JUL 16 1968

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AI-AEC-MEMO COVER SHEET

REPORT TITLE

STUDIES OF TERNARY METAL-NONMETAL-HYDROGEN SYSTEMS

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NAA-SR- ~~AI-AEC~~-MEMO 11849

(This Document Contains _____ Pages.)
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ATOMICS INTERNATIONAL <small>A Division of North American Aviation, Inc.</small>		NAA-SR- TDR NO. 11849		APPROVALS <i>W. L. Korst</i>	
TECHNICAL DATA RECORD		PAGE 1 OF 13		<i>A. E. Bunker</i>	
AUTHOR W. L. Korst		DEPT. & GROUP NO. 741		DATE May 1, 1967 <i>C. L. L.</i>	
		GO NO. 7652 (07707)			
TITLE Studies of Ternary Metal-Nonmetal-Hydrogen Systems		S/A NO. 4552 (28210)		TWR	
		SECURITY CLASSIFICATION			
		(CHECK ONE BOX ONLY)		(CHECK ONE BOX ONLY)	
PROGRAM Reactor Fuels and Materials		SUBACCOUNT TITLE Carbide Type Fuels Research and Development		UNCL. ☒ AEC ☐ DOD ☐ RESTRICTED DATA ☐	
				CONF. ☐ ☐ DEFENSE INFO. ☐	
				SECRET ☐ ☐	
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		ABSTRACT: A report that hexagonal ternary compounds are formed in various M-C-H systems, where M represents various transition metals, suggested the examination of Zr-X-H systems, where X represents B, C, N, O, and Si. The existence of a hexagonal ternary compound, $ZrC \cdot ZrH_x$, has been confirmed, and similar compounds have been discovered in the Zr-N-H and Ti-N-H systems. The hexagonal ternary compound, $ZrN \cdot ZrH_x$, has since been reported in the literature. The hexagonal ternary phases can apparently only be formed by refractory compounds having a high degree of hypostoichiometry. Literature reports indicate that absorption of hydrogen to form such compounds occurs more readily under high pressures of hydrogen. Reports have also appeared of absorption of hydrogen directly into hypostoichiometric fcc MC_{1-x} phases, with retention of the fcc lattice; these cubic ternary phases are reported to exist in equilibrium with the hexagonal ternary phases.			

I. INTRODUCTION

Ternary compound formation in the system Th-C-H has been reported by Peterson and Rexer,^(1,2) who have described the formation of the compounds ThC·ThH₂ and ThC·2ThH₂. X-ray data have shown the former compound to have a hexagonal unit cell, and the latter to have a monoclinic unit cell.

In a later report, Rexer and Peterson⁽³⁾ have described an investigation of the metal-carbon-hydrogen systems of titanium, zirconium, hafnium, yttrium, lanthanum, and vanadium, in which pressure-composition-temperature measurements and X-ray diffraction studies were made. Compounds with the approximate stoichiometry MC·MH_x were found and characterized for each of these metals. All these compounds have hexagonal unit cells, in which they are similar to the ThC·ThH₂ compound described above. No higher hydride analogous to ThC·2ThH₂ has been found for any of these systems, however.

Kramers, et al.⁽⁴⁾ have described what are called "hydro compounds," containing a metal (Zr, Ti, or rare earth), a non-metal (N, C, or O), and hydrogen (more than 0.25 atoms per atom of metal). Ca, Li, or Pu may be added. A Zr-C-H ternary compound having a face-centered cubic (fcc) unit cell similar to ZrC was reported, but no hexagonal ternary compound was found. However, a hexagonal ternary compound was apparently discovered in the Zr-N-H system. A later report by Kramers and Smith⁽⁵⁾ described ternary and quaternary compounds formed by the reaction of oxides and other compounds with hydrogen.

