

# Reaction of Sodium with Ionic Conductors Containing P–O Bonds at Elevated Temperatures

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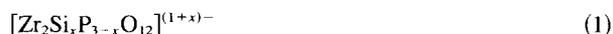
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**Sodium phosphate and a series of compounds containing Na, Zr, Si, P, and O were found to react with sodium at 380°C. The reaction products formed phosphine on hydrolysis. On the basis of these reactions and some thermodynamic calculations, it is not likely that any materials containing P–O bonds will be stable to sodium at the temperatures required for the Na-S battery or Na heat engine operation.**

## I. Introduction

SEVERAL sodium ion-conducting crystalline solids comprised of Na, Zr, Si, P, and O have been reported in the literature and suggested for use in solid electrolyte devices such as the Na-S battery. Although ionic conductivity values comparable to those of polycrystalline  $\beta''$ -Na-Al<sub>2</sub>O<sub>3</sub> (above 300°C) have been reported for some of the materials, relatively little information is available on their resistance to chemical attack. Held in common among several of the potential electrolyte applications is the requirement for resistance to attack by sodium metal. As part of a screening test to evaluate materials for use in batteries, we found that sintered membranes made of several compositions in the system Na-Zr-Si-P-O turned dark and cracked after exposure to sodium at 350° to 380°C for 10 days. On subsequent exposure to moisture, PH<sub>3</sub> was observed. In this paper, we examine the stability of compounds containing sodium, pentavalent phosphorus, and oxygen through the use of experiments which are sensitive to P–O bond breakage and through thermochemical estimation.

The presence of P<sup>(V)</sup>–O bonds is directly related to the high ionic conductivity of the Nasicon class. In one material,<sup>1,2</sup> which is typical of the class of Na-Zr-Si-P-O electrolytes, 1 + x sodium ions move through bottlenecks in a three-dimensional (rhombohedral or monoclinic) skeleton of composition:

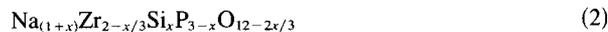


The alkali-ion mobility is enhanced by drawing the O<sup>2-</sup> polarization away by the presence of covalent bonds of two coordinations: tetrahedral in the cases of PO<sub>4</sub><sup>3-</sup> and SiO<sub>4</sub><sup>4-</sup> and octahedral in the case of transition metals with an empty *d* shell, as in the case of Zr. The highest conductivities are found for mixtures of tetrahedral complexes of different formal oxidation numbers. In such mixtures, more near-neighbor vacancies exist on the interstitial sodium sites, leading, in turn, to more successful diffusional jumps. Thus, in the skeletal formula above, the maximum conductivity corresponds to cases for which the variable *x* approaches neither 0 nor 3 in Eq. (1). Consequently, phosphorus–oxygen bonds are needed to obtain high conductivities. For example, with *x* = 2, 22.7% of the oxygen is bound to phosphorus.

For the initial formulation, with *x* = 2 in Eq. (1), evidence for chemical attack is strong. In a patent,<sup>3</sup> a statement appears: "... prolonged immersion in molten sodium showed chemical stability in the environment." In contrast, Schmid *et al.*<sup>4</sup> examined the reaction of Nasicon (of Eq. (1) series) with Na by several physical means (microscopy, X-ray diffraction (XRD), and mechanical properties) after about 2-week exposures to Na metal at 300°C. A unit cell expansion of 2.4% corresponded to extensive

cracking of the Eq. (1) composition with *x* = 2. In the absence of any current passage, a severe deterioration was observed by a physical method.

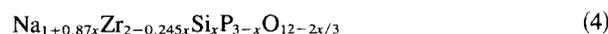
Mixtures of PO<sub>4</sub><sup>3-</sup> and SiO<sub>4</sub><sup>4-</sup> have been retained through the many compositional modifications which have been suggested to obtain single-phase electrolytes. For example, we have two iterations,<sup>5</sup> the first of which is "silica-rich" and has a formulation,



and a specific case (not exactly corresponding to any one value of the variable *x* above),



The second, "near the zirconium oxide solubility limit," is



with a specific case (again, not corresponding to any one value of *x* in Eq. (4)) of



In the two cases of Eqs. (3) and (5), phosphorus–oxygen bonds comprise 15.9 and 18.4% of the oxygen bond count, respectively.

