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ELECTROCHEMICAL OXIDATION OF TITANIUM DIBORIDE

by Warren Philipp

Lewis Research Center

Cleveland, Ohio

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SUMMARY

Titanium diboride was anodically dissolved in various electrolytes including hydrochloric acid, perchloric acid, sodium perchlorate, and buffered acetate solution. When not passive, the titanium diboride dissolved stoichiometrically, that is, in a boron to titanium ratio of 2. The boron and titanium were found in solution in the +3 and +4 oxidation states, respectively. Only for the hydrochloric acid electrolyte was the expected current yield of 10 faradays per mole of dissolved TiB_2 observed; for aqueous sulfuric acid, perchloric acid, and sodium perchlorate, this number of faradays was somewhat less. This deficiency in the number of faradays was most prevalent in runs involving relatively strong perchloric acid solutions at high current densities. For perchloric acid, this deficiency was attributed to chemical oxidation of the TiB_2 by the high concentration of perchlorate at the anode surface. Based on a comparison of the properties of titanium diboride with the already known properties of the other borides, it was concluded that titanium diboride reacts more like an interstitial (metallic) compound than an ionic one.

INTRODUCTION

In the search for high-temperature materials, the refractory nitrides, carbides, and borides have been studied extensively. Little appears in the literature, however, concerning the aqueous chemistry of these compounds. This report deals with the anodic dissolution of titanium diboride (TiB_2) and is an extension of earlier work on the anodic oxidation of titanium nitride (TiN) (refs. 1 and 2). The purpose of these anodic oxidation experiments is to provide further insight as to the metallic nature of these refractories.

In previous papers (refs. 1 and 2), it has been shown that, in dilute $HClO_4$ electrolyte, TiN is anodically oxidized to titanyl ion (TiO^{++}) and nitrogen (N_2). This required 4 faradays of applied current per mole of TiN oxidized. Based on a comparison with an ionic nitride, calcium nitride (Ca_3N_2), in which the nitrogen (N) is converted to ammonium ion (NH_4^+) by acid solutions even in the presence of strong oxidizing agents, it was concluded that TiN does not act chemically as an ionic nitride. Only negligible amounts of NH_4^+ were produced during the anodic dissolution of TiN in acid electrolytes.

The borides differ from the nitrides and carbides in that most of them

have metallic properties regardless of the metal from which they are derived. Thus, it is assumed that these borides are interstitial materials (ref. 3, p. 769). The M_3B_2 borides such as magnesium boride (Mg_3B_2) may be exceptions. Mg_3B_2 reacts with acids to form boron hydrides and hydrogen (H_2), whereas borides of other types are essentially inert. It is thought that Mg_3B_2 is ionic in that it may contain B^{-3} groups (ref. 3, p. 771). Through a comparison of the properties of TiB_2 with the properties of Mg_3B_2, which are already known, the nature of the bonding in TiB_2 can be further understood.

EPXERIMENTAL PROCEDURE

The apparatus (fig. 1) and the general method were essentially the same as those that had been used previously (refs. 1 and 2). The anode consisted of a smooth-surfaced TiB_2 block, 1.5 by 1.5 by 0.8 centimeter, mounted in a polymerized methyl methacrylate holder in such a way that only one side of the block made electrical contact with the anolyte. (Analysis of a representative sample of TiB_2 showed the material to contain 67.88 percent Ti and 30.68 percent B corresponding to a Ti:B mole ratio of 1:2.007.) This holder was then cemented to a polymerized methyl methacrylate rod, which was sealed to the cell proper by means of a standard taper joint. A platinum-foil cathode was contained in a separate compartment. A stable direct-current supply was furnished by a rectifier in parallel with a storage battery. The number of coulombs was determined with an integrating recorder. To minimize the effect of temperature on the results, all the experiments were carried out at a constant temperature of 22° C. At the end of each experiment, the electrolyte was analyzed for total titanium (Ti) (ref. 4) and total boron (B) (ref. 5) and in some cases for reduced ClO_4^- and the lower oxidation states of Ti and B. (To determine the amount of reduced ClO_4^-, an aliquot of the spent electrolyte was treated with ferrous sulfate ($FeSO_4$), and the chloride ion (Cl^-) formed was determined as silver chloride (AgCl). The lower oxidation states of Ti and B were determined by titration with potassium permanganate ($KMnO_4$).) The volume of the gas evolved was measured in a gas buret, and its composition was determined by means of a mass spectrometer. In preliminary experiments, it was discovered that the anode gas consisted mainly of oxygen (O_2). In order to provide an accurate measure of the volume of O_2 evolved, by ensuring that no O_2 would be

