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by Warren H. Philipp

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SUMMARY

Because the group IVA transition metal carbides, nitrides, and borides may possibly be used as high-temperature materials, their physical properties have been given considerable investigation. The reactions of these refractories under study were investigated in various media, including chromic acid solution, hydrochloric acid, acidified hydrogen peroxide, fused potassium hydroxide, and solutions containing hydrofluoric acid. Semiquantitative analyses of the reaction products are presented, including mass-spectrometric determinations of evolved gases. Based on a comparison of the chemical properties of the group IVA caribides, nitrides, and borides with those of known bonding, the nature of the bonding is discussed. The hypothesis used assumes that the outer electrons of the nonmetal (carbon, nitrogen, boron) interact with the d orbitals of the transition metal atom.

INTRODUCTION

Because the group IVA transition metal carbides, nitrides, and borides may possibly be used as high-temperature materials, their physical properties have been given considerable investigation; however, comparatively little is reported in the recent literature on the chemical reactions of these compounds, especially their solution chemistry. The neglect in this field may be attributed to the relative inertness of these refractories to many common laboratory reagents; even in systems in which reactions do occur, the reaction rates are often very slow. It is not surprising that almost all information concerning the chemical bonding of these materials is derived from physical, rather than chemical, properties.

This report presents the results of an experimental investigation into some of the chemical reactions of these refractories. Based on a comparison of these results with results under similar conditions for carbides, nitrides, and borides of known bonding, the chemical bonding for these group IVA transition-metal refractories is discussed with reference to the theories described by Engel (ref. 1) and Samsonov (ref. 2).

Primarily six refractories were investigated: namely, the carbides, nitrides, and diborides of titanium (Ti) and zirconium (Zr). In general, three aqueous systems (chromic acid solution, hydrochloric acid, and acidified hydrogen peroxide) and one non-aqueous high-temperature system (fused potassium hydroxide) were employed as reaction media. This report includes quantitative analyses of the reaction products in solution and the results of mass spectrometric determination of the gaseous products. In certain reactions involving the diborides, special attention was given to the detection of boron hydrides.

TABLE I. - ANALYSIS AND PHYSICAL FORM OF MATERIALS

Compound	Formula	Analysis of material as received		Actual formula based on analysis	Physical form and dimensions as used
		Metal, percent	Nonmetal, percent		
Titanium carbide	TiC	74.60 Ti	17.85 C	$TiC_{0.954}$	Sintered block, 1/2 by 1/2 by 1/4 in.
Titanium nitride	TiN	78.65 Ti	18.60 N	$TiN_{0.809}$	Sintered block, 1/2 by 1/2 by 1/4 in.
Titanium diboride	TiB_2	66.80 Ti	30.49 B	$TiB_{2.01}$	Sintered block, 1/2 by 1/2 by 1/4 in.
Zirconium carbide	ZrC	86.98 Zr	10.95 C	$ZrC_{0.956}$	Sintered cylinder, 1/2 in. diam by 1/4 in.
Zirconium nitride	ZrN	86.22 Zr	11.14 N	$ZrN_{0.841}$	Sintered block, 1/2 by 1/2 by 1/4 in.
Zirconium diboride	ZrB_2	80.37 Zr	18.58 B	$ZrB_{1.95}$	Sintered cylinder, 1/2 in. diam by 1/4 in.
Silicon carbide	SiC	70.70 Si	28.67 C	--------	Sintered cylinder, 1/2 in. diam by 1/4 in.
Chromium carbide	Cr_3C_2	87.08 Cr	12.78 C	--------	Sintered cylinder, 1/2 in. diam by 1/4 in.
Calcium carbide	CaC_2	Commercial grade		--------	Lumps, largest dimension 1/4 to 1/2 in.
Aluminum carbide	Al_4C_3	Uncompacted material 98 percent pure		--------	Compacted cylinder, 1/2 in. diam by 1/4 in.
Cuprous acetylide	Cu_2C_2	Prepared at Lewis Research Center		--------	Precipitate
Calcium nitride	Ca_3N_2	Commercial grade		--------	Lumps
Boron nitride	BN	Uncompacted material 90 to 95 percent pure		--------	Compacted cylinder, 1/2 in. diam by 1/4 in.

EXPERIMENTAL

Materials

In table I are listed the analysis and physical form of the six refractories of interest. Also listed are seven other compounds tested for comparison purposes, namely, silicon carbide (SiC), chromium carbide (Cr_3C_2), calcium carbide (CaC_2), aluminum carbide (Al_4C_3), cuprous acetylide (Cu_2C_2), calcium nitride (Ca_3N_2), and boron nitride (BN). All samples were commercially obtained except the Cu_2C_2, which was prepared at Lewis (ref. 3, p. 435) and dried immediately before testing. Samples were used in compact form, whenever feasible, in order to facilitate handling and to maintain a more consistent surface area. However, because of the ease of hydrolysis of CaC_2 and Ca_3N_2, these materials were used as supplied (lumps). Furthermore, no attempt was made compact Cu_2C_2 because of its explosive nature.

In general, the following reaction media were used: (1) 6M sulfuric acid (H_2SO_4) plus 0.5M chromic acid (CrO_3); (2) 6M hydrochloric acid (HCl); (3) 1M H_2SO_4 plus 1M hydrogen peroxide (H_2O_2); and (4) fused potassium hydroxide (KOH). Occasionally, solutions containing hydrofluoric acid (HF) plus mercuric chloride ($HgCl_2$) and 1M cupric sulfate ($CuSO_4$) plus 0.5M H_2SO_4 were used. Other media used in appropriate cases were aqueous sodium hydroxide (NaOH), fluoroboric acid (HBF_4) plus potassium permanganate ($KMnO_4$), bromine (Br_2) in carbon tetrachloride (CCl_4), and concentrated H_2SO_4. Reagent grade chemicals were used without further purification.

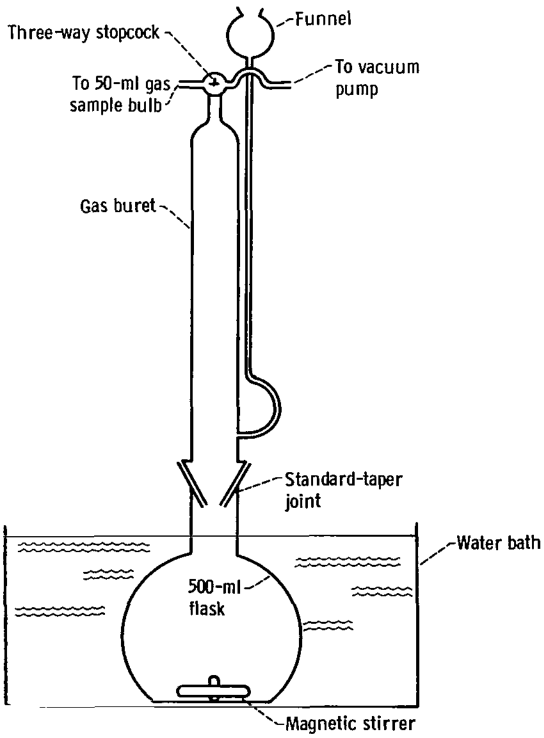

Figure 1. - Apparatus for use with aqueous media.