Early reports of Na<sub>3.1</sub>Zr<sub>1.55</sub>Si<sub>2.3</sub>P<sub>0.7</sub>O<sub>11</sub> of Eq. (3) were that it was stable but with a brown layer,<sup>5</sup> whereas later the same author<sup>6</sup> stated, "... the material is at the silica-rich end of the monoclinic monophasic region in the phase diagram, therefore the material is unstable in contact with sodium at elevated temperatures (300°C)." For the more-recent Na<sub>2.94</sub>Zr<sub>1.49</sub>Si<sub>2.2</sub>P<sub>0.8</sub>O<sub>10.85</sub> composition of Eq. (5), the result of testing<sup>6</sup> at 400°C for 10 days is "... no attack was observed." No supporting details of the observation were given.

## II. Experimental Procedure

Sodium phosphate and the Na<sub>3.1</sub>Zr<sub>1.55</sub>Si<sub>2.3</sub>P<sub>0.7</sub>O<sub>11</sub> composition of Eq. (3) were prepared for tests in sodium metal.

### (1) Na<sub>3</sub>PO<sub>4</sub>

A sample of Na<sub>3</sub>PO<sub>4</sub> · 12H<sub>2</sub>O\* containing 1.7% excess Na<sub>2</sub>O was heated overnight at 400°C in air and then stored over anhydrous magnesium perchlorate. Just prior to use, 1-g samples were heated for 1 h at 400°C under vacuum.

### (2) Na<sub>3.1</sub>Zr<sub>1.55</sub>Si<sub>2.3</sub>P<sub>0.7</sub>O<sub>11</sub>

Only the preparation of the electrolyte involving the use of organometallic zirconium is presented here. A 14.43-g amount of Na<sub>2</sub>CO<sub>3</sub><sup>†</sup> (dried at 270°C, all others dried at 105°C) was added to 66.37 g Zr(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>4</sub>,<sup>‡</sup> 12.12 g SiO<sub>2</sub>,<sup>§</sup> and 7.08 g NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub><sup>¶</sup> in a polypropylene bottle. With 130 mL ethyl alcohol (EtOH) and 10 ZrO<sub>2</sub> grinding media, the precursors were shaker-milled for 10 min and roller-milled for 10 h to mix. After air-drying, the material (in a loosely covered Pt vessel) was ramped to a 600°C initial calcine (in a fume hood) in two days, cooled to ambient, and then inserted into a box furnace at 1125°C and held 16 h (final

\*No. 3836 sodium phosphate, tribasic 12-hydrate crystal, J. T. Baker, Phillipsburg, NJ.

†No. 3602 sodium carbonate, anhydrous powder, J. T. Baker.

‡No. 86133 zirconium 2,4-pentanedionate, Lot No. 042181, Alfa Products Div., Ventron Corp., Danvers, MA.

§No. 88316 silicon oxide, 99.9% (metals basis), -325 mesh, Alfa Products.

¶No. 0776 ammonium phosphate, monobasic crystal, Lot No. 750125, J. T. Baker.

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calcine). Very little fusion accompanied some shrinkage and the observation of a good white coloring. Once more (with 140 mL EtOH) the material was shaker-milled (10 min) and roller-milled (26.5 h) before drying on a hotplate to 40.0 g product (96% yield). X-ray analysis of the calcine showed no significant free  $ZrO_2$ , which had been observed in other (not organometallic) preparations. After addition of polyvinylbutyral binder, 1-cm diameter disks were die-pressed at 103 MPa and isostatically pressed to 414 MPa. On a Pt sheet open to air, the disks were burned out and presintered by heating to 900°C in 2 days. Four final sintering iterations were made: (1) 1260°C, 15.5 h; (2) 1260°C, 68 h; (3) 1270°C, 20 h; and (4) 1280°C, 17.5 h. Based on a theoretical density of 3.30 g/cm<sup>3</sup>, the densities for the sintering conditions were 2.868 g/cm<sup>3</sup> (86%), 2.80 g/cm<sup>3</sup> (85%), 2.84 g/cm<sup>3</sup> (86%), and 2.82 g/cm<sup>3</sup> (85%), respectively. No sticking of the samples to the Pt carrier was observed.

