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Suspension properties of hexagonal BN powders: effect of pH and oxygen content

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Suspension characteristics for two types (HCV and HCP) of hexagonal boron nitride (h-BN) powder have been examined and correlated to the amount of boric oxide present (B_2O_3) on the BN surface. The effects of B_2O_3 on the suspension behavior of HCV-BN and HCP-BN were determined by measuring the zeta (ζ) potential and viscosity as a function of pH. Results indicate the poor suspension quality of HCV-BN powders is linked to the increased presence of B_2O_3 on the particle surface. Because of its weak ionization characteristics, B_2O_3 acts to prevent stable suspension formation by decreasing the double layer length, thereby lowering the barrier to agglomeration. Hence, as the amount of B_2O_3 increases on the HCV-BN powder surfaces, the stability decreases and the particles agglomerate, rapidly settling out of higher viscosity suspensions. In contrast, HCP-BN having less B_2O_3 on the powder surface, exhibits higher ζ-potentials and increased stability against agglomeration. Therefore, HCP-BN forms suspensions of single, unagglomerated particles which are less viscous, settle at a slower rate and are more suitable for slip casting operations. © *1999 Kluwer Academic Publishers*

1. Literature review

Boron nitride is widely used both as a refractory and lubricant and has a layered structure similar to graphite. Its lubricious properties are due to weak bonding between adjacent hexagonal layers which provide easy shear. BN maintains its low frictional coefficient up to 900 °C, whereas other lubricants, including graphite, burn off at lower temperatures [1]. These refractory properties are aided by excellent oxidation and corrosion resistance. Some of the more specific applications for BN include: insulators for high-temperature furnaces, where it is used as connector material for heating elements, protection and insulation for thermocouples, and as break rings for horizontal continuous casting of steel due to its' chemical inertness, thermal stability, and non-wetting properties [1, 2]. BN is also used with alumina for refractories, in silicon nitride composite structures, and with elastomers and thermoplastics [3].

BN powder is produced by reacting boric oxide (B_2O_3) also known as borax, a naturally occurring oxide, with an organic nitrogen compound such as urea or melanine as shown in Equation 1.

$$B_2O_3 + CO(NH_2)_2 \xrightarrow{1000\,^\circ C} 2BN + CO_2 + 2H_2O \quad (1)$$

The majority of these powders are initially in the form of hexagonal or altered hexagonal structure (Turbostratic) [4, 5] which subsequently transform during sintering to a cubic structure. Most methods produce particles having a plate-like particle morphology, a characteristic density of 2.27 g/cm^3 and a melting point of 2600 °C. It is important to note that B_2O_3 is a by-product of BN powder manufacturing and is the most common impurity in h-BN powders.

Due to difficulties associated with sintering, hot pressing (HP) and hot isostatic pressing (HIP) are the primary methods for producing dense BN products from powder. Since consolidation temperatures often exceed 2000 °C for HP and 1500 °C for HIP, sintering aids such as B_2O_3, are added to promote densification. Table I displays properties of h-BN for both HP and HIP samples having various B_2O_3 contents. These measurements show that increased amounts of B_2O_3 yield modest increases in the room temperature flexural strength of h-BN but decreases high temperature flexural strength and increases room temperature electrical resistivity. Thus, for high temperature applications, it is important to limit the B_2O_3 content without jeopardizing component density. Because both HP and HIP often use pre-sintered components which have been slip cast from high solids content suspensions, the relationship(s) between the B_2O_3 content and the slip behavior of the powder suspension must be understood. This study links the level of B_2O_3 in the powders to the suspension processing behavior which in turn effects the green component density, the final density and hence, the resulting mechanical properties.

Slip casting typically involves low viscosity suspensions of well-dispersed particles where the amount of agglomeration, and hence the viscosity, is influenced

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TABLE I Selected characteristic properties of h-BN (taken from Lipp *et al.* [1])

Property	Temperature (°C)	HP-BN ($6.0\,\text{wt}\%\ B_2O_3$)	HP-BN ($1.7\,\text{wt}\%\ B_2O_3$)	HIP-BN ($0.1\,\text{wt}\%\ B_2O_3$)
Sintered density	25	2.1	2.0	2.2
Flexural strength, MPa (4-pt bend)	25	115⊥ 50∥	95⊥ 70∥	60
	1000	20⊥ 10∥	35⊥ 20∥	45
Electrical resistivity, Ω cm	25	9.3×10^{10}	4.9×10^{12}	6.3×10^{13}
	1000		10^{7}	10^{8}

