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Non-polymeric binders for ceramic powders: utilization of neutral and ionic species derived from decaborane(14)

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The pyrolytic conversion of *bis*-Lewis base adducts of decaborane(14), $L \cdot B_{10}H_{12} \cdot L$ (L = neutral monophosphine) and phosphonium salts of the $[B_{10}H_{10}]^{2-}$ anion (e.g. $[Ph_4P^+]_2$, etc.), to ceramic materials has been studied. All species examined served as binders for a variety of non-oxide refractory ceramic powders (e.g. B_4C, BN, BP, $B_{13}P_2$, SiC, Si_3N_4, B, C, AlN).

1. Introduction

Binders are used primarily to help ceramic particles adhere to one another [1, 2]. Both the green strength of a ceramic body and its green density are affected by the binder used. Although many types of material have been employed as binders in ceramic powder processing, organic polymers (e.g. polyvinyl alcohol, polyvinyl butyral, polyethylene, acrylic resins, wax emulsions, etc.) have traditionally played an important role as binder formulations. While the use of such materials as binders often results in the achievement of high green body strength and/or high green body density, there also can be some drawbacks resulting from their use. Major problems can be encountered upon firing of the ceramic body due to binder burnout. Cracking of the part results when the temperature range of the binder burnout is narrow, so that most of the volatiles are released practically simultaneously. Not necessarily always a drawback is that during the non-oxidative firing of the ceramic body there can be substantial retention of carbon, either due to polymer binder pyrolysis (giving nonvolatile, highly carbonaceous residues) or due to polymer–ceramic surface bond formation, preventing degradative volatilization of the binder [3]. In order to avoid these problems, ceramists more recently have become interested in "low loss" inorganic or organometallic polymeric binders [4, 5]. The polymers of choice are those whose pyrolysis gives a high yield of ceramic residue with the release of a minimum quantity of potentially destructive volatiles. Preferably, this ceramic residue also will be the same material of which the powder is composed, but this is not an essential requirement. By use of such "low loss" binders, one may hope to achieve not only the desired high green body strength and density that organic binders bring, but also to obtain ceramic parts of high strength and density. To date, most of the "low loss" organometallic binders that have been investigated have been organosilicon polymers which are used as binders for silicon carbide and silicon nitride powders [6–11].

In our laboratories we have initiated a programme aimed at the development of polymeric precursors for boron-containing ceramic materials: the carbide, nitride and "carbonitride". Successful systems based on known [12–14] and new [15, 16] polymers involving difunctional Lewis-base adducts of decarborane(14) have been developed (Fig. 1). During the course of this research we also prepared and investigated some non-polymeric decaborane(14) derivatives and the report here concerns these and their applications as binders for a variety of non-oxide ceramic powders. As far as binder applications were concerned, we were interested to find out if these non-polymeric boron-containing species might be useful binders for the boron-containing ceramics mentioned above, as well as for elemental boron powder.

2. Experimental details

2.1. General comments

All manipulations were carried out in oven-dried glassware under an inert atmosphere (argon or nitrogen) following standard techniques [17]. All solvents were distilled from appropriate drying agents [18] under a nitrogen atmosphere prior to use. All reagents employed were available commercially and were used as received. All $B_{10}H_{12} \cdot 2L$ complexes* and $[B_{10}H_{10}]^{2-}$ salts† were prepared by published methods (L = Ph_3P, Ph_2PH, $(n\text{-}Bu)_3P$ and $(NMe_2)_2PCl$ [19], L = Ph_2POH, Ph_2PN_3 and Ph_2PNHNH_2 [20], all $[B_{10}H_{10}]^{2-}$ salts [21]). Twice sublimed decaborane(14) was purchased from Callery Chemical Co., Callery, Pennsylvania, and used as-received. All compounds prepared were characterized on the basis of their melting points and spectroscopic (IR; ^{11}B, ^{13}C, ^{31}P, ^1H NMR) properties and comparison with literature values [19–21]. NMR spectra were obtained using a Varian XL-300 NMR spectrometer, IR spectra on a Perkin–Elmer

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*For a discussion of $B_{10}H_{12} \cdot 2L$ complexes, see [19].

†For a discussion of salts of the $B_{10}H_{10}^{2-}$ anion, see [21].