### (3) Exposure Test with Sodium Metal

Sodium phosphate powder ( $\approx 1$  g) and a disk of  $Na_{3.1}Zr_{1.55}Si_{2.3}P_{0.7}O_{11}$  from the fourth sintering were placed separately into dried glass capsules\*\* and evacuated using a rotary vacuum pump with a liquid N<sub>2</sub> cold trap and heated for 1 h at 400°C. Sodium metal<sup>††</sup> was then melted-in and each capsule sealed off. The capsules were held at 380°C for 10 to 14 days.

Residues from the metal exposure tests were dissolved in alcohol-water solutions and the evolved gases were trapped in an H<sub>2</sub>O<sub>2</sub> solution. Soluble phosphorus compounds were determined by treatment of the alcohol-water solution with H<sub>2</sub>O<sub>2</sub>, which would oxidize sodium phosphite, if that were present. The solutions were analyzed by ion chromatography.

## III. Results and Discussion

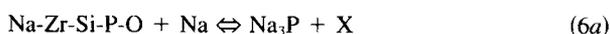
### (1) Sodium Phosphate

The mixture turned dark as a result of exposure at 380°C. When treated with a solution of alcohol and water, phosphine gas (PH<sub>3</sub>) was formed. Approximately 0.41% of the phosphorus in the starting powder was converted to PH<sub>3</sub>.

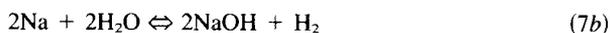
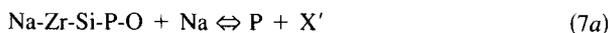
### (2) $Na_{3.1}Zr_{1.55}Si_{2.3}P_{0.7}O_{11}$

The white, smooth membranes turned black and cracked. When the capsule was opened, a pungent odor was observed. From gas analysis, 0.2% of the P was converted to PH<sub>3</sub>. Solution analysis with H<sub>2</sub>O<sub>2</sub>, which would mask any distinction between phosphate and phosphite, revealed that approximately 20% of the P of this Na-Zr-Si-P-O compound had been converted to soluble phosphorus compounds by the Na exposure.

There are two reasonable reaction sequences for the formation of phosphine from the reaction of Na-Zr-Si-P-O compounds and sodium followed by treatment with water:



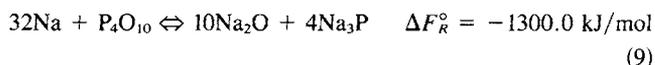
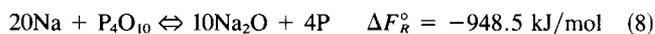
and



Although it is difficult to determine whether the PH<sub>3</sub> was formed by Eq. (6) (with Na<sub>3</sub>P) or Eq. (7) (with P) or a mixture of the two, the presence of PH<sub>3</sub> is clear evidence that P-O bonds were broken.

If only P-O bonds are considered, as in the case of phosphorus oxide, thermodynamic data indicate that the bonds could react

with Na and lead to either the P or the (more probable) Na<sub>3</sub>P reaction product.



These values for the standard free energies of reaction at 350°C were calculated from 298 K data by an extrapolation method, as follows: Values for  $\Delta H_{R,298 K}^\circ$  and  $\Delta S_{R,298 K}^\circ$  were used to obtain the standard free energy of reaction at 298 K:

$$\Delta F_{R,298 K}^\circ = \Delta H_{R,298 K}^\circ - T\Delta S_{R,298 K}^\circ \quad (10)$$

Data for Na(l), P<sub>4</sub>O<sub>10</sub>, Na<sub>2</sub>O, and P(red) are from JANAF<sup>7</sup> with units conversion 1 kcal/mol = 4.184 kJ/mol. For Na<sub>3</sub>P, we have an enthalpy of formation value<sup>8</sup> and an estimate for the entropy<sup>9</sup> of  $110.9 \pm 6.3$  J/mol·K based on the isostructural Li<sub>3</sub>N value (NBS TN 270-8) with adjustment for the greater mass of P over N and Na over Li.

