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AND CHEMICAL BONDING IN THESE COMPOUNDS

by Warren H. Philipp

Lewis Research Center
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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 carbides, 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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Analysis of material as received</th>
<th>Actual formula based on analysis</th>
<th>Physical form and dimensions as used</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Metal, percent</td>
<td>Nonmetal, percent</td>
<td></td>
</tr>
<tr>
<td>Titanium carbide</td>
<td>TiC</td>
<td>74.60 Ti</td>
<td>17.85 C</td>
<td>TiC&lt;sub&gt;0.954&lt;/sub&gt;</td>
</tr>
<tr>
<td>Titanium nitride</td>
<td>TiN</td>
<td>78.65 Ti</td>
<td>18.60 N</td>
<td>TiN&lt;sub&gt;0.809&lt;/sub&gt;</td>
</tr>
<tr>
<td>Titanium diboride</td>
<td>TiB&lt;sub&gt;2&lt;/sub&gt;</td>
<td>66.80 Ti</td>
<td>30.49 B</td>
<td>TiB&lt;sub&gt;2&lt;/sub&gt;&lt;sub&gt;0.01&lt;/sub&gt;</td>
</tr>
<tr>
<td>Zirconium carbide</td>
<td>ZrC</td>
<td>86.98 Zr</td>
<td>10.95 C</td>
<td>ZrC&lt;sub&gt;0.956&lt;/sub&gt;</td>
</tr>
<tr>
<td>Zirconium nitride</td>
<td>ZrN</td>
<td>86.22 Zr</td>
<td>11.14 N</td>
<td>ZrN&lt;sub&gt;0.841&lt;/sub&gt;</td>
</tr>
<tr>
<td>Zirconium diboride</td>
<td>ZrB&lt;sub&gt;2&lt;/sub&gt;</td>
<td>80.37 Zr</td>
<td>18.58 B</td>
<td>ZrB&lt;sub&gt;1.95&lt;/sub&gt;</td>
</tr>
<tr>
<td>Silicon carbide</td>
<td>SiC</td>
<td>70.70 Si</td>
<td>28.67 C</td>
<td></td>
</tr>
<tr>
<td>Chromium carbide</td>
<td>Cr&lt;sub&gt;3&lt;/sub&gt;C&lt;sub&gt;2&lt;/sub&gt;</td>
<td>87.08 Cr</td>
<td>12.78 C</td>
<td></td>
</tr>
<tr>
<td>Calcium carbide</td>
<td>CaC&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Commercial grade</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aluminum carbide</td>
<td>Al&lt;sub&gt;4&lt;/sub&gt;C&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Uncompacted material</td>
<td>98 percent pure</td>
<td></td>
</tr>
<tr>
<td>Cuprous acetylde</td>
<td>Cu&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Prepared at Lewis Research Center</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium nitride</td>
<td>Ca&lt;sub&gt;3&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Commercial grade</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Boron nitride</td>
<td>BN</td>
<td>Uncompacted material</td>
<td>90 to 95 percent pure</td>
<td></td>
</tr>
</tbody>
</table>
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 (Cr3C2), calcium carbide (CaC2), aluminum carbide (Al4C3), cuprous acetylide (Cu2C2), calcium nitride (Ca3N2), and boron nitride (BN). All samples were commercially obtained except the Cu2C2, 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 CaC2 and Ca3N2, these materials were used as supplied (lumps). Furthermore, no attempt was made compact Cu2C2 because of its explosive nature.

In general, the following reaction media were used: (1) 6M sulfuric acid (H2SO4) plus 0.5M chromic acid (CrO3); (2) 6M hydrochloric acid (HCL); (3) 1M H2SO4 plus 1M hydrogen peroxide (H2O2); and (4) fused potassium hydroxide (KOH). Occasionally, solutions containing hydrofluoric acid (HF) plus mercuric chloride (HgCl2) and 1M cupric sulfate (CuSO4) plus 0.5M H2SO4 were used. Other media used in appropriate cases were aqueous sodium hydroxide (NaOH), fluoroboric acid (HBF4) plus potassium permanganate (KMnO4), bromine (Br2) in carbon tetrachloride (CCl4), and concentrated H2SO4. Reagent grade chemicals were used without further purification.