Ternary compounds in the Ti-C-H system have also been reported by Goretzki, Bittner, and Nowotny.⁽⁶⁾ Their findings differ in an important respect from those of Rexer and Peterson.⁽³⁾ They considered that the absorption of hydrogen into the substoichiometric face-centered cubic carbide, TiC_{1-x}, at first occurs with the hydrogen being absorbed into the defect lattice of the monocarbide, believed to possess carbon vacancies. The evidence cited for this conclusion was the absorption of hydrogen by TiC_{1-x} to form a single-phase product, having a fcc structure, with only a very slight change in the lattice constant. One preparation, for example, with TiC_{1-x} containing 31 at. % C, absorbed hydrogen to give a product whose composition corresponded to the formula TiC_{0.46}H_{0.46}. Hydriding at high pressure resulted in the formation of a hexagonal ternary Ti-C-H phase similar to that reported by Rexer and Peterson.⁽³⁾ This hexagonal phase, for which the formula TiC·TiH_x was written, was thought to exist in equilibrium with the fcc phase, for which the formula TiC_{1-x}H_y was written. Dehydriding of samples containing the hexagonal ternary phase was said to lead to α-Ti and TiC_{1-x}. Hydriding at high pressure of samples containing α-Ti and TiC_{1-x}, as well as TiC_{1-x} alone, led to the hexagonal ternary phase. Hexagonal ternary phases were also said to be formed by the action of hydrogen on HfC_{1-x} and ZrN_{1-x}.

Nuclear magnetic resonance studies of the fcc TiC_{1-x}H_y phase have been reported by Bittner,⁽⁷⁾ and neutron diffraction studies of the corresponding

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phase in the Zr-C-H system have been reported by Goretzki, et al.⁽⁸⁾ The aim of these investigations was to discover the positions of the hydrogen atoms. No such structural studies of the hexagonal phase, TiC-TiH_x, were made.

Ternary metal-carbon-hydrogen systems have also been studied by Dean, Lorenzelli, and Pascard.⁽⁹⁾ On the basis of increased lattice parameters after treatment with hydrogen observed in the series UC, PuC, ThC, the authors concluded that hydrogen was absorbed by the hypostoichiometric carbides MC_{1-x} to the extent of two hydrogen atoms for each carbon vacancy in the original monocarbide lattice, and the final products were considered to be carbohydrides of general formula M(C_{1-x}H_{2x}). The fcc NaCl-type structure of the actinide carbides remained unchanged, with only expansion occurring, when hydrogen was absorbed. The lanthanide carbides gave a more complex structure, but were usually hexagonal, probably similar to the compounds reported by Rexer and Peterson.⁽³⁾ In the case of TiC, however, treatment with hydrogen gave only a slight expansion of the fcc lattice, and the hexagonal ternary phase reported by Rexer and Peterson⁽³⁾ and by Goretzki, Bittner, and Nowotny⁽⁶⁾ was not observed. Nor, in the case of ThC, were the two ternary Th-C-H compounds reported earlier by Peterson and Rexer^(1,2) observed.

At the time the investigation to be described in this report began in 1963, only the work by Peterson and Rexer^(1,2) had appeared in the literature. However, we were also familiar with the results reported later by Rexer and Peterson⁽³⁾ on various transition metal-carbon-hydrogen systems, as these had been communicated to J. B. Vetrano of AI,⁽¹⁰⁾ who in turn suggested that studies be made at AI of zirconium-nonmetal-hydrogen systems, where the non-metal could be boron, nitrogen, or oxygen as well as carbon.⁽¹¹⁾ As Peterson had no plans for further work in this area,^(10,12) such an investigation was undertaken. It was extended to the Zr-Si-H and Ti-N-H systems also. Especial attention was directed to the formation of hexagonal ternary compounds in all of these systems.

II. EXPERIMENTAL PROCEDURES AND RESULTS

A. INTRODUCTION

In most of the work done, mixtures of ZrH₂ with one of the refractory compounds ZrC, ZrB₂, ZrN, ZrO₂, and ZrSi₂ were prepared by grinding together the powdered compounds in such proportions as to give the compositions 3Zr·ZrX, Zr·ZrX, and Zr·3ZrX, where X represents each particular nonmetal, and the presence of hydrogen has been disregarded in the formulas. Similar mixtures of TiH₂ and TiN were prepared. These mixtures were subjected to several hydriding and dehydriding cycles, over an extended period of time, with some samples having been heated in hydrogen for several weeks. The longest total treatment in a hydrogen atmosphere for a single sample was 52 days. Heating was usually carried out at 1000°C. During this treatment the samples were contained in molybdenum crucibles in a glass high-vacuum system; no reaction with the crucibles was apparent. Usually only the hydrogen evolved

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from the original sample was used in the first heating cycle; in later hydriding treatments hydrogen obtained from the thermal dissociation of uranium hydride was added to the system, usually to give a pressure approaching 1 atm. The samples were often ground once again after the initial heat treatment.

