears that the beta phase reported by Hägg was zirconium carbide and the gamma phase was zirconium carbohydride.

V. BIBLIOGRAPHY

1. Peterson, D. T. and J. Rexer, Ternary compounds between thorium monocarbide and thorium dihydride. (Mimeo.) Metallurgy Department, Iowa State University of Science and Technology, Ames, Iowa (1959).
2. Mallett, M. W. and I. E. Campbell, J. Am. Chem. Soc. 73, 4850 (1951).
3. Nottorf, R. W., Some problems in the chemistry of uranium and thorium of interest to the development of atomic power. Unpublished Ph.D. Thesis. Library, Iowa State University of Science and Technology, Ames, Iowa (1945).
4. Hume-Rothery, Wm., Phil. Mag. 44, 1154 (1953).
5. Libowitz, G. G. and T. B. P. Gibb, Jr., J. Phys. Chem. 60, 510 (1956).
6. Burgers, W. G. and J. C. Basart, Z. anorg. Chem. 216, 209 (1934).
7. Becker, K., Physik. Z. 34, 185 (1933).
8. Rundle, R. E., C. G. Shull and E. O. Wollam, Acta Cryst. 5, 22 (1952).
9. Sidhu, S. S., L. Heaton and D. D. Zamberis, Acta Cryst. 9, 607 (1956).
10. Lundin, C. E. and D. T. Klodt, Denver Res. Quarterly Progress Rept. No. 8, 1 (1957).
11. Holley, C. E., Jr., R. N. R. Mulford and F. H. Ellinger, J. Phys. Chem. 59, 1226 (1955).
12. Spedding, F. H., K. Gschneidner, Jr. and A. H. Daane, J. Am. Chem. Soc. 80, 4499 (1958).

13. Spedding, F. H., K. Gschneidner, Jr. and A. H. Daane, Trans. Am. Inst. Mining, Met., Petrol. Engrs. 215, 192 (1959).
14. Becker, K. and F. Ebert, Z. Physik 31, 268 (1925).
15. Brauer, G. and R. Hermann, Z. anorg. Chem. 274, 11 (1953).
16. Waite, T. R., W. E. Wallace and R. S. Craig, J. Chem. Phys. 23, 634 (1956).
17. Rostoker, W. and A. Yamamoto, Trans. Am. Soc. Metals 46, 1136 (1954).
18. Hardy, G. F. and J. K. Hulm, Phys. Rev. 93, 1010 (1954).
19. Spedding, F. H., A. S. Newton, J. C. Wharf, O. Johnson, R. W. Nottorf, I. B. Johns and A. H. Daane, Nucleonics 4, 4 (1949).
20. McQuillan, A. D., Proc. Royal Soc. London, Ser. A, 204, 309 (1950).
21. Cadoff, I. and J. P. Nielsen, J. Metals 5, 248 (1953).
22. Peterson, D. T. and J. Rexer, J. Am. Chem. Soc. 81, 4443 (1959).
23. Haag, R. M. and F. J. Shipko, J. Am. Chem. Soc. 78, 5155 (1956).
24. Benesovsky, F. and E. Rudy, Planseeber. Pulvermet. Band 8, 66 (1960).
25. LaGrange, L. D., L. J. Dykstra, J. M. Dixon and U. Merten, J. Phys. Chem. 63, 2035 (1959).
26. Veleckis, E. and R. K. Edwards, The thermodynamic properties in the system hydrogen-hafnium. Unpublished M.S. Thesis. Library, Illinois Institute of Technology, Chicago, Illinois (1957).

27. Edwards, R. K., P. Levesque and D. Cubicciotti, J. Am. Chem. Soc. 77, 1307 (1955).
28. Martin, S. L. H. and A. L. G. Rees, Trans. Faraday Soc. 50, 343 (1954).
29. Libowitz, G. G., J. Nuclear Materials 2, 1 (1960).
30. Mulford, R. N. R. and C. E. Holley, Jr., J. Phys. Chem. 59, 1222 (1955).
31. Cohen, M. U., Rev. Sci. Instru. 7, 155 (1936).
32. Hägg, G., Z. physik. Chem., Ser. B, 11, 433 (1931).

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