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-
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 Cu₂C₂ contacts strong oxidizing acid media, first the Cu₂C₂ 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 TiB₂ or ZrB₂ with HCl, the gaseous products were expanded consecutively into three bulbs containing, respectively, silver nitrate (AgNO₃), HgCl₂, and freshly precipitated mercuric oxide (HgO). The boron hydrides should reduce these compounds, as indicated by darkening of their color be-
cause of the formation of free metal. For one set of experiments (ZrB₂ + 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 (K₂Cr₂O₇) 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 hydro-
scopic 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 inter-
fERENCE 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 am-
monia (NH₃) 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 (H₂),
nitrogen (N₂), oxygen (O₂), carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄), acetylene (C₂H₂), 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 (NH₄⁺, 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 (CO₃⁻²), chemically bound potassium oxide (K₂O), the mercurous ion (Hg⁺²), the trivalent chromium ion (Cr³⁺), 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 (BaCO₃) by addition of barium hydroxide (Ba(OH)₂) to the extract. Correction was made for (CO₃⁻²) originally present in KOH.

The K₂O bound in the complexes TiO₂ · xK₂O and ZrO₂ · xK₂O, was determined by redissolving the alcohol-insoluble material in hot dilute H₂SO₄, 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 H₂SO₄, ignited, and weighed as potassium sulfate (K₂SO₄).

The Hg⁺ ion as mercurous chloride (Hg₂Cl₂) formed in the reaction medium, HF plus HgCl₂, was determined by filtering, drying at 100°C, and weighing. Before Ti could be determined in the solution, the unreacted HgCl₂ was removed by reduction to Hg₂Cl₂ in weakly acid solution by using the stoichiometric amount of stannous chloride (SnCl₂) and subsequent removal of the Hg₂Cl₂ by filtration. The Ti could then be determined by the standard method.

In reactions of carbides and nitrides with CrO₃ solutions, the amount of CrO₃ reduced to Cr⁺³ was determined by double precipitation of chromic hydroxide with ammonium hydroxide. The filtered hydroxide was then oxidized to chromate (CrO₄⁻²) with alkaline H₂O₂ followed by titration. In all redox titrations, the dichromate (Cr₂O₇⁻²) - 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 pri-
mary 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 CuSO₄. With regard to nonaqueous reactants, no reaction occurs with a solution of Br₂ in CCl₄; however, all three carbides are attacked by molten KOH, even in the absence of O₂.

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 CrO₃ solutions as well as H₂O₂ solutions. The X-ray diffraction pattern of such residues is that of TiC. The amount (milliequivalents) of reduction product (Cr⁺³ for CrO₃ medium and H₂ for KOH medium) is given in column 7. Because of the extensive decomposition of the H₂O₂ 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 O₂ 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 CO₃⁻² 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 CrO₃ may be represented by the following chemical equations:
### TABLE II. CHEMICAL REACTIONS OF CARBIDES