The shift in equilibrium with temperature is related to the standard free energy of reaction as follows:<sup>10</sup>

$$\Delta F^\circ = -RT \ln K \quad (11)$$

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (12)$$

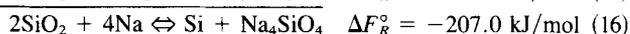
Integrating on the assumption that  $\Delta H_R^\circ$  is a constant, we obtain, after rearrangement:

$$\Delta F_2^\circ = T_2[\Delta F_1^\circ/T_1 - \Delta H_R^\circ(T_2 - T_1)/(T_2T_1)] \quad (13)$$

This formula has been used throughout this paper. A comparison of this extrapolation method with the use of tabulated values at 600 K for Eq. (8) reveals a difference of only 0.6% in the free energy of reaction value calculated.

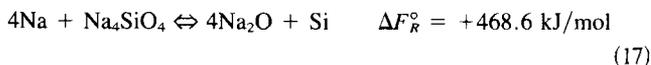
By virtue of the negative standard free energies of Eqs. (8) and (9), P-O bonds are subject to attack by sodium. However, the Na-Zr-Si-P-O compounds do not contain P-O bonds in isolation (as is the case for P<sub>4</sub>O<sub>10</sub>). The presence of other bonds in the system may well be expected to influence the stability and the reactivity of the P<sup>(V)</sup>-O bonds.

A useful analogy can be drawn between the phosphorus-oxygen and silicon-oxygen systems. It is known that some compounds containing Si<sup>(IV)</sup>-O bonds are attacked by Na. For example,



Data for Na<sub>4</sub>SiO<sub>4</sub> are from Elyard and Rawson<sup>11</sup> for the crystalline solid formed from the oxides. The other data are from JANAF.<sup>7</sup>

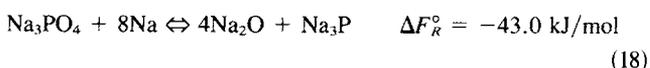
While Si-O bonds are broken and Na-O bonds are formed, the driving force of the reaction is the formation of the silicate. If Eq. (15) is blocked, with no excess SiO<sub>2</sub> to react with the Na<sub>2</sub>O formed, the reaction of sodium with Si-O bonds would be endothermic:



and would not take place spontaneously, unless there were substantial solubility of the product in Na. This argument was put forward by Elyard and Rawson<sup>11</sup> in explanation of the resistance to corrosion displayed by soda-rich glasses.

By analogy with the silicon-oxygen system, sodium phosphate (Na<sub>3</sub>PO<sub>4</sub>) is predicted to be the compound containing P-O bonds that would be most resistant to reaction with sodium. Indeed, sodium phosphate may be thought of as P<sub>4</sub>O<sub>10</sub> that has been fully reacted with Na<sub>2</sub>O. It follows, then, that if any compounds containing P-O bonds are stable to sodium, Na<sub>3</sub>PO<sub>4</sub> would be one.

The free energy of reaction has been estimated for



\*\*Pyrex, Corning Glass Works, Corning, NY.

††Callery Chemical Co., Div. of Mine Safety Appliances Co., Callery, PA.

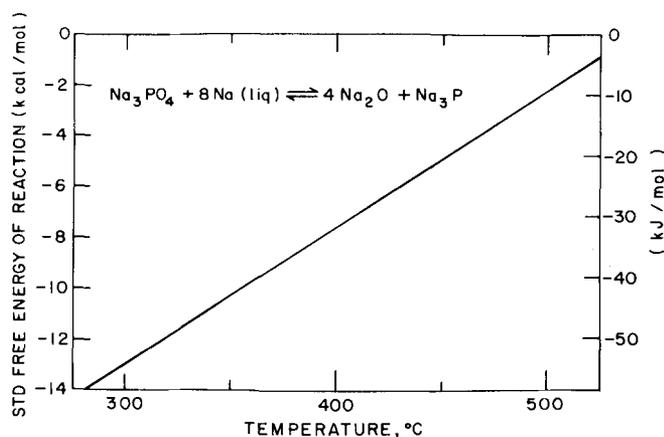


Fig. 1. Standard free energy of reaction of sodium phosphate with sodium.

at 350°C and is plotted as a function of temperature in Fig. 1. Data for  $\text{Na}_3\text{PO}_4$  are available for enthalpy of formation<sup>12</sup> and entropy.<sup>13</sup>  $\text{Na}_3\text{P}$  and others were discussed previously.