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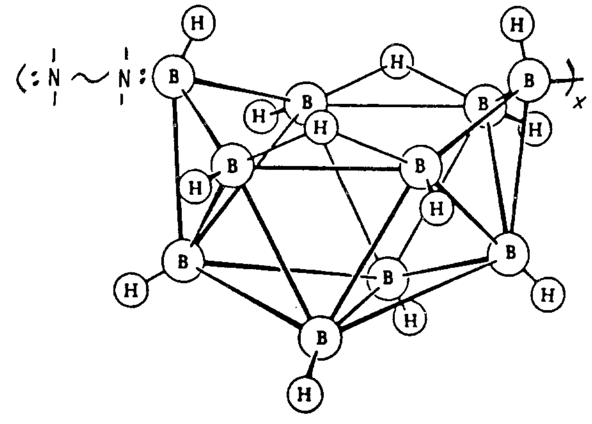

Figure 1 Structure of -[-$B_{10}H_{12}$ · diamine-]-$_x$ polymers.

Model 1430 spectrophotometer. Ceramic analyses were obtained from Galbraith Laboratories, Knoxville, Tennessee.

A hardened stainless steel die in a Carver laboratory press was used for forming 3.75 cm × 1.25 cm bars. Isostatic bar compaction was carried out in a pneumatically driven oil press with the bars wrapped in "Saran Wrap" and contained in evacuated, sealed rubber bags. Lindberg tube furnaces with Eurotherm controllers were used for all preparative scale (> 1 g) pyrolyses (powder and bulk). For pyrolyses to 1000° C, 3.75 cm o.d. quartz tubes and fused silica boats were used; for ones to 1500° C, 6.50 cm o.d. mullite tubes and boron nitride boats supported on alumina dee tubes were used. All pyrolyses were carried out under an atmosphere of flowing argon. For experiments to 1000° C the flow rate was ~ 6 to 8 litre h^{-1} and for experiments to 1500° C it was ~ 16 to 20 litre h^{-1}.

X-ray diffraction patterns were obtained either on a Charles Supper detector and Diano generator instrument or on a Rigaku rotating-anode system. TGA measurements were made on a Perkin–Elmer model TGS2 instrument equipped with a Thermal Analysis System 4 controller. For TGA data, *in situ* data were obtained for powdered samples from ambient to 950° C and mass change data for higher temperatures were collected on bulk samples after they had been heated to the desired temperature and then cooled to ambient conditions.

2.2. General procedure for the preparation of $B_{10}H_{12}$ · 2L complexes [19]

The preparation of $B_{10}H_{12} \cdot 2Ph_3P$ is given as a representative example. A 250 ml Schlenk flask equipped with a stir-bar, gas-inlet tube and a septum was charged under argon with 5.0 g (41 mmol) $B_{10}H_{14}$, 35 ml Et_2O and a solution of 25.0 g (95 mmol) Ph_3P in 150 ml Et_2O, with vigorous stirring during and for 5 min after addition. The precipitate which had formed was filtered, washed with Et_2O and dried at 100° C/0.1 mm Hg to give a nearly quantitative yield of $B_{10}H_{12} \cdot 2Ph_3P$. The complexes where L = Ph_2PH, Ph_2PCl, $(n\text{-Bu})_3P$, and $(Me_2N)_2PCl$, were all prepared by this general procedure. Those where L = Ph_2POH, Ph_2PN_3 and Ph_2PNHNH_2 were prepared by nucleophilic substitution at phosphorus in $B_{10}H_{12} \cdot 2Ph_2PCl$ [20]. The results of their pyrolyses (i.e. their ceramic yields and compositions) are given in Table I.

2.3. General procedure for the preparation of $[B_{10}H_{10}]^{2-}$ salts [21]

The preparation of $[Ph_4P]_2[B_{10}H_{10}]$ is given as a representative example. A solution of 2.00 g $[Et_3NH]_2[B_{10}H_{10}]$ (6.2 mmol) in 30 ml 9/1 water/ethanol was added to a solution of $[Ph_4P][Br]$ (6.00 g, 14.3 mmol) in 50 ml of the same solvent mixture in a 125 ml Erlenmeyer flask. After the mixture had been stirred for 5 min, the precipitate was filtered, washed with water, 5 ml cold (ca. − 10° C) acetone and, finally, with Et_2O. Drying at 60° C/0.1 mm Hg for 5 h gave a white solid in nearly quantitative yield. The following salts were all prepared by the above general metathesis route: $[Ph_3PMe]_2[B_{10}H_{10}]$, $[n\text{-}Bu_3PMe]_2[B_{10}H_{10}]$ and $[Ph_3P(CH_2)_3PPh_3][B_{10}H_{10}]$. The results of their pyrolyses (i.e. their ceramic yields and compositions) are given in Table I.