One set of samples containing zirconium and zirconium carbide in various proportions was prepared by arc melting, but these were found to be very inhomogeneous. One mixture utilizing powdered Zr and ZrC was also used.

Besides the mixtures, the individual compounds ZrB_2 , ZrC, ZrN, and ZrO_2 were also treated with hydrogen over an extended period of time.

The sample of zirconium hydride used in the experiments was unfortunately not of the highest purity. According to the manufacturer, the principal impurities were 1.3 wt % oxygen (8.4 at. %), 482 ppm Fe, and 300 ppm N. The lattice constants of the face-centered tetragonal zirconium hydride were determined from the 440 and 115 lines of the Debye-Scherrer pattern to be: $a = 4.978$, $c = 4.451$ Å, with $c/a = 0.894$, indicating the sample to be quite rich in hydrogen. These lattice constants would correspond approximately to the composition $ZrH_{1.97}$.⁽¹³⁾ No lines other than those of the face-centered tetragonal ϵ -phase of zirconium hydride were observed. A sample of α -Zr prepared by removing the hydrogen from the zirconium hydride by heating it in a dynamic vacuum for several hours at temperatures up to 980°C gave a very excellent Debye-Scherrer pattern, with lattice constants $a = 3.244$, $c = 5.167$ Å found from a Nelson-Riley least-squares extrapolation.⁽¹⁴⁾ These values correspond to 3.237 and 5.157 kX, close to what would be expected for α -Zr containing about 8 at. % oxygen.^(15, p 1036) The other starting materials used are described below in the appropriate sections.

The products resulting from these experiments were examined using X-ray diffraction. Debye-Scherrer photographs were prepared using the powdered, ground samples, either glued to very fine glass rods, or contained in 0.2-mm diameter thin-walled glass capillaries. Nickel-filtered copper radiation was used. Wave-length values used were 1.5418 Å for Cu $K\alpha$, and 1.54051 and 1.54433 Å for Cu $K\alpha_1$ and Cu $K\alpha_2$ radiations, respectively. A 114.6-mm diameter powder camera, with the film mounted asymmetrically, was used, with exposures of about 3 hours. In most cases the unit cell or lattice constants were obtained from individual lines at higher angles for the pattern of the substance in question; in some cases however a Nelson-Riley least-squares extrapolation was carried out.⁽¹⁴⁾

B. ZIRCONIUM-CARBON-HYDROGEN SYSTEM

Although in some preparations reactor grade ZrC was used, in most cases spectrographic grade zirconium carbide was used. According to the manufacturer, it contained 11.72 wt % C, nearly corresponding to the stoichiometric formula ZrC. A Nelson-Riley least-squares extrapolation of the Debye-Scherrer data gave a lattice constant of 4.699 Å for the fcc ZrC, as was also found from the high-angle lines alone. When this ZrC was heated in hydrogen for

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three weeks at 1000°C, no evidence of reaction was observed, either by hydrogen absorption or by change in the X-ray diffraction pattern.

In this system mixtures of ZrH_2 and ZrC in 1:1 and 3:1 gram-formula-weight (gfw) ratios were examined. X-ray diffraction evidence confirmed the existence of the hexagonal ternary compound reported by Rexer and Peterson.⁽³⁾ Removal of hydrogen from the mixture of ZrH_2 , ZrC , and $ZrC \cdot ZrH_x$ resulted in the formation of α -Zr and two fcc zirconium carbide phases. One of these had a lattice constant of 4.699 Å, corresponding to that of the stoichiometric ZrC used as starting material, while the other had a lattice constant of about 4.673 Å, believed to correspond to hypostoichiometric zirconium carbide, ZrC_{1-x} , probably with a composition close to that in equilibrium with α -Zr, about $ZrC_{0.53}$. In addition in some cases there was a band structure in the lines of the X-ray pattern, corresponding to a range of lattice constants extending up to 4.688 Å from the lower value, here about 4.675 Å, indicating a continuous variation in composition from the carbide phase in equilibrium with α -Zr to a composition somewhat richer in carbon.

Kieffer and Benesovsky⁽¹⁶⁾ have described a variation in the lattice parameter of zirconium carbide with composition. The zirconium carbide phase in equilibrium with α -Zr is said to have the composition $ZrC_{0.53}$, and a lattice constant of 4.675 Å. The lattice constant increases with increasing carbon content of the carbide, reaching 4.693 Å at $ZrC_{1.0}$. In a table listing properties of ZrC , however, the lattice constant is given as 4.69764 Å. References are given by the authors to the sources of these data.

