

Fig. 5. Backscattered image of Ti(CN)-30% TiB<sub>2</sub> material (bar=10 μm).

that raw Ti(CN) powder size greatly affects densification and transverse rupture strength. Also, the materials using Ti(C<sub>0.5</sub>N<sub>0.5</sub>) with grain size of <2 μm (No. 2) have ≈0.2 vol% porosity when sintered at 2073 K. Figure 5 is a backscattered image of the materials. The grayish grains are TiB<sub>2</sub>; the white areas are Ti(C<sub>0.5</sub>N<sub>0.5</sub>); and the black areas are pores. It is found that materials using the finer Ti(C<sub>0.5</sub>N<sub>0.5</sub>) powder have fewer pores and higher transverse rupture strength.

#### Effects of Oxygen on the TiB<sub>2</sub> Powder

The surface of fine TiB<sub>2</sub> powders readily became oxidized during the mixing stage. Therefore, in order to examine

the effects of oxidation on the strength and porosity, raw Ti(CN) powder 1 and raw TiB<sub>2</sub> powders 8 and 9 in Table I were used. The results in Table III clearly show that the oxygen in the TiB<sub>2</sub> greatly affects the transverse rupture strength and the porosity of sintered bodies. The reaction  $2\text{TiB}_2 + 5\text{O}_2 \rightarrow 2\text{TiO}_2 + 2\text{B}_2\text{O}_3$  might occur on the near surfaces of TiB<sub>2</sub> grains at the sintering temperature, and B<sub>2</sub>O<sub>3</sub> can be easily volatilized at high temperatures. Accordingly, the sintered bodies may have high porosity.

#### Effects of Co Impurities

The raw Ti(CN) powders tended to have a small amount of Co impurities which came from the WC-Co balls used during crushing. Presumably, the Co impurities will change to CoB and Co<sub>2</sub>B after reacting with TiB<sub>2</sub> at high temperatures,<sup>4</sup> and the CoB and Co<sub>2</sub>B will greatly affect the densification of Ti(CN)-TiB<sub>2</sub> compacts. Therefore, the effects of Co impurities on the densification and transverse rupture strength were examined.

Used in the experiment were Ti(CN) No. 4, TiB<sub>2</sub> No. 6, WC No. 10, and Co No. 11 raw powders. As Fig. 6 shows, higher WC content resulted in greater porosity in Ti(CN)-30% TiB<sub>2</sub> sintered bodies. However, greater additions of WC-10% Co to the Ti(CN)-30% TiB<sub>2</sub> materials resulted in higher transverse rupture strength and lower porosity. Therefore, it is the Co impurities that greatly affect the densification and transverse rupture strength of materials in the Ti(CN)-30% TiB<sub>2</sub> system.

Table III. Porosity and Transverse Rupture Strength of Ti(CN)-30% TiB<sub>2</sub> Sintered Materials Using Different Oxygen Content

Oxygen content of raw TiB <sub>2</sub> powder (wt%)	Transverse rupture strength (MPa)	Porosity (vol%)
0.5	560	1.8
1.9	450	8.8

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## Purity of Aluminum Hydroxide Derived from Triethylaluminum

FRED N. TEBBE,<sup>\*,\*</sup> PATRICIA A. MORRIS,<sup>†,‡</sup> ROGER H. FRENCH,<sup>\*,\*</sup> UMA CHOWDHRY,<sup>\*,\*</sup> AND ROBERT L. COBLE<sup>\*,†</sup>

Central Research and Development Department, Experimental Station, E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware 19898, and Department of Materials Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

*Aluminum hydroxide obtained by hydrolysis of triethylaluminum is free of uranium and thorium at detection limits of 1 to 9 parts per billion (ppb). Other impurities commonly associated with aluminum oxides are present at low levels (Fe, ≈1 ppm; Si, 3 to 6 ppm). When the organoaluminum is intentionally contaminated with an iron salt, purity is restored by a simple distillation.*

WE REPORT the identification of an aluminum hydroxide, formed from hydrolysis of triethylaluminum

(Al(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>, AlEt<sub>3</sub>), free of uranium and thorium at detection limits of 1 to 9 parts per billion (ppb). The sum of other metal-