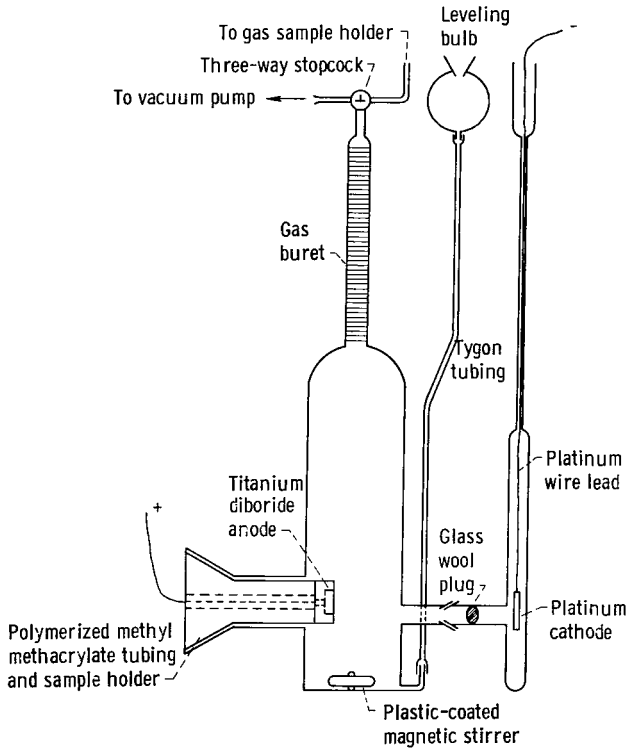

Figure 1. - Apparatus (made of heat-resistant glass except where otherwise specified).

lost because of solubility in the electrolyte, the electrolyte was saturated with O_2 prior to each run.

For most experiments, $HClO_4$ solutions were used as electrolytes because of the stability of ClO_4^- to anodic oxidation; however, to provide further information as to the behavior of the TiB_2 anode, solutions of $NaClO_4$, H_2SO_4, HCl, and sodium hydroxide (NaOH), as well as a mixture of acetic acid (CH_3COOH) and sodium acetate (CH_3COONa), were also used as electrolytes. The total number of coulombs passed in a single experiment ranged from about 4100 to 4500, while the current densities ranged from 6 to 200 milliamperes per square centimeter. The dissolution of TiB_2 in the acid electrolytes was small but not negligible; therefore, it was necessary to run a blank. This was accomplished by observing the loss in weight of the TiB_2 block upon exposing a surface to the electrolyte for a specified time.

In order to identify corrosion products remaining on the corroded TiB_2 surface, X-ray diffraction patterns were taken of this surface. X-ray diffraction patterns were also taken of small amounts of insoluble material found in the electrolyte as a result of slight disintegration of the TiB_2 anode.

RESULTS AND DISCUSSION

The results of the electrochemical oxidation experiments for TiB_2 are shown in table I. Except for the one experiment with 3-molar $HClO_4$ at a current density of 200 milliamperes per square centimeter, the data shown in the table represent an average of two runs for each condition. Column (c) lists the amount of current (coulombs) actually passed for each condition. Column (d) gives the amount of O_2 evolved as calculated from the temperature, the composition, and the total volume of the gas collected in the buret. Col-

TABLE I. - ELECTROCHEMICAL OXIDATION OF TITANIUM DIBORIDE

(a) Electrolyte	(b) Current density, ma/sq cm	(c) Current, coulombs	(d) O_2 evolved, millimoles	(e) Ti in solution, millimoles	(f) B in solution, millimoles	(g) Ratio of B to Ti in solution	(h) TiB_2 in blank,[a] millimoles	(i) Current required for O_2 evolution, percent	(j) Number of electrons per molecule of TiB_2	(k) Total reduced ClO_4^-, millimoles
1 M HCl	10	4324	0.04	4.62	9.18	1.99	0.14	0.35	10.0	----
0.5 M $HClO_4$	6	4083	1.39	4.01	8.23	2.05	0.23	13.2	9.55	----
	10	4214	.94	5.16	10.06	1.95	.12	8.6	8.06	----
1 M $HClO_4$	10	4238	0.70	5.58	11.12	1.99	0.15	6.4	7.59	----
	50	4127	.47	5.42	11.06	2.04	.028	4.4	7.48	----
	100	4332	.36	5.82	11.69	2.01	.010	3.2	7.46	----
3 M $HClO_4$	10	4346	0.46	5.87	11.40	1.94	0.12	4.1	7.66	----
	200	4493	.15	6.86	13.27	1.93	.007	1.3	6.86	4.10
1 M $NaClO_4$	6	4178	1.18	[b]4.14	8.38	[b]2.02	0	10.9	9.25	----
1.5 M H_2SO_4	10	4256	0.27	4.98	9.81	1.97	0.14	2.4	8.98	----
1.5 M CH_3COOH / 1.5 M CH_3COONa	0.5	888	1.27	----	----	----	---	55.2	----	----