Method for Aqueous Systems

Figure 1 is a schematic drawing of the apparatus used in most of the experiments involving aqueous media. The apparatus was Pyrex except when HF was used, in which case the portions exposed to HF were constructed of polyethylene. (Blank runs showed that there was no reaction between HF and polyethylene.) The flask was nearly filled with the solution (reaction medium), the sample dropped in, the gas buret immediately attached, and the remaining solution poured through the funnel until the gas buret was filled with liquid. Reactions were car-

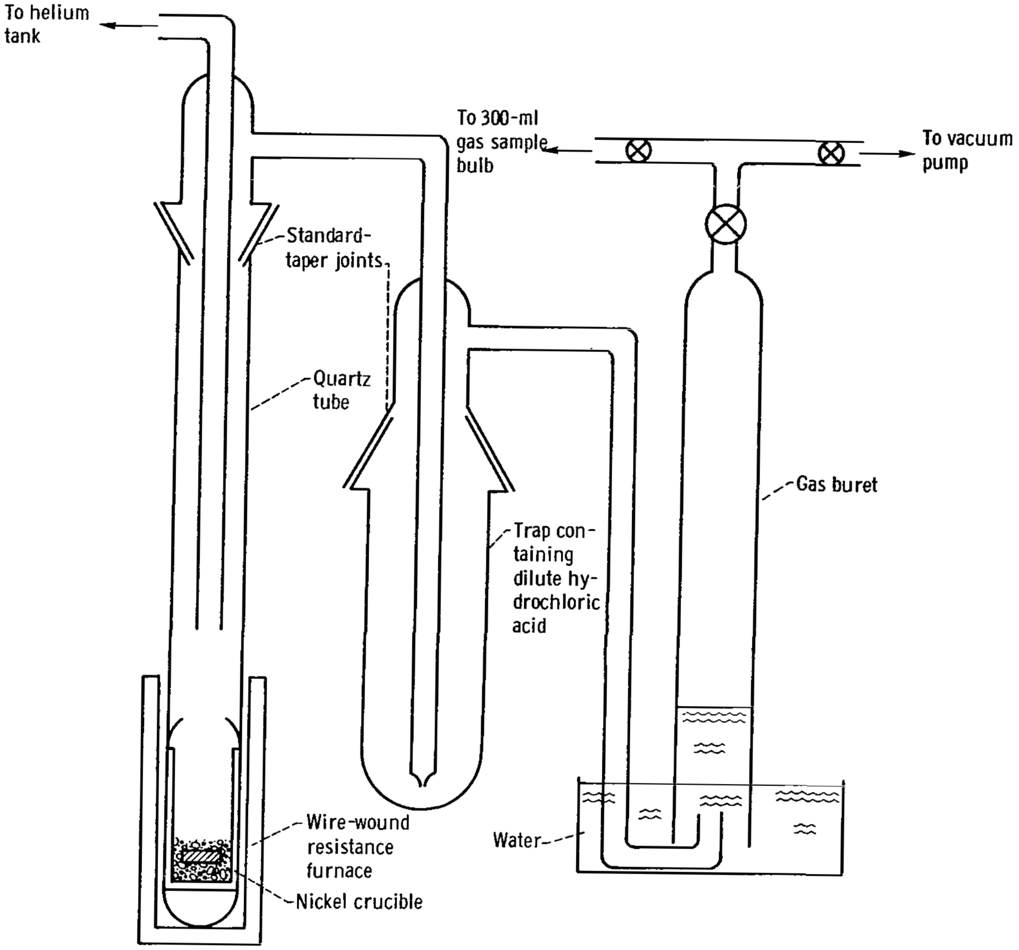

Figure 2. - Apparatus for use with fused potassium hydroxide.

ried out at 23±1° C (room temperature) and at about 100° C by the use of a preheated water bath. Because of the danger of explosion when dry Cu_2C_2 contacts strong oxidizing acid media, first the Cu_2C_2 was added to water (100 ml) in the reaction flask and then the apparatus was filled with the appropriate solution to make the specified reagent concentration.

After the reaction had proceeded a sufficient time (3 to 1500 hr), the gas was analyzed mass spectrometrically, the solution was analyzed chemically, and the change in weight of the sample was determined. A material balance was made when possible. In some cases, a gas analysis was not required; in others, (the majority of cases) only the relative abundance of the gaseous products was desired.

For the detection of boron hydrides from the reaction of TiB_2 or ZrB_2 with HCl, the gaseous products were expanded consecutively into three bulbs containing, respectively, silver nitrate ($AgNO_3$), $HgCl_2$, and freshly precipated mercuric oxide (HgO). The boron hydrides should reduce these compounds, as indicated by darkening of their color because of the formation of free metal. For one set of experiments (ZrB_2 + hot 6M HCl), the boron compounds (e.g., boron hydrides) in the gaseous products were determined semiquantitatively. In these experiments, the flask was modified to include a gas inlet. The flask containing the reactants was flushed with argon (Ar) before the reaction began. The reaction commenced soon after the apparatus had been heated in the water bath. During one of these runs, the gaseous products were flushed with Ar into a measured amount of acidified potassium dichromate ($K_2Cr_2O_7$) solution. A similar run was made in which the gases were flushed into a basic chromate solution. These solutions were then titrated and finally analyzed for the total amount of B (ref. 4).

Method Used at Elevated Temperatures

The apparatus for reactions in fused KOH is shown in figure 2. Because of the hydroscopic nature of KOH, loading and other manipulations were performed in a dry box. The KOH and refractory sample were first placed in the nickel crucible. The amount of KOH added was slightly less than that required for complete reaction of the refractory used. The crucible was wrapped with steel foil. The foil was left open at the top and extended more than 1 inch above the top of the crucible; in this way, it prevented the spray of KOH, resulting from gas evolution, from reaching the quartz walls. The wrapped crucible was then inserted into the quartz tube; this tube was stoppered prior to removal from the dry box and quickly inserted into the rest of the system shown in figure 2. During the time of connection, a stream of helium (He) gas dried in liquid nitrogen was flowing through the system. (Helium was the preferable inert gas because its presence caused no interference with the mass spectrometric analysis.) The flow of helium was maintained throughout the entire experiment. When the system was thoroughly flushed with dry He, the reaction vessel was heated to 400° or 500° C through the use of a wire wound furnace, the system being controlled at that temperature for the required period of time (from 3 to 12 h).