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reaction medium</th>
<th>Temperature, °C</th>
<th>Time, h</th>
<th>Weight loss, g</th>
<th>Metal (Ti, Zr, or Si) found in solution, millimoles</th>
<th>Amount of reduction product (Cr^{3+} or H_2) milliequivalents</th>
<th>Apparent valence change of carbide</th>
<th>( [\text{CO}_3]^{-2} ) in medium after reaction, millimoles</th>
<th>Gaseous products, mole percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC_{0.954}</td>
<td>6M H_2SO_4 + 0.5M CrO_3</td>
<td>100</td>
<td>6</td>
<td>2.3613</td>
<td>24.5</td>
<td>178</td>
<td>7.27</td>
<td>---</td>
<td>21.7</td>
</tr>
<tr>
<td></td>
<td>1M H_2SO_4 + 1M H_2O_2</td>
<td>23</td>
<td>2.1043</td>
<td>21.8</td>
<td>161</td>
<td>7.39</td>
<td>---</td>
<td>3.8</td>
<td>59.9</td>
</tr>
<tr>
<td></td>
<td>KOH</td>
<td>500</td>
<td>3</td>
<td>1.4005</td>
<td>21.2</td>
<td>135</td>
<td>6.37</td>
<td>22</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>6M HCl</td>
<td>100</td>
<td>20</td>
<td>Very slight reaction</td>
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</tr>
<tr>
<td></td>
<td>4M NaOH</td>
<td>100</td>
<td>20</td>
<td>No reaction</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>0.5M H_2SO_4 + 1M CaSO_4</td>
<td>23</td>
<td>200</td>
<td>No reaction</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>Br_2 in CCl_4</td>
<td>23</td>
<td>200</td>
<td>No reaction</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>ZrC_{0.956}</td>
<td>6M H_2SO_4 + 0.5M CrO_3</td>
<td>100</td>
<td>49</td>
<td>2.1573</td>
<td>21.8</td>
<td>161</td>
<td>7.39</td>
<td>---</td>
<td>3.8</td>
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<tr>
<td></td>
<td>1M H_2SO_4 + 1M H_2O_2</td>
<td>23</td>
<td>192</td>
<td>0.6154</td>
<td>5.83</td>
<td>---</td>
<td>---</td>
<td>3.0</td>
<td>1.0</td>
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<tr>
<td></td>
<td>KOH</td>
<td>500</td>
<td>5</td>
<td>9.571</td>
<td>9.91</td>
<td>58.6</td>
<td>5.91</td>
<td>9</td>
<td>.07</td>
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<tr>
<td></td>
<td>1M HF</td>
<td>100</td>
<td>46</td>
<td>0.7222</td>
<td>7.07</td>
<td>---</td>
<td>---</td>
<td>.035</td>
<td>91.7</td>
</tr>
<tr>
<td></td>
<td>6M HCl</td>
<td>100</td>
<td>40</td>
<td>Very slight reaction</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>4M NaOH</td>
<td>100</td>
<td>20</td>
<td>No reaction</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>0.5M H_2SO_4 + 1M CaSO_4</td>
<td>23</td>
<td>200</td>
<td>No reaction</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>Br_2 in CCl_4</td>
<td>23</td>
<td>200</td>
<td>No reaction</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>SiC</td>
<td>6M H_2SO_4 + 0.5M CrO_3</td>
<td>100</td>
<td>40</td>
<td>No reaction</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>KOH</td>
<td>500</td>
<td>4.25</td>
<td>1.1262</td>
<td>111</td>
<td>3.9</td>
<td>21</td>
<td>.06</td>
<td>.15</td>
</tr>
<tr>
<td></td>
<td>6M HCl</td>
<td>100</td>
<td>40</td>
<td>No reaction</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Cr_2C_2</td>
<td>10M HF</td>
<td>100</td>
<td>40</td>
<td>0.9309</td>
<td>29.2</td>
<td>55.0</td>
<td>0.9</td>
<td>0.9</td>
<td>---</td>
</tr>
<tr>
<td>CaC_2</td>
<td>6M H_2SO_4 + 0.5M CrO_3</td>
<td>100</td>
<td>1.75</td>
<td>2.8741</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>78.3</td>
</tr>
<tr>
<td></td>
<td>1M H_2SO_4 + 1M H_2O_2</td>
<td>23</td>
<td>2.25</td>
<td>1.7331</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>0.03</td>
</tr>
<tr>
<td>Al_2C_3</td>
<td>6M H_2SO_4 + 0.5M CrO_3</td>
<td>100</td>
<td>---</td>
<td>Very rapid reaction</td>
<td>(c)</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>1M H_2SO_4 + 1M H_2O_2</td>
<td>23</td>
<td>3.25</td>
<td>1.4745</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>0.25</td>
</tr>
<tr>
<td>Cu_2C_2</td>
<td>2M H_2SO_4 + 0.15M CrO_3</td>
<td>100</td>
<td>20</td>
<td>2.1043</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>1M H_2SO_4 + 1M H_2O_2</td>
<td>23</td>
<td>120</td>
<td>1.2651</td>
<td>---</td>
<td>(d)</td>
<td>1.6</td>
<td>2.9</td>
<td>89.8</td>
</tr>
</tbody>
</table>

*Intense yellow color of peroxytitanic acid.
**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.*

*Green color of Cr^{4+} observed.
*Small amount of amorphous carbon was formed.
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 occurrence of unknown side reactions.