It is apparent from the standard free energy of reaction of Eq. (18) that sodium would be expected to react with sodium phosphate at  $T < 550^\circ\text{C}$ . (A change in the phosphorus standard state is omitted above 407°C.)

While there is some question as to which phosphide results, the basing of the calculations on  $\text{Na}_3\text{P}$  is a conservative choice. For an alternate choice<sup>14</sup> of  $\text{Na}_3\text{P}_5$ , the driving force for reaction would be expected to be larger.

In the experimental test with  $\text{Na}_3\text{PO}_4$  in contact with Na metal at 380°C for 10 days, approximately 0.41% of the P in the starting material was converted to phosphine. Since  $\text{Na}_3\text{PO}_4$  is attacked by sodium, it is reasonable to assume that other, less  $\text{Na}_2\text{O}$ -rich compounds containing phosphorus-oxygen bonds will also be attacked.

The attack of the Eq. (3) composition ( $\text{Na}_{3.1}\text{Zr}_{1.55}\text{Si}_{2.3}\text{P}_{0.7}\text{O}_{11}$ ) is indicated by the  $\text{PH}_3$  evolved and soluble phosphorus, which account for about 20% of the P in the Na-Zr-Si-P-O compound. The composition is lower in Na than  $\text{Na}_3\text{PO}_4$  and is on the  $\text{SiO}_2$ -rich side of a monophasic region<sup>6</sup> which, in turn, suggests lower P activity (and more stability toward reactions affecting P). However, we find that the composition fails by a mechanism that includes P-O bond breakage (indicated by the  $\text{PH}_3$  tests) in addition to, or in place of, the  $\text{SiO}_2$  excess.<sup>6</sup>

The test that we carried out is more severe and more sensitive than those carried out by other investigators. The samples had 15% porosity, which could allow a greater contact surface area than for samples with closed porosity. Also, the test was run at 380°, not at 300°C.<sup>4</sup> (Sodium-sulfur batteries are expected to operate for multi-year periods at temperatures near 350°C.) From tests with phosphate glasses<sup>11</sup> reacting with Na, an increase of temperature from 300° to 400°C is known to play a critical role in the kinetics of corrosion. The chemical detection of reaction products can be more sensitive than microscope observations of cracking or XRD determinations of lattice parameter changes. Due to some decomposition during sintering at 1280°C,  $\text{P}_4\text{O}_{10}$  formation in trace quantities is expected.<sup>15</sup> However, this small decomposition cannot account for the 20% of available P being reduced, as  $\text{Na}_{3.1}\text{Zr}_{1.55}\text{Si}_{2.3}\text{P}_{0.7}\text{O}_{11}$  is 4.6 wt% phosphorus from Eq. (3). The interweaving of densification and decomposition in the same process adds complexity to the class of electrolytes, which was not initially recognized. This aspect appears to be intrinsic to the phosphorus-containing systems.

The tests described here are less severe than those which other electrolytes have passed, which are related to current density, total current passed, and the special requirements for devices which require much-higher temperature stability with sodium metal, such as for the sodium heat engine.<sup>16</sup>

The experiments were carried out with the Eq. (3) composition, which is a representative of the class of electrolytes which retains the high conductivity. As we have seen, P-O bonds are broken even in this  $\text{SiO}_2$ -rich composition. There are many degrees of freedom for compositional variation. An alternate, expressed by Eq. (5), is  $\text{Na}_{2.94}\text{Zr}_{1.49}\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{10.85}$ . It has a higher resistivity ( $7.7 \Omega \cdot \text{cm}$ ) at 300°C than that of Eq. (3), which is significant in comparison to other materials with 4 to 5  $\Omega \cdot \text{cm}$  resistivity. To the extent that the Eq. (5) material is claimed to be near the  $\text{ZrO}_2$  solubility limit of a monophasic region,  $\text{Na}_{2.94}\text{Zr}_{1.49}\text{Si}_{2.2}\text{P}_{0.8}\text{O}_{10.85}$  is the lowest in the relative amounts of tetrahedral (Si and P) bonding to oxygen and may have slower kinetics of corrosion than  $\text{Na}_{3.1}\text{Zr}_{1.55}\text{Si}_{2.3}\text{P}_{0.7}\text{O}_{11}$ . The long-term stability is unlikely to be fundamentally different.