The trap containing dilute HCl was used in experiments with nitrides to trap ammonia (NH_3) from the gas stream; however, in other experiments the trap was bypassed, and the gas was merely collected by water displacement in a graduated tube. At the end of a run the system was flushed with He gas until fresh samples of the exit gas gave negligible mass spectrometric evidence of reaction products.

Analysis

The various gases determined mass spectrometrically included hydrogen (H_2), nitrogen (N_2), oxygen (O_2), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), acetylene (C_2H_2), other hydrocarbons, and boron hydrides. Standard wet chemical analyses were made for Ti and Zr (both were precipitated as hydrous oxides and weighed as dioxides), the ammonium ion (NH_4^+, Kjeldahl method), and boron (B, method of Blumenthal, ref. 4). Some of the analyses, however, involved complex separations or were concerned with specific oxidation states. Included were analyses for residual carbonate (CO_3^{-2}), chemically bound potassium oxide (K_2O), the mercurous ion (Hg^+), the trivalent chromium ion (Cr^{+3}), and the highly reactive boron hydrides. Many of these later methods should only be considered semiquantitative.

Determinations of carbonate in the residue from the carbide-KOH reactions were made by extraction with boiling water followed by precipitation of barium carbonate ($BaCO_3$) by addition of barium hydroxide ($Ba(OH)_2$) to the extract. Correction was made for (CO_3^{-2}) originally present in KOH.

The K_2O bound in the complexes $TiO_2 \cdot xK_2O$ and $ZrO_2 \cdot xK_2O$, was determined by redissolving the alcohol-insoluble material in hot dilute H_2SO_4, evaporating to fumes, adding water, precipitating the hydrous titanium or zirconium oxide with ammonium hydroxide, filtering, and evaporating the filtrate to dryness. The residue was dissolved in a small volume of H_2SO_4, ignited, and weighed as potassium sulfate (K_2SO_4).

The Hg^+ ion as mercurous chloride (Hg_2Cl_2) formed in the reaction medium, HF plus $HgCl_2$, was determined by filtering, drying at 100° C, and weighing. Before Ti could be determined in the solution, the unreacted $HgCl_2$ was removed by reduction to Hg_2Cl_2 in weakly acid solution by using the stoichiometric amount of stannous chloride ($SnCl_2$) and subsequent removal of the Hg_2Cl_2 by filtration. The Ti could then be determined by the standard method.

In reactions of carbides and nitrides with CrO_3 solutions, the amount of CrO_3 reduced to Cr^{+3} was determined by double precipitation of chromic hydroxide with ammonium hydroxide. The filtered hydroxide was then oxidized to chromate (CrO_4^{-2}) with alkaline H_2O_2 followed by titration. In all redox titrations, the dichromate ($Cr_2O_7^{-2}$) - ferrous (Fe^{+2}) system was used with barium diphenyl sulfate indicator.

RESULTS OF REACTIONS OF REFRACTORIES

For clarity, the results of carbide, nitride, and boride experiments are presented and discussed separately. For each, a summary is given followed by an enumeration of the specific details listed in tables II, III, and IV. Each set of data is a composite of at least two experiments. The systems for which no reactions take place are included merely for completeness of the tables. Little comment is made in this section on the reactions of the compounds tested for comparison purposes because these are not of primary interest here; however, use of the results is made in the discussion of the group IVA metal refractory compounds.

Carbides

The group IVA metal carbides, TiC, ZrC, and SiC are practically inert toward attack by strong aqueous acids (HCl) and strong aqueous bases (NaOH) even at 100° C; however, ZrC does react with HF; moreover, both TiC and ZrC are attacked by strong acid solutions of oxidizing agents. SiC is particularly inert toward all the aqueous systems tested, including strongly oxidizing systems. No reaction, neither single or double replacement, occurs between these carbides and acid solutions of $CuSO_4$. With regard to nonaqueous reactants, no reaction occurs with a solution of Br_2 in CCl_4; however, all three carbides are attacked by molten KOH, even in the absence of O_2.

In table II are shown the detailed results of the reactions of TiC, ZrC, and the carbides of known bonding. In the first four columns of table II are listed, respectively, the carbide used, the reactant medium, the temperature, and the duration of the run. When the compact did not break up or disintegrate, the weight loss (column 5) could be used to calculate the amount of Ti or Zr reacted. Such values correspond very well to the amount of Ti or Zr found by analysis of the reacted solution medium (column 6). Breakup of the TiC compact with the formation of a finely divided crystalline residue occurs in CrO_3 solutions as well as H_2O_2 solutions. The X-ray diffraction pattern of such residues is that of TiC. The amount (milliequivalents) of reduction product (Cr^{+3} for CrO_3 medium and H_2 for KOH medium) is given in column 7. Because of the extensive decomposition of the H_2O_2 during the run, no attempt was made to determine the peroxide concentration at the end of a run. Apparently TiC and ZrC catalyze this decomposition, as indicated by the high concentration of O_2 in the gaseous products (column 10). The apparent valence change for the carbide (column 8) is found by dividing the values in column 7 by the corresponding values in column 6.

The apparent valence change (column 8) represents the number of electrons involved in the oxidation of a molecule of carbide, nitride, or boride as a whole and is not intended to denote a specific oxidation state of the metal or nonmetal in the refractory. These values of the apparent valence change are used to determine the relative contribution of reactions which lead to the formation of the reaction products actually found. The amount of CO_3^{-2} in the medium (KOH) after reaction is listed in column 9. In column 10 are given the mass spectrometric semiquantitative analyses of the gaseous reaction products.