[a]TiB_2 dissolved in electrolyte in same time without current.
[b]In this case, reacted Ti was found in a precipitate.

umns (e) and (f) give the amount of Ti and B in the electrolyte after the termination of the run, where the Ti in solution is in the +4 oxidation state and the B appears as boric acid. Column (g) gives the ratio of the amounts of B to Ti found in the electrolyte; in all cases this ratio is about 2. The amount of TiB_2 that dissolves in the electrolyte under the same conditions as used in the experiment with the exception of the passage of current is listed in column (h). The percentage of the current (column (c)) required to form the indicated quantity of O_2 (column (d)) from the decomposition of water is given in column (i). Finally, the number of electrons per molecule of TiB_2 (column (j)) can be calculated.

$$(j) = \frac{\frac{10^3(c)}{F} - 4(d)}{\frac{(e)}{3} + \frac{(f)}{3} - (h)}$$

where F is the faraday constant and each letter in parenthesis represents the value listed in the column designated by that letter for the run being calculated. In one experiment, the total reduced ClO_4^- was determined (column (k)).

The anodic oxidation of TiB_2 to form Ti in the +4 oxidation state and B in the +3 state, as was determined experimentally, requires the use of 10 faradays per mole of TiB_2 oxidized according to the equation

$$TiB_2 + 7H_2O = 2H_3BO_3 + 8H^+ + TiO^{++} + 10e$$

In experiments with HCl as the electrolyte, this electrical requirement was satisfied; moreover, the ratio of B to Ti of corrosion products in solution was 2. In view of this, it appears that, in HCl, the total reaction to form B and Ti in the +3 and +4 oxidation states, respectively, is one of electron transfer from the TiB_2 molecule to the electrode proper. In this experiment, the small amount of gas evolved contained mainly O_2. A low concentration of H_2 (about 0.5 percent by volume) was found, but no boron hydrides could be detected. It is reasonable that this small amount of H_2 came from the solution in the cathode compartment. Based on the results, it appears that the chemistry of TiB_2 bears little resemblance to that of Mg_3B_2, which is thought to be ionic (ref. 3, p. 771). The hydrolysis of Mg_3B_2 in HCl produces a variety of products including boron hydrides and H_2(ref. 6). It is felt that, if TiB_2 contained boride ions similar to those in Mg_3B_2, there would be a side reaction of boride ions to produce boron hydrides or at least decomposition products of these hydrides detectable in the form of a significant amount of H_2. In HCl electrolyte such a hydrolysis reaction would result in a number less than 10 for the number of faradays involved in the dissolution of a mole of TiB_2.

In experiments with acid electrolytes, HCl, $HClO_4$ and H_2SO_4, examination by X-ray diffraction of the corroded anode surface and small quantities of insoluble residue (formed by disintegration of the anode) found in the electrolyte showed the presence of no substance other than TiB_2.

In all runs, only small amounts of H_2(about 0.5 percent by volume) were detected in the gas evolved at the anode. Based on these results, it is surmised that the electrochemical reaction does not involve the preferential dissolution of either B or Ti by the applied current followed by dissolution of the remaining species Ti, B, or titanium monoboride (TiB) through chemical action of the electrolyte. It is unlikely, therefore, that a reaction involving the reduction of H^+ by a metal is an important step in these reactions.