In experiments using acidic H\(_2\)O\(_2\), 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\(_2\)CO\(_3\)) (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\(_2\)O and ZrO\(_2\) \( \cdot \) xK\(_2\)O. Thus, the two important reactions appear to be

\[
\text{MC} + 8\text{KOH} - \text{MO} \cdot x\text{K}_2\text{O} + \text{K}_2\text{CO}_3 + 4\text{H}_2 + (3 - x) \text{K}_2\text{O} \quad (3)
\]

\[
\text{MC} + 4\text{KOH} - \text{MO} \cdot x\text{K}_2\text{O} + \text{CH}_4 + (2 - x) \text{K}_2\text{O} \quad (4)
\]

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 → ZrF$_6^{2-}$ + CH$_4$ + 2H$^+$

(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$^\circ$ 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$^\circ$ C. TiN is slightly attacked by concentrated H$_2$SO$_4$ at 100$^\circ$ 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$_2$SO$_4$ plus 0.5M CrO$_3$, 1M H$_2$SO$_4$ plus 1M H$_2$O$_2$, 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$_3$N$_2$ 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:

$$6\text{MN} + 8\text{CrO}_3 + 36\text{H}^+ \rightarrow 6\text{MO}^{2+} + 8\text{Cr}^{3+} + 3\text{N}_2 + 18\text{H}_2\text{O}$$

(6)

$$3\text{MN} + \text{CrO}_3 + 12\text{H}^+ \rightarrow 3\text{MO}^{2+} + \text{Cr}^{3+} + 3\text{NH}_4^+$$