A more recent report by Storms,⁽¹⁷⁾ however, describes measurements made using very pure preparations, indicating a maximum in the lattice parameter variation. The lattice constants listed are 4.691 Å for $ZrC_{0.55}$, the composition in equilibrium with α -Zr; 4.7017 Å for $ZrC_{0.82}$, the maximum value of the lattice constant and the corresponding composition; and 4.6983 Å for $ZrC_{0.95}$, the phase in equilibrium with carbon. Elsewhere in the report this composition is given as $ZrC_{0.98}$, as an approximate composition. The lower lattice constants reported by earlier workers are said to be due to the presence of oxygen or nitrogen, both of which are said to cause such a decrease.

It is considered justifiable therefore to conclude that in this work lattice constants approximating 4.699 and 4.673 Å correspond to zirconium carbide phases having approximate compositions $ZrC_{1.0}$ and $ZrC_{0.53}$.

When a dehydrided sample, containing α -Zr, ZrC , and ZrC_{1-x} , with ZrC_{1-x} in greater proportion than ZrC , is hydrided, resulting in the formation of the ternary compound, $ZrC \cdot ZrH_x$, and ZrH_2 , the proportion of ZrC_{1-x} present becomes much less than that of ZrC , which it had previously exceeded, indicating that ZrC_{1-x} must react to form the ternary compound. The α -Zr reacts to form ZrH_2 , and the ZrC remains unaffected. If such a hydrided sample is treated with a solution of bromine in acetonitrile, both the ZrH_2 and the ternary compound are removed, leaving ZrC and the unreacted small proportion of ZrC_{1-x} behind, with the latter still in much smaller proportion than the ZrC . Neither ZrC nor ZrC_{1-x} is believed to be attacked by bromine.

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Treatment of a dehydrated sample, containing α -Zr, ZrC, and ZrC_{1-x} , with bromine resulted in the removal of nearly all the α -Zr, and left behind the two zirconium carbide phases. Perhaps some α -Zr was coated with carbide, and therefore was unattacked by bromine. It would be expected to be completely removed by the bromine treatment.

An X-ray diffraction pattern for the ternary compound has been published by Korst, (18) for a composition approximating $\text{ZrC} \cdot \text{ZrH}_2$. The lattice constants derived from this pattern, using a Nelson-Riley extrapolation in a least-squares calculation, were $a = 3.3467 \pm 0.0001 \text{ \AA}$, $c = 5.4898 \pm 0.0001 \text{ \AA}$, $c/a = 1.640$. The lattice constants reported by Rexer and Peterson (3) for the composition $\text{ZrC} \cdot \text{ZrH}_{1.46}$ are $a = 3.347 \text{ \AA}$, $c = 5.469 \text{ \AA}$, $c/a = 1.634$. The lattice constants doubtless vary with both carbon and with hydrogen content.

One of the lines listed in the X-ray pattern for the ternary compound is believed to be due to the 115 reflection (hexagonal indexing). Such a reflection is not contributed to by atoms in the closest-packed positions, which are apparently occupied by the Zr atoms, since the reflections $hk\ell$ with $h-k = 3n$, $\ell = 2n+1$ are absent. A close examination of the pattern indicated that there may also be present some of the 00ℓ reflections with $\ell = 2n+1$, although these are extremely weak indeed. Reexamination of patterns for earlier preparations of the ternary compound supported these observations. The appearance of these reflections may be due to contributions by the carbon and hydrogen atoms present, and may make it possible to draw some conclusions concerning the positions of these atoms in the unit cell. There are however difficulties in the choice of a suitable space group which have not been resolved.

C. ZIRCONIUM-BORON-HYDROGEN SYSTEM

In this system the starting materials used were powdered zirconium hydride and zirconium diboride, which were mixed in 1:1, 5:3, 3:1, and 7:1 gfw ratios. The zirconium diboride was said to be of 98.0% purity by the supplier, but no other analytical data were available. A Debye-Scherrer pattern gave lattice constants $a = 3.1665$, $c = 3.529 \text{ \AA}$, calculated from the 300 and 104 lines.