By judging from the reaction products (columns 6 and 10) the reaction of TiC and ZrC with strongly acid solutions of CrO_3 may be represented by the following chemical equations:

TABLE II. - CHEMICAL REACTIONS OF CARBIDES

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)							
Compound	Reaction medium	Temperature, °C	Time, h	Weight loss, g	Metal (Ti, Zr, or Si) found in solution, millimoles	Amount of reduction product (Cr^{+3} or H_2), milliequivalents	Apparent valence change of carbide	$(CO_3)^{-2}$ in medium after reaction, millimoles	Gaseous products, mole percent							
									CO	CO_2	CH_4	H_2	N_2	O_2	C_2H_2	Others
$TiC_{0.954}$	6M H_2SO_4 + 0.5M CrO_3	100	6	2.3613	24.5	178	7.27	---	21.7	77.3	-----	-----	-----	1.0	-----	------------
	1M H_2SO_4 + 1M H_2O_2	23	372	1.3478	15.0	(a)	----	---	15.4	8.3	0.02	0.15	0.50	75.6	-----	------------
	KOH	500	3	1.4005	21.2	135	6.37	22	.14	.16	5.9	91.00	2.8	.46	-----	He(carrier)
	6M HCl	100	20	Very slight reaction	------	-----	----	---	-----	-----	-----	-----	-----	-----	-----	------------
	4M NaOH	100	20	No reaction	------	-----	----	---	-----	-----	-----	-----	-----	-----	-----	------------
	0.5M H_2SO_4 + 1M $CuSO_4$	23	200	No reaction	------	-----	----	---	-----	-----	-----	-----	-----	-----	-----	------------
	Br_2 in CCl_4	23	200	No reaction	------	-----	----	---	-----	-----	-----	-----	-----	-----	-----	------------
$ZrC_{0.956}$	6M H_2SO_4 + 0.5M CrO_3	100	49	2.1573	21.8	161	7.39	---	3.8	93.9	0.04	0.08	1.2	1.0	-----	------------
	1M H_2SO_4 + 1M H_2O_2	23	192	.6154	5.83	-----	----	---	3.0	1.0	.44	.07	.39	95.1	0.03	------------
	KOH	500	5	.9571	9.91	58.6	5.91	9	.07	.10	8.9	86.4	4.0	.52	.02	He(carrier)
	10M HF	100	46	0.7222	7.07	-----	----	---	-----	0.35	91.7	5.7	1.3	0.44	-----	Ethane: 0.61
	6M HCl	100	40	Very slight reaction	------	-----	----	---	-----	-----	-----	-----	-----	-----	-----	------------
	4M NaOH	100	20	No reaction	------	-----	----	---	-----	-----	-----	-----	-----	-----	-----	------------
	0.5M H_2SO_4 + 1M $CuSO_4$	23	200	No reaction	------	-----	----	---	-----	-----	-----	-----	-----	-----	-----	------------
	Br_2 in CCl_4	23	200	No reaction	------	-----	----	---	-----	-----	-----	-----	-----	-----	-----	------------
SiC	6M H_2SO_4 + 0.5M CrO_3	100	40	No reaction	------	-----	----	---	-----	-----	-----	-----	-----	-----	-----	------------
	KOH	500	4.25	1.1262	[b]28.4	111	3.9	21	0.06	0.15	18.7	75.2	5.0	0.87	0.01	------------
	6M HCl	100	40	No reaction	------	-----	----	---	-----	-----	-----	-----	-----	-----	-----	------------
Cr_3C_2	10M HF	100	40	0.9309	------	-----	----	---	-----	-----	29.2	55.0	0.9	0.9	-----	Ethylene: 8.1 Ethane: 2.0 Propene: 2.0 Propane: 1.7 Butane: 0.1 Pentane: 0.1
CaC_2	6M H_2SO_4 + 0.5M CrO_3	100	1.75	2.8741	-----	-----	----	---	-----	78.3	-----	0.13	-----	0.08	21.5	------------
	1M H_2SO_4 + 1M H_2O_2	23	2.25	1.7331	-----	-----	----	---	-----	.03	-----	1.2	0.41	26.0	72.4	------------
Al_4C_3	6M H_2SO_4 + 0.5M CrO_3	100	------	Very rapid reaction	-----	(c)	----	---	-----	-----	-----	-----	-----	-----	-----	------------
	1M H_2SO_4 + 1M H_2O_2	23	3.25	1.4743	-----	-----	----	---	-----	0.25	83.9	1.1	0.11	11.5	0.65	Ethane: 2.5
Cu_2C_2	2M H_2SO_4 + 0.15M CrO_3	100	20	2.1042	-----	-----	----	---	2.4	33.3	-----	0.18	3.5	0.40	57.9	Biacetylene: 2.4
	1M H_2SO_4 + 1M H_2O_2	23	120	1.2651	-----	(d)	----	---	-----	1.6	-----	-----	2.9	89.8	5.7	Biacetylene: 0.09

[a] Intense yellow color of peroxytitanic acid.

[b] The actual amount of Si in solution was not determined. This value was calculated from the weight loss. It was found that, for TiC and ZrC, when there was no sample disintegration, the metal actually found in solution by analysis corresponded quite closely to the value calculated from the weight loss.

[c] Green color of Cr^{+3} observed.

[d] Small amount of amorphous carbon was formed.

$$3MC + 8CrO_3 + 30H^+ \rightarrow 3MO^{++} + 3CO_2 + 8Cr^{+3} + 15H_2O \qquad (1)$$

$$MC + 2CrO_3 + 8H^+ \rightarrow MO^{++} + CO + 2Cr^{+3} + 4H_2O \qquad (2)$$

where M represents the metals. Equations (1) and (2) involve, respectively apparent 8 and 6 valence changes for the carbide (MC); however, by taking into account the actual compositions ($TiC_{0.954}$ and $ZrC_{0.956}$) the apparent valence changes for reactions corresponding to equations (1) and (2) become, respectively, 7.82 and 5.91. The experimental value of 7.27 (column 8) for TiC indicates that about 3/4 of the carbide reacts according to equation (1), and 1/4 according to equation (2); while for ZrC the experimental value of 7.39 indicates that equation (1) constitutes about 4/5 of the reaction, and equation (2) the remaining 1/5. The gas analysis (column 10) supports this ratio for TiC; however, for ZrC the low concentration of CO in the gaseous products suggests that equation (2) contributes very little to the over-all reaction. This apparent disagreement may be due to the occurence of unknown side reactions.

In experiments using acidic H_2O_2, both CO and CO_2 are formed (column 10); however, in contrast to experiments in CrO_3 solution, the CO-producing reaction predominates. Because the amount of reduction product was not determined, a more detailed account of the reactions cannot be ascertained. In the reactions with TiC, the intense yellow color of peroxytitanic acid was noted.

In reactions of TiC, ZrC, and SiC with fused KOH, most of the C goes to potassium carbonate (K_2CO_3) (column 9); the remainder for the most part is converted to CH_4. Based on similar experiments with nitrides, the Ti and Zr probably form, respectively, the complexes $TiO_2 \cdot xK_2O$ and $ZrO_2 \cdot xK_2O$. Thus, the two important reactions appear to be

$$MC + 8KOH \rightarrow MO_2 \cdot xK_2O + K_2CO_3 + 4H_2 + (3 - x)\,K_2O \qquad (3)$$

$$MC + 4KOH \rightarrow MO_2 \cdot xK_2O + CH_4 + (2 - x)\,K_2O \qquad (4)$$

The apparent valence changes for the carbide are, respectively, 8 and 0 for equations (3) and (4), or 7.82 and 0.18, if the actual composition of the carbide is considered. In equation (4) use is made of the convention that the hydrogen does not change valence; that is, its valence in CH_4 is plus 1. The experimental values of 6.37 and 5.91 for TiC and ZrC, respectively, imply that, for TiC, equation (3) accounts for about 4/5 of the reaction and equation (4) accounts for the remaining 1/5, while for ZrC the relative contributions of equations (3) and (4) are 3/4 and 1/4, respectively. This distribution agrees with the large fraction of carbon found as carbonate (column 9, table II).