(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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reaction medium</th>
<th>Temperature, °C</th>
<th>Time, h</th>
<th>Weight loss, g</th>
<th>Metal (Ti, Zr, B) found in solution, milli-moles</th>
<th>Amount of reaction product (CrO\textsuperscript{2+} or Hg\textsuperscript{2+}), milli-equivalents</th>
<th>Apparent valence change of nitride</th>
<th>NH\textsubscript{4}\textsuperscript{+} in solution or HCl trap, milli-moles</th>
<th>N as NH\textsubscript{4}\textsuperscript{+} percent of total N</th>
<th>Molar ratio of NH\textsubscript{4}\textsuperscript{+} to reacted metal</th>
<th>N\textsubscript{2}</th>
<th>H\textsubscript{2}</th>
<th>O\textsubscript{2}</th>
<th>CO\textsubscript{2}</th>
<th>CH\textsubscript{4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN\textsubscript{0.809}</td>
<td>6M H\textsubscript{2}SO\textsubscript{4} + 0.5M CrO\textsubscript{3}</td>
<td>100</td>
<td>110</td>
<td>0.3484</td>
<td>5.69</td>
<td>14.8</td>
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<td>2.80</td>
<td>60.9</td>
<td>0.492</td>
<td>44</td>
<td>96.4</td>
<td>0.2</td>
<td>2.8</td>
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</tr>
<tr>
<td></td>
<td>2M H\textsubscript{2}SO\textsubscript{4} + 0.5M CrO\textsubscript{3}</td>
<td>100</td>
<td>100</td>
<td>0.3119</td>
<td>5.11</td>
<td>---</td>
<td>2.55</td>
<td>61.7</td>
<td>0.499</td>
<td>---</td>
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</tr>
<tr>
<td></td>
<td>1M H\textsubscript{2}SO\textsubscript{4} + 1M H\textsubscript{2}O\textsubscript{2}</td>
<td>23</td>
<td>1300</td>
<td>0.3202</td>
<td>5.22</td>
<td>(a)</td>
<td>---</td>
<td>3.83</td>
<td>90.8</td>
<td>0.734</td>
<td>&gt;10</td>
<td>1.9</td>
<td>2</td>
<td>0.6</td>
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</tr>
<tr>
<td></td>
<td>1M H\textsubscript{2}SO\textsubscript{4} + 1M H\textsubscript{2}O\textsubscript{2}</td>
<td>100</td>
<td>47</td>
<td>0.8000</td>
<td>13.13</td>
<td>(a)</td>
<td>---</td>
<td>10.18</td>
<td>95.7</td>
<td>0.774</td>
<td>---</td>
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</tr>
<tr>
<td></td>
<td>10M HF + 0.3M H\textsubscript{2}SO\textsubscript{4}</td>
<td>100</td>
<td>96</td>
<td>2.9370</td>
<td>49.1</td>
<td>34.7</td>
<td>0.7</td>
<td>41.0</td>
<td>100</td>
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<tr>
<td></td>
<td>6M HCl</td>
<td>100</td>
<td>50</td>
<td>No reaction</td>
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<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
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</tr>
<tr>
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<td>10M HF</td>
<td>100</td>
<td>50</td>
<td>Very slight reaction</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
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<td>---</td>
<td>---</td>
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</tr>
<tr>
<td></td>
<td>Aqueous HBF\textsubscript{4} + KMnO\textsubscript{4} Concentrated H\textsubscript{2}SO\textsubscript{4}</td>
<td>100</td>
<td>50</td>
<td>No reaction</td>
<td>---</td>
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<td>---</td>
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<td>---</td>
</tr>
<tr>
<td></td>
<td>1M CuSO\textsubscript{4} + 0.5M H\textsubscript{2}SO\textsubscript{4}</td>
<td>23</td>
<td>100</td>
<td>No reaction</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
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</tr>
<tr>
<td></td>
<td>KOH</td>
<td>500</td>
<td>7</td>
<td>1.1222</td>
<td>18.5</td>
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<td>---</td>
<td>5.50</td>
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<td>66</td>
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<td>KOH</td>
<td>400</td>
<td>12</td>
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</tr>
<tr>
<td></td>
<td>KOH</td>
<td>6M NaOH</td>
<td>100</td>
<td>20</td>
<td>No reaction</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
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<td>---</td>
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</tr>
<tr>
<td>ZrN\textsubscript{0.841}</td>
<td>6M H\textsubscript{2}SO\textsubscript{4} + 0.5M CrO\textsubscript{3}</td>
<td>100</td>
<td>50</td>
<td>0.9857</td>
<td>9.50</td>
<td>24.2</td>
<td>2.55</td>
<td>5.04</td>
<td>63.0</td>
<td>0.550</td>
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<td>(b)</td>
<td>---</td>
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<tr>
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<td>1M H\textsubscript{2}SO\textsubscript{4} + 1M H\textsubscript{2}O\textsubscript{2}</td>
<td>23</td>
<td>1500</td>
<td>0.1175</td>
<td>1.16</td>
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<td>---</td>
<td>0.450</td>
<td>46.0</td>
<td>0.387</td>
<td>---</td>
<td>8.6</td>
<td>0.2</td>
<td>91.0</td>
<td>0.1</td>
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<tr>
<td></td>
<td>1M H\textsubscript{2}SO\textsubscript{4} + 1M H\textsubscript{2}O\textsubscript{2}</td>
<td>100</td>
<td>40</td>
<td>0.1127</td>
<td>1.07</td>
<td>---</td>
<td>---</td>
<td>0.450</td>
<td>60.2</td>
<td>0.507</td>
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<tr>
<td></td>
<td>6M HCl</td>
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<td>28</td>
<td>1.7860</td>
<td>16.49</td>
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<td>13.82</td>
<td>99.6</td>
<td>0.638</td>
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<td>0.9</td>
<td>94.7</td>
<td>0.4</td>
<td>1.38</td>
</tr>
<tr>
<td></td>
<td>1M CuSO\textsubscript{4} + 0.5M H\textsubscript{2}SO\textsubscript{4}</td>
<td>23</td>
<td>100</td>
<td>Very slight reaction</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
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<tr>
<td></td>
<td>KOH</td>
<td>500</td>
<td>5</td>
<td>0.1798</td>
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<td>---</td>
<td>0.464</td>
<td>31.5</td>
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<td>(b)</td>
<td>---</td>
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</tr>
<tr>
<td></td>
<td>KOH</td>
<td>400</td>
<td>7</td>
<td>Slight reaction</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
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</tr>
<tr>
<td></td>
<td>4M NaOH</td>
<td>100</td>
<td>20</td>
<td>No reaction</td>
<td>---</td>
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<td>---</td>
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<td>---</td>
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</tr>
<tr>
<td>BN</td>
<td>KOH</td>
<td>500</td>
<td>4</td>
<td>1.6956</td>
<td>59.3</td>
<td>---</td>
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<td>57.0</td>
<td>99.7</td>
<td>0.961</td>
<td>---</td>
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</tr>
<tr>
<td>Ca\textsubscript{2}N\textsubscript{2}</td>
<td>6M H\textsubscript{2}SO\textsubscript{4} + 0.5M CrO\textsubscript{3}</td>
<td>100</td>
<td>10</td>
<td>1.5827</td>
<td>---</td>
<td>---</td>
<td>17.5</td>
<td>99.1</td>
<td>---</td>
<td>---</td>
<td>---</td>
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</tr>
</tbody>
</table>