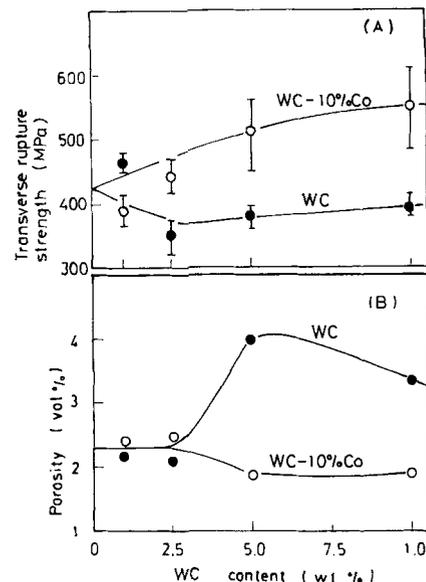


Fig. 6. (A) Transverse rupture strength and (B) porosity versus WC or WC-10% Co content. The materials were sintered at 2173 K for 5400 s in argon.

#### CONCLUSION

Particle sizes of TiB<sub>2</sub> and Ti(CN) powders, oxygen content in TiB<sub>2</sub> powders, and Co impurities greatly affect the densification and bending strength of Ti(CN)-30% TiB<sub>2</sub> compacts.

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ion impurities is ≈10 to 20 parts per million (ppm).

There is interest in the generation of ceramics of high purity for scientific and technological purposes. For example, studies have recently appeared on techniques for processing alumina without introduction of contaminants<sup>1</sup> and on the effects of traces of foreign ions on sintering of alumina.<sup>2</sup> Uranium and thorium are widely distributed in natural minerals in concentrations >25 ppb. When these contaminated

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\*Member, the American Ceramic Society.

\*E. I. du Pont de Nemours & Co., Inc.

†Massachusetts Institute of Technology.

‡Present address: P.A.M., Bell Communications Research, Red Bank, NJ 07701.

minerals are incorporated in materials for packaging of random-access-memory devices,  $\alpha$ -particle emission form the radioactive elements may interfere with the electronics.<sup>3,4</sup> Impurities such as iron ( $\approx 10$  ppm) and calcium ( $\approx 20$  ppm)<sup>5</sup> affect the performance of sodium vapor lamps constructed of alumina. It has been recognized that it is desirable to eliminate liquid-phase-forming impurities which segregate at grain boundaries of ceramics made for use at high temperatures.

The availability of convenient sources of aluminum oxides of high purity is of interest to us. Following our determination<sup>4,6</sup> that many of the commercially available aluminas contain impurities in concentrations sufficient to interfere with their use in electronics packaging and in some other applications, we were prompted to seek a synthetic method for an alumina of higher quality. Triethylaluminum is known to be converted by hydrolysis to  $\text{Al}(\text{OH})_3$ .<sup>7</sup> It appeared to us that  $\text{AlEt}_3$  might easily be obtained in a state of relatively high purity and converted to  $\text{Al}(\text{OH})_3$  of comparable purity. Our initial study<sup>1</sup> on the  $\text{Al}(\text{OH})_3$  derived from  $\text{AlEt}_3$  demonstrated that the hydroxide could be calcined and partially sintered without introduction of impurities.

## EXPERIMENTAL PROCEDURE

### Reagents

Triethylaluminum,<sup>8</sup> commercial, production-grade, was used as-received, or was distilled (see *Procedures*). Toluene<sup>9</sup> was distilled in glass, and the water azeotrope was discarded. Water, initially purified by reverse osmosis, was further purified to 18 M $\Omega$ -cm resistivity by treatment with carbon black, ion exchange, and filtration columns.<sup>10</sup> The iron chloride was anhydrous.<sup>11</sup> Aqueous standardized solutions of iron and uranium were obtained from a commercial source.<sup>12</sup>

### Procedures

Attempts were made to minimize the exposure of reagents and equipment to contaminants, although clean-room facilities were not used. Equipment was washed with 50% nitric acid and deionized water. Polymeric fluorocarbon vessels were used for storage of reagents and solvent and for the hydrolysis reaction. Triethylaluminum was routinely distilled before use except where the purity of the material as it is supplied was of interest. Cautions applicable to the use of  $\text{AlEt}_3$  are noted below.