Debye-Scherrer patterns of the dehydrated products in all cases indicated ZrB_2 and α -Zr to be present, with the lattice constants of α -Zr gradually becoming larger as the treatment time increased. The largest values observed were $a = 3.251$ and $c = 5.178 \text{ \AA}$, found for the 5:3 sample. The increase in these parameters may be due to additional oxygen impurity; these values correspond to 15 at. % oxygen (15, p 1036). No subsequent analyses were made for oxygen, however. It is also possible that there was some solution of boron in the α -Zr, as an increase in lattice spacings from $a = 3.229$, $c = 5.139 \text{ \AA}$ for pure α -Zr to $a = 3.249$, $c = 5.203 \text{ \AA}$ at the solid solubility limit of about 1 at. % B has been reported. (15, p 910)

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Of more interest were the results of the hydriding treatment, as the principal object of the investigation was to discover whether any ternary compounds existed. This was at first thought to have occurred for the 1:1 sample. After heating in hydrogen, dehydriding, and then heating again in hydrogen for seven days at 1000°C, this sample reabsorbed a quantity of hydrogen equivalent to about 90% of that originally present. The Debye-Scherrer pattern showed ZrB_2 and ZrH_2 to be present, together with a number of unidentified lines, most of which could be indexed on the basis of a hexagonal unit cell with $a = 3.33$, $c = 5.59$ Å. Some of the lines of such a cell coincided with lines of the hydride and diboride, also, and the evidence for such a cell was not considered to be conclusive.

Similar results were obtained with the other samples used. However, these additional lines did not become appreciably stronger after successive cycles, and attempts to index them satisfactorily were not successful. Although there are indications, therefore, of a possible hexagonal ternary compound in this system, no definite conclusion can be drawn.

D. ZIRCONIUM-NITROGEN-HYDROGEN SYSTEM

The zirconium nitride sample used in earlier experiments was not very pure, although the supplier claimed its purity to be 98-99%. An X-ray diffraction pattern showed α -Zr and fcc δ -zirconium hydride to be present, together with zirconium nitride having a fcc unit cell constant of 4.578 Å. An analysis for nitrogen by the Kjeldahl method indicated 6.89 and 7.17 wt % nitrogen in two determinations, for an average of 7.03 wt % N. Since stoichiometric ZrN contains 13.3 wt % N, it is seen that this sample is very hypostoichiometric.

In this system 1:1, 3:1 and 1:3 gfw ratio mixtures of ZrH_2 and ZrN were used. The original zirconium nitride sample alone was also heated in hydrogen. All of these experiments led to products for which the Debye-Scherrer patterns indicated a hexagonal unit cell to be present, considered to be that of a ternary compound, $ZrN \cdot ZrH_x$. Debye-Scherrer photographs showing very strong and complete hexagonal patterns were obtained.

A treatment of a hydrided 1:3 $ZrH_2:ZrN$ sample with bromine in acetonitrile partially removed the ternary compound; probably all would be removed under more vigorous conditions than those used.

Dehydriding of the samples led to α -Zr with enlarged lattice constants, with $a = 3.251$ and $c = 5.208$ Å, and $c/a = 1.602$. These lattice constants for α -Zr are much larger than those found for the α -Zr obtained by dehydriding the original ZrH_2 starting material ($a = 3.244$, $c = 5.167$ Å), which contained

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8 at. % oxygen. Perhaps there is some dissolution of nitrogen in the α -Zr phase. The solubility of nitrogen in α -Zr has been reported to be 20 at. % (14, p 1002)

In later experiments a somewhat better sample of zirconium nitride was used. The manufacturer reported it to contain 10.98 wt % N ($\text{ZrN}_{0.81}$), with 3340 ppm oxygen and 1820 ppm carbon as the principal impurities. A Kjeldahl analysis for nitrogen gave 11.5 wt % N, corresponding approximately to $\text{ZrN}_{0.85}$. The lattice constant for this sample of ZrN was 4.577 Å. When this material was heated together with zirconium hydride in a 1:1 mixture, there also resulted the hexagonal unit cell ascribed to the ternary compound, with $a = 3.286$, $c = 5.489$ Å, $c/a = 1.670$, found from the 302 and 213 lines. The dehydrided sample, after a couple of cycles, gave indications of two zirconium nitride phases, with $a = 4.577$, corresponding to the original starting material, and with $a = 4.581$ Å, considered to be hypostoichiometric ZrN_{1-x} , derived from the decomposition of the ternary compound. According to Storms, (17) the cell constant for ZrN is constant at 4.577 Å at compositions above $\text{ZrN}_{0.78}$, while it increases to 4.584 Å at the phase boundary with α -Zr, where the composition is approximately $\text{ZrN}_{0.54}$.