On the one hand, P must be retained to keep the high conductivity. On the other hand, in view of the reactivity of  $\text{Na}_3\text{PO}_4$  and  $\text{Na}_{3.1}\text{Zr}_{1.55}\text{Si}_{2.3}\text{P}_{0.7}\text{O}_{11}$ , one really needs to substantially lower the P activity for stability. This pair of conditions leads to a reduced probability of finding Na-Zr-Si-P-O compositions for skeletal ion conductors which are stable to Na metal for extended periods at elevated temperatures.

Many other skeletal systems (such as hollandites and zeolites) have been studied without finding low resistivities. In the previously cited patent,<sup>3</sup> another class of skeletons based on (Mg, Si) pairs instead of (Si, P) is noted (which have higher resistivities for the case described). The discussion here is restricted to the phosphorus-containing ones, but would be expected to apply to cases of substitutes such as Hf or Ta for Zr. Potassium fits so poorly through the bottlenecks of the Eq. (1) skeleton that Na is, in practice, the only alkali metal considered. Use of Na-Zr-Si-P-O materials with diluted alkali metals (as has been suggested for the  $\text{Li}_3\text{N}$  electrolyte) or in lower-temperature applications (below 300°C) such as electrochromic devices are alternatives, but the consequences of lower cell voltages and markedly higher resistivities restrict even these applications. Here, we have considered aspects needed for the Na-S battery and the sodium heat engine. Compositional variation does not appear to be a promising avenue to obtain stability for the electrolytes which require a substantial P content to obtain high conductivity. Additional requirements, such as stability with sodium polysulfides, must also be retained for the battery application.

#### IV. Summary

Phosphorus is the key to the conductivity of the Na-Zr-Si-P-O skeletal ion conductors. Previously masked by processing complexities and the use of only physical (microscope and XRD) methods, the severity of deterioration of the electrolyte (in the absence of any current passage) is clearly indicated by chemical tests of the reaction products.  $\text{Na}_3\text{PO}_4$ , which should be more stable than the electrolytes by analogy to sodium silicates, also produces  $\text{PH}_3$  on hydrolysis after contact with Na metal for 10 days at 380°C. This is evidence of  $\text{P}^{(\text{V})}$ -O bond breakage. It appears unlikely that minor compositional variation in the system Na-Zr-Si-P-O will lead to structures with  $\text{P}^{(\text{V})}$ -O bonds that are not attacked by Na.

**Acknowledgments:** The authors thank F.D. Runkle, G.E. Fisher, and L.C. Westwood for experimental assistance, J.T. Kummer and N. Weber for discussions, and W. Evans of the National Bureau of Standards for an entropy estimate.

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<sup>6</sup>U. von Alpen and M. F. Bell, "Structural and Electrochemical Investigations of New Compounds in the Phase System  $\text{Na}_2\text{O-ZrO}_2\text{-SiO}_2\text{-P}_2\text{O}_5$ "; The Electrochemical Society, Extended Abstracts, Volume 82-1, 1982; pp. 1170-71.

<sup>7</sup>JANAF Thermochemical Tables, 2d ed. Edited by D. R. Stull and H. Prophet. No. NSRDS-NBS-37, U.S. Government Printing Office, Washington, DC, 1971.

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<sup>9</sup>W. Evans; private communication, Dec. 18, 1981.

<sup>10</sup>R. R. Wenner, Thermochemical Calculations. McGraw-Hill, New York, 1941; esp. p. 91.

<sup>11</sup>C. A. Elyard and H. Rawson, "The Resistance of Glasses of Simple Composition to Attack by Sodium Vapor at Elevated Temperatures"; pp. 270-86 in *Advances in*

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# Sintering and Properties of Titanium Diboride Made from Powder Synthesized in a Plasma-Arc Heater

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The pressureless sintering to near theoretical density of high-purity titanium diboride powder, produced in a plasma arc from halogen vapor reactants, is described. Physical and mechanical property measurements between 25° and 1400°C are reported for materials densified at  $T=1800^\circ$  to 2275°C. Titanium diboride exhibits several unusual and interesting properties, which include high electronic conductivity, a large positive strength-vs-temperature coefficient, and an intrinsic resistance to high-temperature slow crack growth (negative  $N$ ). Property trends are explained in terms of microstructural development and residual grain-boundary stresses.