The ZrC is readily attacked by hot HF solution according to the equation

$$ZrC + 6HF \rightarrow ZrF_6^{-2} + CH_4 + 2H^+ \quad (5)$$

The gaseous products consist almost entirely of CH_4 and as can be expected from the known chemistry of Zr, the Zr forms the complex hexafluorozirconate ion (ZrF_6^{-2}) in solution.

Nitrides

No apparent reaction occurs between either TiN or ZrN and aqueous NaOH. TiN is practically inert to even strong acids, including HCl and HF. ZrN reacts with 6M HCl at 100° C, with NH_4^+ being a major product. There appears to be no reaction of either TiN or ZrN with acid solutions of $CuSO_4$ at 23° C. TiN is slightly attacked by concentrated H_2SO_4 at 100° C. No reaction is observed for TiN with hot HBF_4 plus $KMnO_4$; however, TiN is readily attacked by hot aqueous HF containing an oxidizing agent such as $HgCl_2$. Both TiN and ZrN react with hot 6M H_2SO_4 plus 0.5M CrO_3, 1M H_2SO_4 plus 1M H_2O_2, and molten KOH (in the absence of O_2).

In table III are shown the detailed results of reactions of TiN, ZrN, BN, and Ca_3N_2 in various media. The designations of the first eight columns of table III are the same as has been described for table II. Column 9 (amount of NH_4^+ found) is self-explanatory. In column 10 is given the mole percent of the total reacted nitrogen found as NH_4^+ (based on metal found in solution, and the percent N in the original sample). In column 11 the molar ratio of NH_4^+ to reacted metal is obtained by dividing each value in column 9 by the corresponding value in column 6. For calculated systems (column 12) within the limits of the analyses, the N not found as NH_4^+ was found as N_2 (based on the amount of gas and its analysis). The mass spectrometric analysis of the gaseous reaction products is given in column 13.

Because both NH_4^+ and N_2 are found in the products resulting from the reaction of TiN (as well as ZrN) in acid solutions of CrO_3, two equations may be written:

$$6MN + 8CrO_3 + 36H^+ \rightarrow 6MO^{+2} + 8Cr^{+3} + 3N_2 + 18H_2O \quad (6)$$

$$3MN + CrO_3 + 12H^+ \rightarrow 3MO^{+2} + Cr^{+3} + 3NH_4^+ \quad (7)$$

Equation (6) involves an apparent valence change of 4 for the compound MN, while equation (7) involves a change of 1. When the actual composition of the nitrides ($TiN_{0.809}$ and $ZrN_{0.841}$) is taken into account, the valence change for equation (6) is still 4, but for equation (7), the valence change becomes 1.57 for $TiN_{0.809}$ and 1.48 for $ZrN_{0.841}$. The experimental values of 2.60 and 2.55 for TiN and ZrN, respectively,

TABLE III. - CHEMICAL REACTIONS OF NITRIDES

(1) Compound	(2) Reaction medium	(3) Temperature, °C	(4) Time, h	(5) Weight loss, g	(6) Metal (Ti, Zr, B) found in solution, millimoles	(7) Amount of reaction product (Cr^{+3} or Hg^{+1}), milliequivalents	(8) Apparent valence change of nitride	(9) NH_4^+ in solution or HCl trap, millimoles	(10) N as NH_4^+, percent of total N	(11) Molar ratio of NH_4^+ to reacted metal	(12) N as N_2, percent of total N	(13) Gaseous products, mole percent				
												N_2	H_2	O_2	CO_2	CH_4
$TiN_{0.809}$	6M H_2SO_4 + 0.5M CrO_3	100	110	0.3484	5.69	14.8	2.60	2.80	60.9	0.492	44	96.4	0.2	2.8	---	---
	2M H_2SO_4 + 0.5M CrO_3	100	100	.3119	5.11	----	----	2.55	61.7	.499	---	----	----	----	---	---
	1M H_2SO_4 + 1M H_2O_2	23	1300	.3202	5.22	(a)	----	3.83	90.8	.734	>10	1.9	.2	97.3	0.6	---
	1M H_2SO_4 + 1M H_2O_2	100	47	.8000	13.13	(a)	----	10.16	95.7	.774	---	----	----	----	---	---
	10M HF + 0.3M $HgCl_2$	100	96	2.9370	49.1	34.7	0.71	41.0	100	.835	---	----	----	----	---	---
	6M HCl	100	50	No reaction	-----	----	----	------	-----	-----	---	----	----	----	---	---
	10M HF	100	50	Very slight reaction	-----	----	----	------	-----	-----	---	----	----	----	---	---
	Aqueous HBF_4 + $KMnO_4$	100	50	No reaction	-----	----	----	------	-----	-----	---	----	----	----	---	---
	Concentrated H_2SO_4	100	50	Slight reaction	-----	----	----	------	-----	-----	---	----	----	----	---	---
	1M $CuSO_4$ + 0.5M H_2SO_4	23	100	No reaction	-----	----	----	------	-----	-----	---	----	----	----	---	---
	KOH	500	7	1.1322	18.5	----	----	5.50	36.7	0.297	66	----	----	----	---	---
	KOH	400	12	.2748	4.28	----	----	1.47	42.5	.344	---	----	----	----	---	---
	4M NaOH	100	20	No reaction	-----	----	----	------	-----	-----	---	----	----	----	---	---
$ZrN_{0.841}$	6M H_2SO_4 + 0.5M CrO_3	100	50	0.9857	9.50	24.2	2.55	5.04	63.0	0.530	---	(b)	----	----	---	---
	1M H_2SO_4 + 1M H_2O_2	23	1500	.1175	1.16	----	----	.450	46.0	.387	---	8.6	0.2	91.0	0.1	---
	1M H_2SO_4 + 1M H_2O_2	100	40	.1127	1.07	----	----	.450	60.2	.507	---	----	----	----	---	---
	6M HCl	100	28	1.7860	16.49	----	----	13.82	99.6	.838	---	.9	94.7	.4	.1	3.8
	1M $CuSO_4$ + 0.5M H_2SO_4	23	100	Very slight reaction	-----	----	----	------	-----	-----	---	----	----	----	---	---
	KOH	500	5	.1798	1.75	----	----	.464	31.5	.265	---	(b)	----	----	---	---
	KOH	400	7	Slight reaction	-----	----	----	------	-----	-----	---	----	----	----	---	---
	4M NaOH	100	20	No reaction	-----	----	----	------	-----	-----	---	----	----	----	---	---
BN	KOH	500	4	1.6956	59.3	----	----	57.0	99.7	0.961	---	----	----	----	---	---
Ca_3N_2	6M H_2SO_4 + 0.5M CrO_3	100	10	1.5827	-----	----	----	17.5	99.1	-----	---	----	----	----	---	---

[a] Intense yellow color of peroxytitanic acid was noted in all reactions involving TiN and solutions containing H_2O_2.