\textsuperscript{a}Intense yellow color of peroxotitanic acid was noted in all reactions involving TiN and solutions containing H\textsubscript{2}O\textsubscript{2}.

\textsuperscript{b}Mass-spectrographic analysis showed the presence of N\textsubscript{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$_2$O$_2$. 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$_2$SO$_4$ plus H$_2$O$_2$, the NH$_4^+$ forming reaction at 100$^\circ$C accounts
for only about 3/5 of the reaction products. The same reaction carried out at a lower
temperature, 23$^\circ$C, gave a somewhat lower yield, 46 percent of NH$_4^+$. Again, the re-
fractory materials catalyze the decomposition of H$_2$O$_2$, as indicated by the high concen-
tration of O$_2$ in the gas; furthermore, the color of peroxytitanic acid is observable for
TiN even at 100$^\circ$C.

The reaction of TiN in HF plus HgCl$_2$ results in an essentially quantitative conver-
sion (column 10) of the N to NH$_4^+$ according to the equation

$$2\text{TiN} + 2\text{Hg}^{+2} + 12\text{F}^- + 8\text{H}^+ + 2\text{Cl}^- \rightarrow 2\text{TiF}_6^{2-} + 2\text{NH}_4^+ + \text{Hg}_2\text{Cl}_2$$

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

$$2\text{TiN} + 12\text{HF} \rightarrow 2\text{H}^+ + 2\text{TiF}_6^{2-} + 2\text{NH}_4^+ + \text{H}_2$$

Titanium nitride appears to be considerably more reactive than ZrN in fused KOH. At
400$^\circ$C there is some attack of the TiN by fused KOH, but with ZrN under these con-
ditions 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$_2 \cdot x$K$_2$O and ZrO$_2 \cdot x$K$_2$O,
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,

$$2\text{MN} + 8\text{KOH} \rightarrow 2\text{MO}_2 \cdot x\text{K}_2\text{O} + \text{N}_2 + 4\text{H}_2 + (4 - x) \text{K}_2\text{O} \quad (10)$$

$$2\text{MN} + 8\text{KOH} \rightarrow 2\text{MO}_2 \cdot x\text{K}_2\text{O} + 2\text{NH}_3 + \text{H}_2 + (4 - x) \text{K}_2\text{O} \quad (11)$$