**Distillation of  $\text{AlEt}_3$ .** **Caution:** As the use of aluminum alkyls has become

routine in some applications, considerable attention has been devoted to definition of their hazards and development of safe handling procedures. Consultation of the literature<sup>8,13</sup> is recommended. Aluminum alkyls are treated with the care accorded highly pyrophoric and moisture-sensitive materials. Dilution with properly chosen solvents reduces the potential for spontaneous inflammation in air. Solvents are chosen with care. Aluminum alkyls can act as strong reducing agents; contact with oxidizing solvents or reagents could be hazardous. Halogenated solvents are avoided except in special cases.<sup>9</sup> Attention is given to methods of deactivation of byproducts and wastes. They are protected from air, diluted with copious amounts of a solvent such as xylene<sup>8(b)</sup> or toluene, and deactivated by controlled hydrolysis or alcoholysis with a higher alcohol,<sup>8(b)</sup> or by controlled incineration.

The borosilicate glass<sup>14</sup> still (Vigreux design, 8-mm ID by 17 cm) was contained within a nitrogen-purged drybox.<sup>15</sup> Triethylaluminum, 370 mL, was distilled under reduced pressure. The distillate, 300 mL, bp 64° to 67°C was collected in a fluorocarbon vessel. Samples intentionally contaminated with iron salts were distilled by a similar procedure.

**Hydrolysis of  $\text{AlEt}_3$ .** (See cautionary statement above.) A solution of 33 g (0.29 mol) of  $\text{AlEt}_3$  in 330 mL of toluene was prepared in the drybox. In a shielded hood, the vessel was connected to a vented bubbler and a source of nitrogen. With nitrogen supplied to maintain a slight positive pressure in the system, the vessel was chilled in an ice bath. With stirring, 25 g (0.14 mol) of water were added as small droplets over 2.5 h. The rate of addition was controlled so that the temperature of the solution remained below the boiling point, and the quantity of ethane produced was easily released through the bubbler. The end of the reaction was signaled when ethane ceased to form. The suspension was centrifuged, liquids decanted, and the product dried under vacuum to a weight of 18.7 g. Anal. Calcd for  $\text{Al}(\text{OH})_3$ : Al, 34.6; ash, 65.4. Found: Al, 32.3; ash, 61.6; C, 1.8; surface area 241 m<sup>2</sup>/g. Other properties of the product are reported separately.<sup>1</sup>

### Analytical Information

Uranium and thorium analyses were performed by neutron-activation procedures.<sup>16</sup> Analytical data for other metal ions and for anionic species were obtained by spark-source mass spectroscopy.<sup>17</sup>

**Uranium and Thorium.** Some information was obtained on the reliability of the uranium analysis. The deionized water was found to contain <0.05 ppb of uranium. Water doped with a known amount of uranium was examined. Anal. Calcd for U: 6.4 ppb. Found: U, 6.6 ppb. A sample of  $\text{Al}(\text{OH})_3$  prepared from this uranium-doped water was examined. Anal. Calcd for U: 7.4 ppb. Found: U, 9.1 ppb.

Separate samples of  $\text{Al}(\text{OH})_3$  from  $\text{AlEt}_3$ , hydrolyzed as it was received, were free of uranium at detection limits of 5 and 7 ppb and of thorium at detection limits of 5 and 4 ppb, respectively. Samples of  $\text{Al}(\text{OH})_3$  from distilled  $\text{AlEt}_3$  were free of uranium at detection limits of 4.7, 3, and 7 ppb and of thorium at detection limits of 5, 7, and 9 ppb. Traces of sodium in the samples increased the detection limits. In one case, a sample was washed three times with deionized water. Neutron-activation analysis showed that washing reduced the amount of sodium in the sample. After washing, the detection limits for uranium and thorium were 0.7 and 1.3 ppb, respectively. Neither element was detected.

**Broad-Spectrum Analyses of Impurities.** The data presented are based on spark-source mass spectrographic determinations. The concentrations of individual elements determined by mass spectrography were reported to us to be accurate, in general, within a factor of 2 in 65% of the cases and within a factor of 3 in 85% of the analyses. The accuracy of the balance of the determinations was less than these limits.