[b] Mass-spectrographic analysis showed the presence of N_2 as the only nitrogen containing species in the gaseous reaction products.

indicate that, for both, about 3/5 of the nitride reacts according to equation (7), the remaining 2/5 reacting according to equation (6). This distribution is in agreement with the fact that about 3/5 of the total N is found as NH_4^+, as shown in column 10 of table III.

Two equations similar to equations (6) and (7) can be written for the reactions of nitrides with H_2O_2. For TiN the NH_4^+ forming reaction predominates (over 90 percent; column 10, table III) to a greater extent than when a CrO_3 solution is used. For the reaction of ZrN with 1M H_2SO_4 plus H_2O_2, the NH_4^+ forming reaction at 100° C accounts for only about 3/5 of the reaction products. The same reaction carried out at a lower temperature, 23° C, gave a somewhat lower yield, 46 percent of NH_4^+. Again, the refractory materials catalyze the decomposition of H_2O_2, as indicated by the high concentration of O_2 in the gas; furthermore, the color of peroxytitanic acid is observable for TiN even at 100° C.

The reaction of TiN in HF plus $HgCl_2$ results in an essentially quantitative conversion (column 10) of the N to NH_4^+ according to the equation

$$2TiN + 2Hg^{+2} + 12F^- + 8H^+ + 2Cl^- \rightarrow 2TiF_6^{-2} + 2NH_4^+ + Hg_2Cl_2 \tag{8}$$

The reaction requires one equivalent weight of Hg^{+2} per mole of TiN, or 1.6 for $TiN_{0.809}$. The lower value actually found may be due to the simultaneous reduction of H^+ as shown by the equation

$$2TiN + 12HF \rightarrow 2H^+ + 2TiF_6^{-2} + 2NH_4^+ + H_2 \tag{9}$$

Titanium nitride appears to be considerably more reactive than ZrN in fused KOH. At 400° C there is some attack of the TiN by fused KOH, but with ZrN under these conditions there is only a slight reaction. In all reactions involving TiN and ZrN in fused KOH, extraction of the solid reaction products with hot absolute ethyl alcohol results in an insoluble residue corresponding to the compositions $TiO_2 \cdot xK_2O$ and $ZrO_2 \cdot xK_2O$, respectively, x varying between 0.25 and 0.35. The equations for these reactions are similar to those for the reactions of TiC and ZrC with KOH,

$$2MN + 8KOH \rightarrow 2MO_2 \cdot xK_2O + N_2 + 4H_2 + (4 - x) K_2O \tag{10}$$

$$2MN + 8KOH \rightarrow 2MO_2 \cdot xK_2O + 2NH_3 + H_2 + (4 - x) K_2O \tag{11}$$

From the data in column 10 it is evident that equation (10) represents the major contribution to the overall reaction.

BN is readily attacked by KOH. The reaction begins as soon as the KOH melts; NH_3

is evolved. In the acidified solution of the solid reaction products, the B is found as boric acid. The total N in BN was calculated by assuming the sample to be 0.95 BN and 0.05 boric oxide (B_2O_3). Ca_3N_2 is rapidly hydrolysed by acid solutions; however, in 6M H_2SO_4 plus 0.5M CrO_3 this hydrolysis is slow enough, probably because of the formation of insoluble calcium sulfate ($CaSO_4$) on the nitride lumps, to permit adequate control of the reaction.

Borides

The diborides of Ti and Zr are more reactive to strongly acid solutions than the corresponding carbides and nitrides. Unlike the carbides and nitrides, TiB_2 and ZrB_2 reduce metal salt solutions such as $CuSO_4$ to the corresponding free metal. Both of the diborides, when exposed to an acidified $CuSO_4$ solution at 23° C for about 72 hours, result in the formation of an adherent smooth copper deposit which covered the compact (Cu was identified by X-ray diffraction; no copper boride was detectable.)

In table IV are presented the detailed results of the reactions of TiB_2 and ZrB_2. The table designations are similar to those described for tables II and III. The action of HCl on TiB_2 yields essentially titanous ion (Ti^{+3}), as indicated by the violet color of the used solution. Column 8 gives a quantitative measure of the amount of Ti^{+3} formed, the remaining Ti in solution being in the form TiO^{++}.

No boron hydrides are detected from TiB_2 reactions either mass spectrometrically or by reduction of $AgNO_3$. In the reaction of ZrB_2 with HCl, small amounts of boron hydrides may be produced; the gaseous reaction products caused a slight blackening of $AgNO_3$, but there appeared to be no reduction of $HgCl_2$ or freshly precipitated HgO. Furthermore, in the mass spectrometric data (after compensating for the major constituents) a small peak at mass 26 and another at 27 may be due to trace quantities of diborane (B_2H_6) (ref. 5, p. 1). When the reaction flask containing the ZrB_2 and 6M HCl was continuously flushed with Ar throughout a run, a relatively large amount of boron compounds was found in the gas (column 9). The volatile B was probably a plus 3 boron species (ref. 6, p. 751). In the same experiment, quantitative measure of the reducing species (assumed to be boron hydrides) in these gaseous products is given in column 10.