From the data in column 10 it is evident that equation (10) represents the major contri-
bution 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 (B₂O₃). Ca₃N₂ is rapidly hydrolysed by acid solutions; however, in 6M H₂SO₄ plus 0.5M CrO₃ this hydrolysis is slow enough, probably because of the formation of insoluble calcium sulfate (CaSO₄) 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, TiB₂ and ZrB₂ reduce metal salt solutions such as CuSO₄ to the corresponding free metal. Both of the diborides, when exposed to an acidified CuSO₄ solution at 25° 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 TiB₂ and ZrB₂. The table designations are similar to those described for tables II and III. The action of HCl on TiB₂ 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 TiB₂ reactions either mass spectrometrically or by reduction of AgNO₃. In the reaction of ZrB₂ with HCl, small amounts of boron hydrides may be produced; the gaseous reaction products caused a slight blackening of AgNO₃, but there appeared to be no reduction of HgCl₂ 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 (B₂H₆) (ref. 5, p. 1). When the reaction flask containing the ZrB₂ 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, CaC₂ (composed of acetylide (C₂⁻²) ions), and a
<table>
<thead>
<tr>
<th>Compound</th>
<th>Reaction medium</th>
<th>Temperature, °C</th>
<th>Time, h</th>
<th>Weight loss, g</th>
<th>Analysis (Ti or Zr) in solution, millimoles</th>
<th>Ti$^3+$ in solution, millimoles</th>
<th>B in gaseous products, millimoles</th>
<th>Reducing species in gaseous products found by bubbling through dichromate, milliequivalents</th>
<th>Gas analysis, mole percent</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiB$_2$.01</td>
<td>6M HCl</td>
<td>100</td>
<td>8.25</td>
<td>0.3450</td>
<td>4.57</td>
<td>9.12</td>
<td>3.48</td>
<td>----</td>
<td>----</td>
<td>99.1</td>
</tr>
<tr>
<td></td>
<td>1M H$_2$SO$_4$</td>
<td>23</td>
<td>6.25</td>
<td>3.0385</td>
<td>41.0</td>
<td>83.7</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>1M CuSO$_4$</td>
<td>23</td>
<td>100</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
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<tr>
<td></td>
<td>0.5M H$_2$SO$_4$</td>
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<tr>
<td>ZrB$_1$.95</td>
<td>6M HCl</td>
<td>100</td>
<td>----</td>
<td>----</td>
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<td>----</td>
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<td>99.1</td>
<td>0.69</td>
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<tr>
<td></td>
<td>$^a$6M HCl</td>
<td>100</td>
<td>17</td>
<td>2.5435</td>
<td>22.41</td>
<td>41.24</td>
<td>----</td>
<td>3.47</td>
<td>0.083</td>
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</tr>
<tr>
<td></td>
<td>$^a$1M CuSO$_4$</td>
<td>23</td>
<td>100</td>
<td>----</td>
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<td></td>
<td>$^a$0.5M H$_2$SO$_4$</td>
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$^a$With continuous flow of Ar.
somewhat less ionic Cu$_2$C$_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$_2$H$_2$; moreover, Cu$_2$C$_2$ in a more diluted acid solution of CrO$_3$ yields essentially C$_2$H$_2$. Even more pronounced are the results of reactions in 1M H$_2$SO$_4$ plus 1M H$_2$O$_2$. 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$_2$C$_2$) forms C$_2$H$_2$, and C-4 (methanide ion present in Al$_4$C$_3$) 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$_2$C$_2$, which is less ionic than CaC$_2$ and thus would have less tendency to undergo hydrolysis, a small amount of the C in Cu$_2$C$_2$ in acid solutions of H$_2$O 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$_3$C$_2$ and ZrC with strong HF solution, the Cr$_3$C$_2$ 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$_3$C$_2$ 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 \( \text{CH}_4 \) formation, and conversely, positive C atoms favor CO and \( \text{CO}_2 \) formation.

On examination of the reactions of these carbides with fused KOH, it is seen that the ratio of \( \text{CH}_4 \) to \( \text{H}_2 \) 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 covalently bonded with slight ionic character of the type \( M^-\text{C}^+ \), 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 (\( \text{N}_2, \text{NH}_3, \text{NH}_4^+, \) and possibly hydrazine) is feasible.

Ionic nitrides, such as \( \text{Ca}_3\text{N}_2 \), which contain the nitrogen minus 3 ion (\( N^{-3} \)) are hydrolyzed in acid solution to \( \text{NH}_4^+ \) (ref. 8, p. 578). The results in table III show that, even under strong oxidizing, hot acid solutions of \( \text{CrO}_3 \), no oxidation of \( N^{-3} \) is observed, the formation of \( \text{NH}_4^+ \) being practically quantitative. Also, quantitative formation of \( \text{NH}_4^+ \) is observed on reaction of \( \text{Ca}_3\text{N}_2 \) with acid solutions of \( \text{H}_2\text{O}_2 \) and \( \text{KMnO}_4 \) (ref. 9); however, under similar circumstances, especially in acid solutions of \( \text{CrO}_3 \), significant amounts of \( \text{N}_2 \) 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 NH₃ or NH₄⁺ formation. The order of increasing negativity of the N in the four nitrides used experimentally is TiN, ZrN, BN, and Ca₃N₂; thus, the tendency to form NH₃ or NH₄⁺ should increase in that order.