Some information on the reliability of iron determinations by spark-source mass spectrography was obtained. The deionized water used for hydrolysis was reported to contain 0.05 ppm of Fe. A sample of this water was combined with a standardized solution of the iron ion, and the mixture used to hydrolyze distilled  $\text{AlEt}_3$ . Anal. Calcd for Fe in  $\text{Al}(\text{OH})_3$ : 5 ppm. Found: Fe, 2 ppm. A solution of  $\text{FeCl}_3$  in distilled  $\text{AlEt}_3$  was hydrolyzed with deionized water, and the product was examined for its iron content. Anal. Calcd for Fe: 12 ppm. Found, Fe: 5 ppm.

Typical sets of mass-spectrographic data for impurities in  $\text{Al}(\text{OH})_3$  from  $\text{AlEt}_3$  are reported in Table I. Elements not found at detection limits of  $\approx 0.02$  ppm were Be, F, Sc, Co, Ge, Se, Br, Rb, Sr, Y, Zr, Nb,

Table I. Impurities in  $\text{Al}(\text{OH})_3$  from  $\text{AlEt}_3$

Impurity	Impurity concentration by weight in $\text{Al}(\text{OH})_3$ from $\text{AlEt}_3$ , as-received (ppm)	Impurity concentration by weight in $\text{Al}(\text{OH})_3$ from $\text{AlEt}_3$ , distilled (ppm)
Li	$\leq 0.1$	<0.1
B	0.3	0.1
Na	0.2	0.5
Mg	$\leq 1$	<1
Si	6	3
P	0.06	0.03
S	<3	<3
Cl	45	20
K	0.1	0.3
Ca	0.4	0.3
V	$\leq 0.05$	<0.05
Cr	0.1	0.2
Mn	0.06	0.1
Fe	0.6	0.3
Ni	0.2	$\leq 0.1$
Cu	0.2	$\leq 0.06$
Zn	$\leq 0.1$	<0.1
Ga	0.2	<0.1
As	0.4	0.2

<sup>8</sup>Ethyl Corp., Baton Rouge, LA.

<sup>9</sup>Fisher Scientific Co., Pittsburgh, PA.

<sup>10</sup>Millipore Super Q apparatus, Millipore Corp., Bedford, MA.

<sup>11</sup>Spex Industries, Inc., Edison, NJ.

<sup>12</sup>See also the manufacturer's safety information sheets for the specific compounds of interest.

<sup>13</sup>Pyrex, Corning Glass Works, Corning, NY.

<sup>14</sup>Vacuum Atmospheres Co., Hawthorne, CA.

<sup>15</sup>General Activation Analysis, Inc., San Diego, CA.

<sup>16</sup>Northern Analytical Laboratory, Inc., Amherst, NH.

Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th, and U. Among the light elements not analyzed were H, C, N, and O.

*Distillation of Intentionally Contaminated AlEt<sub>3</sub>.* A portion of the solution of FeCl<sub>3</sub> in AlEt<sub>3</sub> described above was distilled with recovery of 96% of the AlEt<sub>3</sub>. Hydrolysis with deionized water yielded Al(OH)<sub>3</sub> which was found to contain 1 ppm of Fe.

## RESULTS AND DISCUSSION

Triethylaluminum is among the most readily available of the organometallics. If the purity or other properties of this compound were found to be attractive, we could consider it as a source of the aluminum ion for a number of ceramic and glass materials. Although we have focused on means of obtaining aluminum oxides with low concentrations of  $\alpha$ -particle-emitting and other impurities, the results reported here should also bear on the purity which could be anticipated for other materials generated from AlEt<sub>3</sub>.

The conditions of its synthesis and the chemical and physical properties of AlEt<sub>3</sub> would seem to favor its ability to be isolated with low concentrations of many of the contaminants usually associated with mineral sources of the aluminum ion. It is normally made from aluminum metal under highly reducing conditions,<sup>10</sup> where other metals which are unstable as their ethyl or hydride complexes may be excluded from the product. Since AlEt<sub>3</sub> distills at reduced pressures as a stable liquid, it can be separated from a number of potential impurities. It possesses significant reducing power which, in some cases, may assist in its separation from complexes of other metal ions. For example, volatile titanium(IV) chloride, is reduced by AlEt<sub>3</sub> to the titanium(III) salt,<sup>11,12</sup> which has much lower volatility. In some cases, however, triethylaluminum complexes with and enhances the volatility of metal ions. The volatility of Ca(AlEt<sub>4</sub>)<sub>2</sub>, although lower than that of AlEt<sub>3</sub>, is exceptional for a calcium salt.<sup>13</sup>

The alkyls are normally much stronger reducing agents than the alkoxides of aluminum. It would be useful to know if this or other differences in the properties (or methods of synthesis) of the two classes of compounds significantly affect the relative ease of their purification.