In one hydriding experiment it was evident that insufficient hydrogen was present in the system to saturate the product, as all of it was absorbed by the sample. The cell constants of the hexagonal ternary compound in the pattern for this product were found to be $a = 3.283$, $c = 5.350$ Å, $c/a = 1.630$. These are seen to be somewhat smaller than the values given above.

It is apparently very difficult to convert the mixture of ZrN and Zr completely to a single phase, which would form only the ternary compound on hydriding. This is also true of mixtures of ZrC and Zr. It would be advantageous to start with hypostoichiometric single-phase material, having a composition close to that at the phase boundary with α -Zr. Such a sample would be better suited for the obtaining of dissociation pressure data.

E. ZIRCONIUM-OXYGEN-HYDROGEN SYSTEM

In this system mixtures of ZrH_2 and powdered spectrographic grade ZrO_2 in 5:3, 3:1, and 7:1 gfw ratios were heated at about 1000°C, for 15, 7, and 9 days respectively under the pressure of the evolved hydrogen in each case. In each of these experiments all the hydrogen was not reabsorbed. No substantial changes were found in the Debye-Scherrer patterns for the products, in which there appeared only the lines of ZrH_2 and ZrO_2 .

A sample of ZrO_2 alone was also heated in hydrogen, under a pressure of about 700 mm, for a period of 12 days at 1000°C. This sample was found to absorb hydrogen to the extent indicated by the formula $\text{ZrO}_2\text{H}_{0.13}$. This apparent absorption of hydrogen was accompanied by a loss in weight of the

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sample of about 0.062%. There was also a slight increase in the values of the unit cell constants accompanying the absorption, indicated by the slight shift of the lines to smaller angles than in the pattern for the untreated ZrO_2 .

F. ZIRCONIUM-SILICON-HYDROGEN SYSTEM

In the only experiment carried out in the Zr-Si-H system, a 3:1 gfw ratio mixture of powdered ZrH_2 and $ZrSi_2$ of 98.0% minimum purity, according to the manufacturer, was heated for about 15 days at $1000^\circ C$, under about 400 mm pressure of hydrogen, which had been evolved from the zirconium hydride in the sample. About three-fourths of this hydrogen was not reabsorbed on cooling. A Debye-Scherrer pattern prepared for the product indicated that there had been a reaction between Zr and $ZrSi_2$ to form one or more silicides richer in Zr than is $ZrSi_2$. The Zr-Si system is not yet completely characterized--there are two different crystal structures reported for $ZrSi$, and lines ascribable to both of these structures appeared in the pattern.⁽¹⁹⁾ $ZrSi$ is the next compound adjacent to $ZrSi_2$ in the system. There were also indications of the presence of Zr_2Si .⁽²⁰⁾ The starting composition could lead theoretically down to Zr_2Si --there are three additional compounds between Zr_2Si and $ZrSi$, and it is possible that some quantity of one or more of these was formed, as the conditions of the experiment doubtless did not lead to a state of equilibrium. There were also lines of face-centered tetragonal zirconium hydride in the product, and a great many unidentified lines.

G. TITANIUM-NITROGEN-HYDROGEN SYSTEM

Titanium hydride, TiH_2 , of 99.9% purity, according to the manufacturer, was used. Its lattice constant was found to be 4.450 Å. The purity of the titanium nitride was not specified by the manufacturer. It was analyzed by AI for nitrogen content, using Kjeldahl and caustic fusion methods. The former led to 18.35 wt % nitrogen, corresponding to $TiN_{0.88}$, while the latter led to 19.8 wt % nitrogen, corresponding to $TiN_{0.93}$. The titanium nitride may therefore be considered to have the approximate composition $TiN_{0.9}$, somewhat hypostoichiometric. Its lattice constant was found to be 4.240 Å.