## I. Introduction

TITANIUM DIBORIDE ceramics are of interest for aluminum evaporation boats, cutting tools, armor, and electrodes. Of these, the use of titanium diboride as an inert, energy-saving cathode in Hall-Heroult reduction cells has commanded probably the most interest in previous<sup>1</sup> and more recent<sup>2</sup> times. Many of the early titanium diboride cathode failures have been ascribed to impurity contamination,<sup>3,4</sup> particularly that by oxygen. Since the early efforts, significant advances have been made in titanium diboride materials technology which, in no small part, are responsible for the renewed interest in the cathode application. One goal of this paper is to report these material advances.

The densification of diborides was the subject of a recent review.<sup>5</sup> Hot-pressing and large amounts of sintering aids have been used to prepare dense bodies of titanium diboride.<sup>5-8</sup> Both approaches can leave deleterious impurities in the final product,<sup>9</sup> since the impurities were necessary for densification. In addition, hot-pressing has limited shape-forming capability. Attempts<sup>5,7</sup> to sinter relatively pure titanium diboride have produced densities of up to 95% of theoretical, but more frequently much less.

Published mechanical-property data on relatively pure, single-phase titanium diboride are rather scarce. General property summaries are available,<sup>10-12</sup> as are strength and microstructural information on hot-pressed materials.<sup>8,13</sup> Recently, the strengths of many of the newer materials in aluminum were reported.<sup>14</sup>

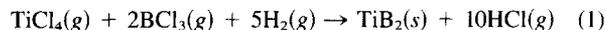
This paper describes the essentially complete densification of a titanium diboride powder by pressureless sintering. The powder is produced in an arc-plasma reactor and is of high purity and sub-micrometer particle size. This method of powder manufacture is distinct from the more traditional carbothermic process.<sup>15</sup> The successful densification has produced a reconsideration of the relevant sintering mechanisms of titanium diboride. Measurements of se-

lected physical and mechanical properties of the sintered material are presented and discussed in terms of microstructure, purity, and residual stresses. A subsequent publication<sup>16</sup> will cover the influence of aluminum environments on mechanical properties.

## II. Experimental Methods

### (1) Powder Characteristics

The titanium diboride powder was produced<sup>17,18</sup> in an arc plasma by the reaction of titanium tetrachloride and boron trichloride gases in the presence of excess hydrogen according to:



A chlorinated hydrocarbon was fed into the reactor to introduce a small amount of carbon into the titanium diboride powder. The carbon assists densification by inhibiting grain growth of the diboride.

The titanium diboride powder was examined by transmission electron microscopy and found to consist of submicrometer-sized crystals, of equiaxed and tabular forms, with only small amounts of crystal intergrowth. The tabular crystals were predominately hexagonal platelets having a diameter-to-thickness ratio of about 1.5:1 to 10:1. A photomicrograph of the powder is shown in Fig. 1. Titanium diboride powders of a surface area of approximately 7 m<sup>2</sup>/g, as determined by BET nitrogen adsorption, have been found to sinter well.

### (2) Sample Preparation

The ceramic powder was mixed with 2.5 wt% of paraffin wax binder. Because of the pyrophoric nature of the powder, all powder processing was conducted under an inert gas atmosphere to preclude contamination from air. Rectangular bar specimens of various sizes for strength and modulus studies were mechanically pressed in steel dies at a pressure of 17 MN/m<sup>2</sup> and then isopressed at 69 MN/m<sup>2</sup>. Similar powder consolidation procedures have been used to fabricate sintered components up to 3 kg in weight.

The compacts were densified by sintering under vacuum ( $P < 3$  Pa) in a furnace with graphite heating elements. Samples were sintered for one hour at maximum sintering temperatures at  $T = 1800^\circ$  to 2275°C.

### (3) Characterization of Sintered Material

(A) *Microstructure and Density*: Specimens were prepared for metallographic examination by polishing initially with diamond grits and ending with chrome oxide to produce a mirror finish. Polished samples were etched 15 to 30 s in a fresh solution of three drops concentrated HF/10 cm<sup>3</sup> concentrated HNO<sub>3</sub>/3 cm<sup>3</sup> concentrated HCl/10 cm<sup>3</sup> glycerine. The predominant grain-size range for each sintering temperature was determined by microscopic

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