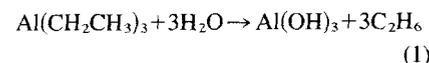
Attention has previously been given to the purity of aluminum oxides prepared from AlEt<sub>3</sub>.<sup>14</sup> We are not aware of information similar to that presented here, where a broad spectrum of impurities at detection limits of <1 ppm are examined. When we initiated this study we anticipated that the commercial, production grade of AlEt<sub>3</sub> would likely contain small amounts of im-

purities, the concentrations of which might be reduced by distillation. We were surprised to find few impurities in Al(OH)<sub>3</sub> made from AlEt<sub>3</sub> (either as-received or after distillation), many of which were present in concentrations near the detection limits of the analytical techniques available. In particular, we found no uranium and thorium in Al(OH)<sub>3</sub> prepared from AlEt<sub>3</sub> at detection limits as low as 0.7 and 1.3 ppm, respectively. With the exception of the silicon ion, present in concentrations of 1 to 6 ppm, the impurities detected were at levels of  $\leq 1$  ppm. Thus, in order to determine the effectiveness of a single distillation of AlEt<sub>3</sub>, we combined it with a small quantity of FeCl<sub>3</sub> and distilled it from the mixture. The distillation, performed with an inefficient glass column, was sufficient to restore the material to the state of purity in metal ions found before contamination.

Our results on distillations of AlEt<sub>3</sub> thus apply to separations from FeCl<sub>3</sub>. It is to be determined to what extent other metal-ion complexes are removed by distillation, and whether the use of more-efficient distillation techniques, or equipment other than glass, could enhance purity. Also unknown to us are relationships between the purities of AlEt<sub>3</sub> and the materials used for its synthesis. We have limited information on the consistency of the purity of commercial triethylaluminum. Several lots obtained over  $\approx 2$  yr, however, consistently yielded Al(OH)<sub>3</sub> with a total of 10 to 20 ppm of metal-ion impurities.

Except for chloride, the concentrations of anionic impurities detected in our Al(OH)<sub>3</sub> are on the order of 3 ppm (sulfur) or less. Chloride, 45 ppm, was found in Al(OH)<sub>3</sub> from one sample of AlEt<sub>3</sub>, while Al(OH)<sub>3</sub> from another sample contained 1 to 3 ppm.<sup>1</sup> Distillation did not significantly reduce the quantity of chloride in AlEt<sub>3</sub>, probably because it is present as AlEt<sub>2</sub>Cl, which boils near AlEt<sub>3</sub>. While distillation of AlEt<sub>3</sub> from its mixture with FeCl<sub>3</sub> effectively separated aluminum from iron, the concentration of chloride in Al(OH)<sub>3</sub> prepared from the distillate was increased from 45 to 115 ppm.

Triethylaluminum and water react to form Al(OH)<sub>3</sub> and ethane.<sup>7</sup>



When the hydrolysis is conducted in the liquid phase, a solvent assists in dissipation of the heat of reaction and in dispersing the hydroxide. We used toluene as the solvent because it may be less likely to become contaminated with metal-ion impurities than more polar solvents. The reaction, and the particle characteristics of Al(OH)<sub>3</sub> resulting from it, are expected to be more easily controlled by use of a solvent in which both reagents for the reaction are soluble.

## CONCLUSIONS

Aluminum hydroxide and  $\alpha$ -alumina<sup>1</sup> derived from commercial, production-grade triethylaluminum contain significantly lower quantities of metal-ion impurities than aluminum oxides from mineral sources. When triethylaluminum is intentionally contaminated with iron chloride, purification is achieved by a simple distillation of the organoaluminum from the mixture. Oxides prepared from the organoaluminum are potentially of value in studies of the effects of impurities on the transformations and sintering of alumina and in applications where low levels of  $\alpha$ -particle-emitting and other impurities are important.

## ACKNOWLEDGMENT

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