Removal of hydrogen from the TiH_2 reagent led to α -Ti having the lattice constants $a = 2.952$, $c = 4.691$, $c/a = 1.589$. According to Pearson^(15, p 872) the best values for α -Ti are $a = 2.9504$, $c = 4.6833$ Å, $c/a = 1.587$. The presence of oxygen and nitrogen both increase the c lattice spacing while having little effect on the a spacing. The larger c spacing found here is probably therefore indicative of oxygen or nitrogen impurities.

In this system 1:1, 1:3, and 3:1 gfw ratio mixtures of TiN and TiH_2 were used. The hydrided 1:1 and 1:3 mixtures apparently resulted in the formation of a ternary compound, $TiN \cdot TiH_x$, with lattice constants $a = 3.042$, $c = 5.037$ Å, $c/a = 1.656$, determined from the 302 and 205 lines for the best pattern, found for the 1:3 sample of TiN and TiH_2 .

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The dehydrided 1:1 and 1:3 samples of $\text{TiN}:\text{TiH}_2$ contained:

- 1) $\alpha\text{-Ti}$, with expanded cell constants $a = 2.966$, $c = 4.798$ Å, $c/a = 1.618$, probably containing nitrogen in solution. (15, p 997)
- 2) Titanium nitride, with $a = 4.222$ Å, probably considerably hypostoichiometric. The TiN_{1-x} composition existing in equilibrium with $\alpha\text{-Ti}$ is about $\text{TiN}_{0.45}$. (15, p 997; 17, p 113)
- 3) ϵ (Ti-N), with the pattern reported by Palty, Margolin, and Nielsen. (21) This phase is said to be either Ti_4N or Ti_3N . (22)

The 3:1 $\text{TiN}:\text{TiH}_2$ sample did not give a positive indication of the ternary compound after being heated in hydrogen, perhaps because relatively little of the hypostoichiometric nitride had formed. Both the hydrided and the dehydrided samples, however, did give an indication of splitting of the TiN lines, indicating that some TiN_{1-x} had formed.

III. SUMMARY AND DISCUSSION

As an extension of reports that hexagonal ternary compounds in systems M-C-H had been observed, where M represents any of several transition metals, a study was undertaken of Zr-X-H systems, where X represents B, N, or O as well as C. Also examined were the Zr-Si-H and Ti-N-H systems.

In most of the work done, mixtures of ZrH_2 with one of the refractory compounds ZrC , ZrB_2 , ZrN , ZrO_2 and ZrSi_2 were prepared by grinding together the powdered compounds in such proportions as to give the compositions $3\text{Zr}\cdot\text{ZrX}$, $\text{Zr}\cdot\text{ZrX}$, and $\text{Zr}\cdot 3\text{ZrX}$, where X represents each particular nonmetal, and the presence of hydrogen has been disregarded in the formulas. Similar mixtures of TiH_2 and TiN were also prepared. These mixtures were subjected to several hydriding and dehydriding cycles, and a Debye-Scherrer pattern was prepared for the product resulting from each step in the cycle. Note was also taken of the amount of hydrogen absorbed during the hydriding runs.

In the Zr-C-H system the existence of the hexagonal ternary compound, $\text{ZrC}\cdot\text{ZrH}_x$, was confirmed. Similar phases were discovered in the Zr-N-H and Ti-N-H systems, and an inconclusive indication of such a phase also appeared in the Zr-B-H system. There have since been additional reports in the literature of the hexagonal phases in the Zr-C-H, Ti-C-H, and Zr-N-H systems, but there has been no other report of a hexagonal Ti-N-H phase. There have been other reports of the absorption of hydrogen by hypostoichiometric monocarbides of various transition metals to give hexagonal ternary phases, and also to form fcc $\text{MC}_{1-x}\text{H}_y$ phases.

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Later work on the Ti-C-H system reported in the literature indicates that the absorption of hydrogen by fcc hypostoichiometric TiC_{1-x} to form both the fcc phase containing hydrogen and the ternary hexagonal phase takes place much more readily at high pressures of hydrogen.

The observation that stoichiometric refractory compounds, such as $ZrC_{1.0}$, do not absorb hydrogen, coupled with other observations indicating that dehydriding of the ternary phase $ZrC \cdot ZrH_x$ leads to hypostoichiometric ZrC_{1-x} , and also that hydriding of a mixture of $ZrC_{1.0}$ and ZrC_{1-x} leads to formation of the hexagonal ternary compound by the ZrC_{1-x} phase, leads to the conclusion that the hexagonal ternary phase can only be formed by the hypostoichiometric refractory phases. Therefore ternary phases would not be expected to be formed by compounds existing only as the stoichiometric compound, but are more likely to be formed by compounds having a wide range of hypostoichiometry, such as is the case for the carbides and nitrides of zirconium and titanium.