DISCUSSION IN TERMS OF CHEMICAL BONDING

Carbides

In contrast to an ionic carbide, CaC_2 (composed of acetylide (C_2^{-2}) ions), and a

TABLE IV. - CHEMICAL REACTIONS OF BORIDES

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)					(12)
Compound	Reaction medium	Temperature, °C	Time, h	Weight loss, g	Metal (Ti or Zr) in solution, millimoles	Analysis of B in solution, millimoles	Ti^{+3} in solution, millimoles	B in gaseous products, millimoles	Reducing species in gaseous products found by bubbling through dichromate, milliequivalents	Gas analysis, mole percent					Remarks
										H_2	N_2	CO_2	CH_4	O_2	
$TiB_{2.01}$	6M HCl	100	8.25	0.3450	4.57	9.12	3.48	----	-----	99.1	0.67	0.08	0.05	0.13	------------------
	1M H_2SO_4 + 1M H_2O_2	23	6.25	3.0385	41.0	83.7	----	----	-----	5.2	.48	.59	.17	93.5	1.12 millimoles of H_2
	1M $CuSO_4$ + 0.5M H_2SO_4	23	100	------	-----	-----	----	----	-----	----	----	----	----	-----	Cu deposit on boride
$ZrB_{1.95}$	6M HCl	100	------	------	-----	-----	----	----	-----	99.1	0.69	0.03	0.03	0.12	Possible trace of B_2H_6 in gas less than 0.01 percent
	[a]6M HCl	100	17	2.5435	22.41	41.24	----	3.47	0.083	----	----	----	----	-----	------------------
	1M $CuSO_4$ + 0.5M H_2SO_4	23	100	------	-----	-----	----	----	-----	----	----	----	----	-----	Cu deposit on boride

[a] With continuous flow of Ar.

somewhat less ionic Cu_2C_2, TiC and ZrC yield essentially no hydrocarbon when treated with acid solutions containing CrO_3. The small amount of CH_4 formed with ZrC (0.04 percent of the gaseous products) is attributed to the hydrolysis of other metal carbides present in the sample as impurities. Under the same conditions CaC_2 forms a significant amount of C_2H_2; moreover, Cu_2C_2 in a more diluted acid solution of CrO_3 yields essentially C_2H_2. Even more pronounced are the results of reactions in 1M H_2SO_4 plus 1M H_2O_2. With TiC and ZrC, the predominant reactions involve the formation of CO and CO_2, while, under similar conditions, carbides composed of negatively charged carbon species form, almost exclusively, the hydrocarbon corresponding to that species; thus, C_2^{-2} (CaC_2 and Cu_2C_2) forms C_2H_2, and C^{-4} (methanide ion present in Al_4C_3) yields CH_4.

Thermodynamic considerations alone indicate that, under oxidizing conditions, the carbon in these carbides would be converted to the oxides; however, with the negative C species relative reaction rates become important. Apparently, the hydrolysis reaction rate is rapid compared to the rate of the redox reaction resulting in the formation of CO and CO_2. With regard to Cu_2C_2, which is less ionic than CaC_2 and thus would have less tendency to undergo hydrolysis, a small amount of the C in Cu_2C_2 in acid solutions of H_2O is oxidized to free C and CO_2. On the basis of the results of these reactions, it appears that TiC and ZrC are not ionic carbides in the sense that the C is negatively charged.

Under reducing conditions as encountered in the reaction of Cr_3C_2 and ZrC with strong HF solution, the Cr_3C_2 produces a mixture of hydrocarbons, the amounts decreasing with increasing number of C atoms. The formation of hydrocarbons of more than one C atom is indicative of some sort of carbon to carbon bonding in the carbide; Cr_3C_2 is thought to be composed of zigzag chains of C atoms extending throughout the crystal with Cr atoms inserted between the chains (ref. 7, p. 260). On the other hand, although under different conditions (fused KOH), essentially the only hydrocarbon being formed with SiC is CH_4, which implies no carbon to carbon bonding in SiC. This behavior is in agreement with the established structure, in which the Si and C atoms have alternate positions, and each type is surrounded tetrahedrally by the other. This reasoning indicates that there is no carbon to carbon bonding in TiC or ZrC because the only hydrocarbon produced in significant quantity in reactions of TiC (with fused KOH) and ZrC (with aqueous HF and fused KOH) is CH_4. Thus, it is concluded that the C atoms have significant bonding only to Ti or Zr atoms.

A concept of the metal-nonmetal bonding in transition metal carbides, nitrides, and borides described by Engel (ref. 1) is as follows: The outer electrons of the nonmetal at atom are distributed between the outer bonding positions and d levels in the transition metal atoms. If these d levels are strong acceptors and the ionization potential of the nonmetal electrons is low, the electron concentration is greater near the metal atom, and some ionic character results (e.g., Ti^-C^+). The acceptor ability of the metal atom is expressed qualitatively by Samsonov (ref. 2) according to the relation,

$$\text{Acceptor ability} = \frac{1}{Nn}$$

where N is the principal quantum number of the unfilled d level and n is the number of electrons in this unfilled d level. When this concept is used for the group IVA carbides, Ti, having an unfilled 3d shell, has a greater acceptor ability for electrons than Zr, with an unfilled 4d shell. On the other hand, SiC is bonded solely by sp orbitals, there being practically no localization of electrons near the Si core. The order of increasing positivity of the C atom in these carbides is SiC, ZrC, TiC. Greater negativity of C atoms favors CH_4 formation, and conversely, positive C atoms favor CO and CO_2 formation. On examination of the reactions of these carbides with fused KOH, it is seen that the ratio of CH_4 to H_2 in the gaseous products decreases in the order of increasing positivity of the C atom; this is to be expected.

It is concluded that TiC and ZrC are essentially convalently bonded with slight ionic character of the type M^-C^+, this ionic character being most pronounced in TiC.

Nitrides

Unfortunately, the results of these chemical experiments allow less understanding of the structure of nitrides than do those for carbides. With the carbides many stable compounds may be formed (such as numerous hydrocarbons), while the formation of only a limited number of N species (N_2, NH_3, NH_4^+, and possibly hydrazine) is feasible.

Ionic nitrides, such as Ca_3N_2, which contain the nitrogen minus 3 ion (N^{-3}) are hydrolyzed in acid solution to NH_4^+ (ref. 8, p. 578). The results in table III show that, even under strong oxidizing, hot acid solutions of CrO_3, no oxidation of N^{-3} is observed, the formation of NH_4^+ being practically quantitative. Also, quantitative formation of NH_4^+ is observed on reaction of Ca_3N_2 with acid solutions of H_2O_2 and $KMnO_4$ (ref. 9); however, under similar circumstances, especially in acid solutions of CrO_3, significant amounts of N_2 are evolved from TiN and ZrN. In view of this difference in chemistry, TiN and ZrN are not ionic nitrides in the sense that N is present as a discrete N^{-3} ion.

Based on the bonding concept described for the carbides, where the electrons of the nonmetal atom are accepted in the d and s orbitals of the metal, TiN and ZrN represent a system where the metal has high acceptor ability; however, the N is strongly electronegative (ref. 10, p. 93). Thus, there is less tendency for localization of electrons near the Ti and Zr core than there is for carbides and borides. Nevertheless, because of the strong acceptor ability of the metal atom, the electrons tend to be drawn away from the N, and thus it is less negative than the N in a sp covalently bonded nitride such as BN. The sp orbitals of B would have relatively lower acceptor ability than the d and s orbitals of Ti and Zr. It is logical to assume that greater negativity of the N atoms in a compound results in greater tendency for NH_3 or $NH_4{}^+$ formation. The order of increasing negativity of the N in the four nitrides used experimentally is TiN, ZrN, BN, and Ca_3N_2; thus, the tendency to form NH_3 or $NH_4{}^+$ should increase in that order.