2.4. General procedure for the preparation of ceramic composite bars using $B_{10}H_{12}$ · 2L complexes and $[B_{10}H_{10}]^{2-}$ salts as binders for ceramic powders (Scheme 1)

One of the three following procedures was used for sample preparation:

(A) Weighed quantities (see Table II) of $B_{10}H_{12}$ · 2L

TABLE I Pyrolysis of $B_{10}H_{12}$ · 2L adducts and $[B_{10}H_{10}]^{2-}$ salts

Compound	Ceramic yield (%)*	Ceramic composition (%)			
		B	C	P	Other
$B_{10}H_{12} \cdot 2Ph_2PH$	83	23.17	60.75	13.71	
$B_{10}H_{12} \cdot 2Ph_3P$	86	18.20	69.59	9.88	
$B_{10}H_{12} \cdot 2Ph_2PCl$	73	20.62	57.09	13.17	Cl, 0.02
$B_{10}H_{12} \cdot 2Ph_2POH$	77	21.38	55.65	11.93	O, 10.57
$B_{10}H_{12} \cdot 2Ph_2PN_3$	72†				
$B_{10}H_{12} \cdot 2Ph_2PNHNH_2$	71	27.69	43.80	8.20	N, 16.56
$B_{10}H_{12} \cdot 2(n\text{-Bu})_3P$	58	35.94	46.43	15.34	
$B_{10}H_{12} \cdot 2(NMe_2)_2PCl$	55†				
$[Ph_3PMe]_2[B_{10}H_{10}]$	83†				
$[Ph_4P]_2[B_{10}H_{10}]$	93	6.87	73.06	13.01	
$[Ph_3P(CH_2)_3PPh_3][B_{10}H_{10}]$	91	15.96	69.33	8.33	
$[(n\text{-Bu})_3PMe][B_{10}H_{10}]$	68	30.10	49.03	11.96	

*Yield to 1000° C at a rate of 10° C min^{-1} under an argon atmosphere as determined in a tube furnace on ~ 1 g samples as follows: ceramic yield = [(wt residue)/(wt sample pyrolysed)] × 100.

† Composition not determined.

TABLE II $B_{10}H_{12} \cdot 2L$ binder experiments with 16.7 wt % binder

L	Ceramic powder	Mixture method*	Shape retention†	Colour
Ph_2PH	B_4C	A	E	Black
Ph_2PCl	B_4C	A	E	Black
Ph_2PNHNH_2	B_4C	A	G	Black
Ph_2POH	B_4C	A	G	Black
Ph_2PN_3	B_4C	A	G	Black
$(NMe_2)_2PCl$	B_4C	A	F	Black
$(n\text{-Bu})_3P$	B_4C	B	G	Black
Ph_3P	B_4C	B	E	Black
Ph_3P	B_4C	C	E	Black
Ph_2PH	B_4C	B	E	Black
Ph_2PH	B_4C	C	E	Black
Ph_3P	B	A	E	Dark Red
Ph_3P	Si_3N_4	A	E	Grey
Ph_3P	α-SiC	A	G	Dark grey
Ph_3P	β-SiC	A	G	Dark grey
Ph_3P	BN	A	G	Grey
Ph_3P	AlN	A	G	Silver/grey
Ph_3P	BP	A	F	Grey
Ph_3P	$B_{13}P_2$	A	E	Dark grey
Ph_3P	Rayon	B	G	Black

*See Section 2; method A, without solvent; method B, in acetone; method C, in pentane.

†Based on the fired ceramic composite bar as compared to the unfired, pressed composite bar. Qualitative order: E = excellent > G = good > F = fair.

or of a $[B_{10}H_{10}]^{2-}$ salt and the ceramic powder were mixed and ground for 15 min in a mortar and pestle in an inert atmosphere box.

(B) The $B_{10}H_{12} \cdot 2L$ or $[B_{10}H_{10}]^{2-}$ salt (0.5 g) was dissolved in 50 ml solvent (usually acetone) and 2.5 g ceramic powder was added. The stoppered flask was immersed into a Branson B-220 ultrasonicator containing ~7.5 cm ambient temperature water and vibrated for 15 min. Afterwards, the solvent was removed at 100° C and 0.1 mm Hg.

(C) The $B_{10}H_{12} \cdot 2L$ or $[B_{10}H_{10}]^{2-}$ salt (0.5 g) and the ceramic powder (2.5 g) were suspended in ~75 ml non-solvent (usually pentane) in a 100 ml stoppered round bottomed flask. Further processing was carried out as described in B, above.