The greater tendency of NH₃ 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 NH₃ almost quantitatively; whereas, with TiN and ZrN under these conditions most of the N is liberated as N₂. For TiN even at a relatively low temperature, 400°C (which minimizes thermal decomposition of any NH₃ formed), the yield of NH₃ is small. Because of the great stability of NH₄⁺ in acid media, reactions of ZrN in nonoxidizing acids (HCl) yield NH₄⁺ quantitatively. Although TiN is not appreciably attacked by HF or HCl alone, it reacts with aqueous HF plus Hg²⁺ to form NH₄⁺ quantitatively. It is proposed that the oxidizing action of Hg²⁺ merely converts the Ti⁺³ intermediate to TiF₆⁻².

In experiments of TiN and ZrN in H₂SO₄ plus CrO₃ solutions and of ZrN in hot 1M H₂SO₄ plus H₂O₂, there is a consistency of results which was reproducible in several independent runs. In these about 60 percent of the total N formed NH₄⁺ (column 10, table III), while the remaining 40 percent was evolved as N₂. 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 NH₄⁺ formed to the Ti or Zr found in solution (column 11, table III). In other words, the reaction of 1 mole of TiN₀.₈₀₉ or ZrN₀.₈₄₁ yields 1/2 mole of NH₄⁺, 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 TiB₂ and ZrB₂ readily displace H⁺ from strong acids, the TiB₂ forming Ti⁺³ as does metallic Ti under similar conditions. In addition, the metallic properties of TiB₂ and ZrB₂ are shown by the replacement of the cupric ion (Cu⁺²) from solution to form Cu.

Unlike Mg₃B₂, 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), TiB₂ produces no boron hydrides and ZrB₂ produces only small amounts on treatment with aqueous HCl. If the formation of boron hydrides is due to the hydrolysis of B⁻³ ions, TiB₂ and ZrB₂ are not ionic in the sense that magnesium bromide (Mg₃B₂) is.
The diborides do not have a simple interstitial structure. In TiB₂ and ZrB₂ 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 TiB₂ and ZrB₂ 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 (CrO₃), hydrochloric acid (HCl), acidified hydrogen peroxide (H₂O₂), 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 (Cr₃C₂), calcium carbide (CaC₂), aluminum carbide (Al₄C₃), cuprous acetylide (Cu₂C₂), calcium nitride (Ca₃N₂), 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 H₂O₂ containing sulfuric acid (H₂SO₄), TiC and ZrC react to form carbon monoxide (CO) and carbon dioxide (CO₂); whereas, under similar conditions, other carbides such as CaC₂ and Al₄C₃ react to form hydrocarbons. This tendency of TiC and ZrC to form CO and CO₂ 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, Cr₃C₂ 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\textsubscript{2}) as the main nitrogen species. In another experiment, by using the strong oxidizing aqueous media, hot CrO\textsubscript{3}-H\textsubscript{2}SO\textsubscript{4} solution, the ionic nitride Ca\textsubscript{3}N\textsubscript{2} reacts with the quantitative formation of the ammonium ion (NH\textsubscript{4}\textsuperscript{+}). For TiN and ZrN in the same medium, a significant quantity of N\textsubscript{2} is formed. This tendency of TiN and ZrN to form N\textsubscript{2} is indicative of a more positive nitrogen species in TiN and ZrN than is present in BN and especially Ca\textsubscript{3}N\textsubscript{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\textsubscript{4}\textsuperscript{+} 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\textsubscript{2} and ZrB\textsubscript{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\textsubscript{2} with HCl; however, from the reaction of ZrB\textsubscript{2} with HCl, trace amounts of boron hydrides may be produced.

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

REFERENCES


"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

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