The greater tendency of NH_3 formation for BN as compared with TiN and ZrN is demonstrated in reactions in fused KOH. The BN is rapidly attacked by KOH to form NH_3 almost quantitatively; whereas, with TiN and ZrN under these conditions most of the N is liberated as N_2. For TiN even at a relatively low temperature, 400° C (which minimizes thermal decomposition of any NH_3 formed), the yield of NH_3 is small. Because of the great stability of $NH_4{}^+$ in acid media, reactions of ZrN in nonoxidizing acids (HC1) yield $NH_4{}^+$ quantitatively. Although TiN is not appreciably attacked by HF or HCl alone, it reacts with aqueous HF plus Hg^{+2} to form $NH_4{}^+$ quantitatively. It is proposed that the oxidizing action of Hg^{+2} merely converts the Ti^{+3} intermediate to $TiF_6{}^{-2}$

In experiments of TiN and ZrN in H_2SO_4 plus CrO_3 solutions and of ZrN in hot 1M H_2SO_4 plus H_2O_2, there is a consistency of results which was reproducible in several independent runs. In these about 60 percent of the total N formed $NH_4{}^+$ (column 10, table III), while the remaining 40 percent was evolved as N_2. Because of the uniformity of this result under a variety of conditions, it is believed to be characteristic of the nitride itself. As a consequence of this same uniformity of results, it is found that a simple fraction, 1/2, closely approximates the mole ratio of $NH_4{}^+$ formed to the Ti or Zr found in solution (column 11, table III). In other words, the reaction of 1 mole of $TiN_{0.809}$ or $ZrN_{0.841}$ yields 1/2 mole of $NH_4{}^+$, but at this time the significance of the phenomenon is not readily apparent.

Borides

Chemically, the borides appear to be more metallic than the corresponding carbides and nitrides. Both TiB_2 and ZrB_2 readily displace H^+ from strong acids, the TiB_2 forming Ti^{+3} as does metallic Ti under similar conditions. In addition, the metallic properties of TiB_2 and ZrB_2 are shown by the replacement of the cupric ion (Cu^{+2}) from solution to form Cu.

Unlike Mg_3B_2, an ionic boride composed of boron minus 3 groups (B^{-3}) (ref. 8, p. 771), which reacts with acids to form significant yields of boron hydrides (ref. 11), TiB_2 produces no boron hydrides and ZrB_2 produces only small amounts on treatment with aqueous HCl. If the formation of boron hydrides is due to the hydrolysis of B^{-3} ions, TiB_2 and ZrB_2 are not ionic in the sense that magnesium bromide (Mg_3B_2) is.

The diborides do not have a simple interstitial structure. In TiB_2 and ZrB_2 the B atoms are arranged in two-dimensional nets, being bound to each other covalently as B-B. The metallic properties of the borides are a result of overlap of the bonding orbitals of the metal with one another and of the metallic nature of the M-B bond (ref. 2). In view of the low electronegativity and the low ionization potential of B and the strong acceptor ability of the d orbitals of Ti and Zr, the presence of B^{-3} ions in TiB_2 and ZrB_2 is very unlikely.

SUMMARY OF RESULTS

The reactions of the carbides, nitrides, and diborides of titanium and zirconium in compact form were investigated in various media, including chromic acid solution (CrO_3), hydrochloric acid (HCl), acidified hydrogen peroxide (H_2O_2), fused potassium hydroxide (KOH), and in some cases solutions containing hydrofluoric acid (HF). Semiquantitative determinations of the reaction products are presented, including mass-spectrometric analyses of the gaseous products. For comparison purposes, the results are also reported for reactions of compounds of known bonding, such as silicon carbide (SiC), chromium carbide (Cr_3C_2), calcium carbide (CaC_2), aluminum carbide (Al_4C_3), cuprous acetylide (Cu_2C_2), calcium nitride (Ca_3N_2), and boron nitride (BN). In view of these results, the bonding of the group IVA carbides, nitrides, and diborides is discussed considering the hypothesis that the outer electrons of the nonmetal atom (carbon (C), nitrogen (N), and boron (B) interact with the d orbitals of the transition metal atom (titanium (Ti) and zirconium (Zr)).

Under mild oxidizing conditions such as are encountered in dilute solutions of H_2O_2 containing sulfuric acid (H_2SO_4), TiC and ZrC react to form carbon monoxide (CO) and carbon dioxide (CO_2); whereas, under similar conditions, other carbides such as CaC_2 and Al_4C_3 react to form hydrocarbons. This tendency of TiC and ZrC to form Co and CO_2 is attributed to the somewhat positive nature of the carbon atom resulting from the strong attraction of the outer electrons of the carbon by the d orbitals of Ti and Zr. A relative measure of the acceptor ability of these d orbitals is shown in reactions with fused KOH where a comparison is made with SiC in which only s and p bonding is involved; the relative amount of methane produced increases in the order TiC, ZrC, SiC. In the reaction of ZrC with aqueous HF, methane is essentially the only hydrocarbon produced, which indicates no carbon-to-carbon bonding in this compound. In contrast, Cr_3C_2 which does contain carbon-to-carbon bonds produces a mixture of hydrocarbons in similar reactions.

Results of the reaction of the nitrides in fused KOH show that BN, a covalent nitride, reacts readily to form ammonia in practically stoichiometric yield, while TiN and ZrN form nitrogen gas (N_2) as the main nitrogen species. In another experiment, by using the strong oxidizing aqueous media, hot CrO_3-H_2SO_4 solution, the ionic nitride Ca_3N_2 reacts with the quantitative formation of the ammonium ion (NH_4^+). For TiN and ZrN in the same medium, a significant quantity of N_2 is formed. This tendency of TiN and ZrN to form N_2 is indicative of a more positive nitrogen species in TiN and ZrN than is present in BN and especially Ca_3N_2. This positive nitrogen species in TiN and ZrN is believed to arise from the strong electron attraction of the available d orbitals of the parent transition metal. In several experiments under a variety of conditions, a consistent value of 1/2 is obtained for the ratio of moles of NH_4^+ formed to the moles of TiN or ZrN reacted. This phenomenon is thought to be characteristic of the nitride, although a definite explanation is not given because of insufficient data.

The chemistry of TiB_2 and ZrB_2 is typical of a metal; both diborides readily displace copper from acid solutions of cupric sulfate and react with strong acids, such as HCl, to produce hydrogen. No boron hydrides are detected in the products of the reaction of TiB_2 with HCl; however, from the reaction of ZrB_2 with HCl, trace amounts of boron hydrides may be produced.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, April 6, 1966.

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