IV. ACKNOWLEDGMENTS

This investigation was initiated at the suggestion of J. B. Vetrano. The treatment of various samples with a solution of bromine in acetonitrile was carried out by L. Silverman, who developed the procedure.

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V. REFERENCES

1. D. T. Peterson and J. Rexer, "Ternary Compounds between Thorium Monocarbide and Thorium Dihydride," *J. Inorg. Nucl. Chem.* 24, 519 (1962); IS-247 (1962).
2. D. T. Peterson and J. Rexer, "Self-Moderating Fertile Compounds," U. S. Patent 3,044,847 (1962).
3. J. Rexer and D. T. Peterson, "Ternary Metal-Carbon-Hydrogen Compounds of Some Transition Metals," *Nuclear Metallurgy* 10, 327 (1964).
4. W. J. Kramers, et al., "Refractory Metal Compounds," British Patent 960,720. First filed 1958; published 1964. Abstracted in *Nuclear Science Abstracts* 18: 27877 (1964).
5. W. J. Kramers and J. R. Smith, "Chemical Interaction of Oxides with Metals at High Temperatures," *Nature* 202, 39 (1964).
6. H. Goretzki, H. Bittner, and H. Nowotny, "Der Einfluss von Wasserstoff auf Titancarbid," *Monatsh. Chem.* 95, 1521 (1964).
7. H. Bittner, "Magnetische Kernresonanzuntersuchungen an Ti-C-H Legierungen," *Monatsh. Chem.* 95, 1514 (1964).
8. H. Goretzki, E. Ganglberger, H. Nowotny and H. Bittner, "Zum Problem der Carbohydride," *Monatsh. Chem.* 96, 1563 (1965).
9. G. Dean, R. Lorenzelli, and R. Pascard, "Reaction a Temperature Moyenne entre les Monocarbures de Lanthanides et d'Actinides et l'Hydrogene," *CEA-R 2602* (1964); translated into English by A. Cornell, *AI-TRANS.* 69 (1965).
10. D. T. Peterson, telephone conversation with J. B. Vetrano of AI, November 27, 1962, and subsequent direct conversation held at Ames, Iowa, December 11, 1962. Reported by Vetrano in an Inter-Office Letter to G. D. Calkins, December 18, 1962; a copy may be found in W. L. Korst's AI Laboratory Notebook, p A-073107.
11. J. B. Vetrano, "Structure and Stability of Ternary Compounds in the System Zr-X-H where X = B, C, N or O," pp 36-38 of "A Proposed Program of Synthesis, Structure, and Behavior of Metal-Hydrogen Systems," edited by J. B. Vetrano, December 28, 1962. A copy may be found in W. L. Korst's AI Laboratory Notebook p A-073105.
12. D. T. Peterson, Letter to W. L. Korst, October 9, 1963.

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NO. NAA-SR-TDR-11849

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13. W. L. Korst, "X-Ray Studies of δ and ϵ Zirconium Hydrides," NAA-SR-6880 (1962).
14. W. L. Korst, I. R. Tannenbaum, and K. T. Miller, "Precision Determination of Lattice Constants Using Computer Program OW-335," NAA-SR-TDR-6206 (1961).
15. W. B. Pearson, "A Handbook of Lattice Spacings and Structures of Metals and Alloys," Pergamon Press (1958).
16. R. Kieffer and F. Benesovsky, "Hartstoffe," Vienna: Springer-Verlag, 1963, p 109.
17. E. K. Storms, "A Critical Review of Refractories," LA-2942 (1964).
18. W. L. Korst, "X-Ray Diffraction Data for $ZrC \cdot ZrH_2$," NAA-SR-TDR-11542 (1965).
19. ASTM Powder Diffraction File, Cards 9-226 and 10-267.
20. ASTM Powder Diffraction File, Card 6-0517.
21. A. E. Palty, H. Margolin, and J. P. Nielsen, "Titanium-Nitrogen and Titanium-Boron Systems," Trans. ASM 46, 312 (1954).
22. M. Hansen and K. Anderko, "Constitution of Binary Alloys," New York: McGraw-Hill, 1958, p 989.