Unlike the experiments in HCl electrolyte, anodic dissolution of TiB_2 in $HClO_4$ and H_2SO_4 solutions involved less than 10 faradays per mole of TiB_2 dissolved, although the final oxidation states of the B and Ti were the same as in the case of HCl, namely, +3 for B and +4 for Ti. In the $HClO_4$ electrolyte this number of faradays is lowest at higher $HClO_4$ concentrations and higher current densities. Apparently, the actual mechanism for the oxidation of TiB_2 in acids containing an oxygenated anion is complex; however, a plausible explanation for this deficiency in the number of coulombs may be given that is in accord with the experimental results. In addition to the reaction involving an electron transfer to the electrode, a second purely chemical reaction could take place involving the dissolution of the TiB_2 surface (cleaned by anodic oxidation) in a high concentration of the anion because of the anode potential. In $HClO_4$, the chemical reaction would be the reduction of ClO_4^- by TiB_2 to form the lower oxidation states of chlorine (Cl). In all experiments with perchlorate electrolytes, the odor of Cl_2 was noted, and Cl^- was detected in a spent electrolyte on addition of silver nitrate ($AgNO_3$). In one run using 3-molar $HClO_4$ at a current density of 200 milliamperes per square centimeter, the amount of reduced ClO_4^- was determined quantitatively. It has been demonstrated experimentally that TiB_2 reacts with strong $HClO_4$ solutions to produce Cl_2 and Cl^-. It should be noted that, upon increasing the $HClO_4$ concentration and the current density, the O_2 producing a side reaction becomes less significant. Apparently the O_2 is produced by the decomposition of water; therefore, as the ClO_4^- concentration at the anode surface increases, the contribution of the reaction of TiB_2 with ClO_4^- becomes more prevalent at the expense of other reactions, including the one involving the decomposition of water to form O_2.

In an attempt to dissolve anodically the B in preference to Ti in TiB_2 and also to detect the formation of hypoborates and subborates, TiB_2 was anodically oxidized in weakly acid, neutral, and alkaline electrolytes. In 1-molar NaOH, TiB_2 became passive with the formation of a visible film over the surface. Even in a buffered acetate electrolyte (1.5 M CH_3COOH and 1.5 M CH_3COOHa), which has a pH of about 4.8, the TiB_2 became passive to a degree where only a small current could be passed. In this case the visible coating that formed on the TiB_2 surface occasionally exfoliated. Unfortunately, the coating did not give an X-ray diffraction pattern and, therefore, was not identifiable. Only traces of Ti and B were found in solution, these quantities being too low to report as quantitative results. During the anodic dissolution of TiB_2 in 1-molar $NaClO_4$, a white precipitate formed in the anolyte, although the anode did not become passive. This insoluble portion contained the bulk of the Ti formed from the anodic oxidation of TiB_2 and was probably $TiO_2 \cdot xH_2O$; the B was found in solution as boric acid. No hypoborates or subborates were detected and, as was the case in all electrolytes tested where the TiB_2 did not

passivate, the B to Ti ratio in the reaction products was 2.

CONCLUSIONS

The results of these experiments on the anodic dissolution of titanium diboride indicate that titanium diboride acts chemically as though it were a metallically bonded boride. Attempts to dissolve preferentially either the titanium or the boron failed. The experimental evidence suggests that the titanium diboride anodically dissolves as a unit rather than by the preferential dissolution of either titanium or boron and the remainder is left to react with the electrolyte itself.

Because of good agreement in the electrochemical yield of oxidation products with hydrochloric acid as the electrolyte, it seems that the mechanism for the dissolution of titanium diboride in that electrolyte is simply one of electron transfer from the titanium diboride to the electrode proper. In those electrolytes containing an oxygenated anion, such as perchloric acid, the scheme is more complex in that the quantity of oxidation products formed is greater than that calculated from the amount of current passed. Until more data on the aqueous chemistry of titanium diboride become available, the mechanism for this latter process cannot be definitely established.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, May 22, 1964

REFERENCES

1. Philipp, W.: Evidence of Metallic Bonding in TiN. Acta. Met., vol. 10, no. 5, May 1962, pp. 583-584.

2. Phillip, W.: Reply to Comments on "Evidence of Metallic Bonding in TiN." Acta Met., vol. 12, no. 6, June 1964, pp. 740-742.

3. Moeller, Therald: Inorganic Chemistry. John Wiley & Sons., Inc., 1955.

4. Sandell E. G.: Colorimetric Determination of Traces of Metals. Second ed., Interscience Pub., 1950, p. 572.

5. Blumenthal, Herman: Determination of Boron in Metal Borides. Analytical Chem., vol. 23, no. 7, July 1951, pp. 992-994.

6. Stock, Alfred: Hydrides of Boron and Silicon. Cornell Univ., Press, 1933, pp. 162-167.

NASA-Langley, 1964 E-2405

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