The samples thus prepared were placed in a 1.25 cm × 3.75 cm rectangular die and formed into bars in a Carver laboratory press at 2250 kg ($4.6 \times 10^7\,\text{nt}\,\text{m}^{-2}$ uniaxially), wrapped in "Saran Wrap", placed in an evacuated, sealed rubber bag, removed to an ambient temperature isostatic press and further compacted to $3.45 \times 10^8\,\text{nt}\,\text{m}^{-2}$. The uniaxial pressing time duration was ~5 min and the isostatic pressing time duration was ~15 min. The resulting bar was pyrolyzed in a stream of argon to 1000° C (10° C min^{-1} heating rate, hold at 1000° C for 30 min) and subsequently allowed to cool to ambient temperature over a period of ~3.5 h. The pyrolysed sample was handled in an inert atmosphere box. The results of the individual experiments are given in Table II.

For the purposes of this initial screening test, a ceramic composite bar was considered to be "excellent" if it met both the criteria of being a uniform, rectangular monolithic body that had retained its shape (compared with the polymer composite bar before pyrolysis) in all three dimensions without undergoing any discernable shrinkage or bloating above the detectable level of 3 to 5%, as well as having a strength such that it could not be broken manually without mechanical means (e.g. a vise and pliers).

3. Results and discussion

We began this investigation with the preparation and study of the pyrolysis of several known monomeric decarborane(14)–Lewis-base adducts in which the Lewis base was a trivalent phosphorus compound, and also of some phosphonium salts of the $[B_{10}H_{10}]^{2-}$ anion. This initial thrust was due to the fact that the known processable decaborane(14) polymers involved diphosphines as the difunctional Lewis base [22–25]. Both of these classes of compounds have a high boron content, and this is what is needed in a B_4C precursor. The $B_{10}H_{12}$–Lewis base compounds, written as $B_{10}H_{12} \cdot 2L$ or, to indicate better their structure, as $L \cdot B_{10}H_{12} \cdot L$, are readily prepared by the reaction of $B_{10}H_{14}$ with two molar equivalents of the Lewis base in a suitable organic solvent such as diethyl ether or benzene (Equation 1) [19]. Among the Lewis bases

$$B_{10}H_{14} + 2{:}L \rightarrow L \cdot B_{10}H_{12} \cdot L + H_2 \qquad (1)$$

that react with $B_{10}H_{14}$ in this way are amines, phosphines, organic sulphides and nitriles. When an $R_3N \cdot B_{10}H_{12} \cdot NR_3$ adduct is heated, proton transfer from boron to nitrogen occurs and salts of the very stable $[B_{10}H_{10}]^{2-}$ anion, $[R_3NH]_2[B_{10}H_{10}]$, are formed. A wide variety of $[B_{10}H_{10}]^{2-}$ salts can be prepared by cation exchange reactions [21]. Such proton transfer processes had not been demonstrated for phosphine adducts, $R_3P \cdot B_{10}H_{12} \cdot PR_3$, but we have found that they do occur. Thus, when a sample of $B_{10}H_{12} \cdot 2Ph_3P$ was heated to 250° C at 10° C min^{-1} under a stream of argon, transformation to $[Ph_3PH]_2[B_{10}H_{10}]$ took place as evinced by the infrared spectrum of the sample after it had cooled to room temperature. A medium intensity band at 2395 cm^{-1}, not present in the spectrum of the neutral adduct, was observed. This band may be assigned to ν (P–H) of the $[Ph_3PH]^+$ cation [26].

The $L \cdot B_{10}H_{12} \cdot L$ compounds and $[B_{10}H_{10}]^{2-}$ salts that we prepared and studied are shown in Table I. Of initial interest were the yield and elemental composition of the ceramic residue obtained when they were pyrolysed to 1000° C in a stream of argon. According to the results in Table I, the precursors can be divided into two classes: (1) those having phenyl groups attached to phosphorus, whose pyrolysis gives a high (> 70%) yield of ceramic residue that contains a large fraction of the carbon present in the precursor, and (2) those that do not contain phenyl groups, whose pyrolysis gives lower yields of ceramic residue. As Table I shows, pyrolysis of powder samples of the various phosphorus-containing compounds or salts under the stated conditions resulted in retention of phosphorus in the residue. However, on further heating to 2350° C under argon, nearly total loss of phosphorus occurred when polymeric precursors such as $\text{-[-}B_{10}H_{12} \cdot Ph_2POPPh_2\text{-]-}_x$ were pyrolysed [12–14].

In all examples studied, the ceramic residue from the pyrolysis under argon to 1000° C was amorphous.

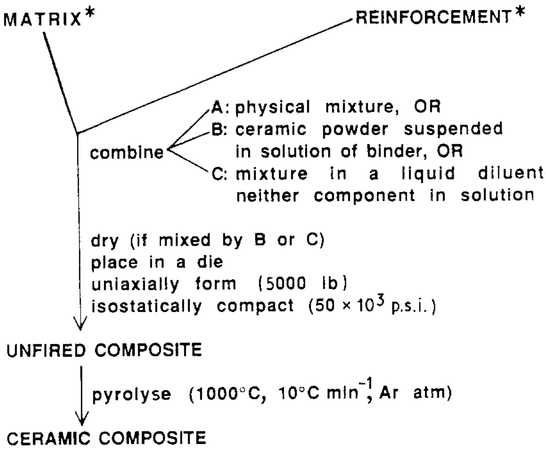

Figure 2 Schematic representation of the preparation of ceramic composites utilizing derivatives of $B_{10}H_{14}$ as binders for ceramic powders. *Typical binder/ceramic powder ratio is 16.7 wt % binder (matrix)/83.3 wt % ceramic powder (reinforcement).

Firing at 1500° C for 10 h resulted in materials whose powder X-ray diffraction (XRD) pattern showed broad lines indicative of weakly crystalline B_4C-containing material. The ceramic residues derived from the precursors in Table I are all black solids. Those precursors in Class 1 above gave freely flowing powders that were quite hard, often scoring the agate mortar used to prepare XRD samples. The precursors in Class 2 gave brittle, foamy solids, as might be expected when there is more substantial evolution of volatiles.

The determination of a nominal composition of amorphous materials is merely an accounting game using elemental analysis data. At that point no identifiable crystalline phases are present. Further firing at higher temperatures, as already noted, does cause crystallization, but also can cause changes in elemental composition. By elemental accounting, we assume that all phosphorus in the amorphous material is present as BP. The remaining boron then is assigned to B_4C. This leaves unbound carbon that we assume to be present in its elemental form. Such an accounting gives a molar formulation of 1 B_4C + 0.94 BP + 16 C to the pyrolysis product of $B_{10}H_{12} \cdot 2Ph_3P$, or, on a weight per cent basis, 21.2% B_4C, 13.3% BP and 65.5% C. However, we stress that this is only a *nominal* formulation for this material. It is possible that these elements are randomly bound in the amorphous product. A more detailed study of the *crystalline* phases obtained by firing to higher temperatures was made for the $-[-B_{10}H_{12} \cdot Ph_2POPPh_2-]-_x$ polymer [12–14]. One fact, however, is a certainty in the case of the ceramic products of the pyrolysis of the Class 1 precursors in Table I: they contain a substantial amount of free carbon.

The $B_{10}H_{12} \cdot 2L$ adducts and $[B_{10}H_{10}]^{2-}$ salts listed in Table I proved to be useful as binders for B_4C and other ceramic powders such as BN, SiC, $B_{13}P_2$, Si_3N_4 and elemental boron (Table II). Fig. 2 shows the procedure used. The best results were obtained when the phosphorus-containing ligand had phenyl substituents on phosphorus. This is very likely due to the high ceramic yields obtained in the pyrolysis of the Class 1 precursors. Because, in this application, the compounds used as binders are present in the green body to the extent of about 17% by weight (Table II), the excess of carbon in their pyrolysis residue is less of a disadvantage than when the pure precursors are pyrolysed. Other weight ratios of binder to ceramic powder were investigated, but, in general, the 17% binder content gave the best results. Of the various systems studied (Table II), the one in which $B_{10}H_{12} \cdot 2Ph_3P$ was used as binder for elemental boron powder should be the best in terms of potential useful application. Firing at higher temperature should result in reaction of elemental boron with the free carbon to form boron carbide, a process that is known to take place at around 1600° C [27]. It should be noted that our evaluation of binders as "excellent", "good" and "fair" is based on the degree of shape retention of a fired composite bar as compared to the unfired, pressed composite bar, as well as on a qualitative estimate of strength. Quantitative strength tests were not undertaken for every sample in this orientational study.*

Covalent, unimolecular compounds, in general, would not be expected to be suitable "low loss" binders due to their volatility at temperatures prior to complete thermal decomposition. In the $L \cdot B_{10}H_{12} \cdot L$ adducts, however, we are dealing with covalent, unimolecular compounds which are converted to nonvolatile salts, $[LH^+]_2[B_{10}H_{10}^{2-}]$, by relatively mild heating, so that on further heating no material is lost except for the volatiles released in the pyrolysis itself. This unique chemistry makes these materials unexpectedly good binders.

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*A fired composite bar produced as described in Fig. 2 from B_4C and $B_{10}H_{12} \cdot 2Ph_3P$ gave a strength of $\sim 1 \times 10^8$ nt m^{-2}. We thank Mr. Garry Garvey of the Massachussetts Institute of Technology, Department of Materials Science, for this measurement.

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