The mechanical and thermal properties of hot-pressed BN (HP-BN) are anisotropic—they differ when measured perpendicular (⊥) and parallel (∥) to the pressing axis. On the other hand, these same properties are isotropic for hot isostatic pressed BN (HIP-BN).

by the powder surface characteristics. Upon contact with the liquid medium, surface species may ionize, producing a net charge at the particle surface. This surface charge attracts oppositely charged species from the fluid, which migrate and absorb at the particle surface. The density of this layer varies directly with the strength of the surface potential and is known as the Stern layer [6]. The Stern layer is generally considered to be one ionic radius thick, and varies with the size of the ions present in the media [6]. Other molecules interact with the newly formed surface layer but show a dramatic decrease in attachment strength. These weakly held ions are easily removed and replaced through collisions with other molecules. This layer represents the shear layer which is not as tightly bound to the particle surface as the Stern layer [7].

One factor affecting particle ionization is the type of electrolyte solution used. Electrolyte ions with a high affinity for surface groups will create a high potential, while low potentials are a result of a low affinity. The electrolyte concentration affects ionization by changing the number of ions present in the suspension. Similarly, the pH or the acid/base nature of the solution will change the double layer thickness, altering the degree of agglomeration. The attraction of negative surface ions will be higher in acidic solutions whereas positive ionization occurs in more basic media. Thus, there exists a dependence of double layer thickness on pH, electrolyte type, and electrolyte concentration. The thickness of the double layer, known as the Debye length ($1/\kappa$), is measured according to the following equation.

$$\kappa = \sqrt{\frac{e^2 \Sigma n_i^0 z_i^0}{kT}} \tag{2}$$

It is the combination of attractive (van der Waals) and repulsive forces acting on the particles which yields either agglomerated or a dispersed suspension according to Derjaguin and Landau [8], and Verwey and Overbeek [9] (DLVO) theory. Here the net interaction between particles is given by a summation of the attractive and repulsive energies V_A and V_R, given in Equation 3.

$$V_T = V_R + V_A \tag{3}$$

A repulsive force arises when particle double layers overlap. Upon close approach, these ion layers are pushed together, generating a repulsive force. For spherical particles of equal radii, this repulsive force is given by [6]:

$$V_R = 2\varepsilon_0 \varepsilon_R \psi^2 \ln[1 + \exp(-\kappa H)] \tag{4}$$

where ε_0 and ε_R are the permitivity in a vacuum and the relative permitivity, respectively, while ψ is the particle surface potential and H is the distance between the particle surfaces. This surface potential however, is not readily measurable because of the continuous ion activity at the particle/fluid interface. Therefore, the surface potential is estimated at the double layer by the experimentally obtainable zeta (ζ) potential.

Charge density at the shear plane varies with the double layer thickness because the surface potential decreases with increasing distance from the particle surface. Thus, there is a direct dependence of ζ-potential on double layer thickness. The ζ-potential in turn is related to the concentration of ions in the medium, their valence, and the type of electrolyte used. The ζ-potential is a measure of the potential difference arising from a particle exposed to an electric field. The Smoluchowski equation [7]:

$$\zeta = \frac{\eta v}{\varepsilon_0 \varepsilon_R} \tag{5}$$

describes the ζ-potential assuming a large κa, where a is a measure of the particle radius of curvature, η is the fluid viscosity and v is the electrophoretic velocity.

Attractive energies in DLVO theory are governed by van der Waals forces [10]:

$$V_A = -A\left(\frac{a}{12H}\right) \tag{6}$$

where a is the radius of the particle (μm), H is the interparticle distance (μm) and A is the Hamaker constant which acts as a correction term for molecular interactions between particles and the liquid medium.

2. Experimental

The focus of this study was to determine the ζ-potential as a function of pH for several electrolyte concentrations and to correlate these results to viscosity measurements, B_2O_3 surface content and visual observations for two different types of commercially available h-BN powders. The ζ-potential was experimentally calculated from electrokinetic sonic amplitude (ESA) data as a function of pH. This method applies an alternating electric field to a suspension, thereby oscillating the particles, producing acoustic waves. Analysis of these wave oscillations provides information on the mobility of the particle which is used to calculate the ζ-potential. ESA measurements[*] were collected as a function of pH according to the following procedure. 0.5 vol % (1 ml) powder samples were dispersed into a stirred $NaNO_3$ electrolyte solution at a concentration of 10^{-3} N. The suspension pH was lowered to pH 3 using 1 M HNO_3. Ultrasonic agitation was employed to disrupt any agglomerates before ESA measurements were taken. The pH range for ESA analysis was from 3 to 10 using a basic titrant (1 M NaOH).

Type HCV-BN[†] powder has a spherical morphology and a manufacturers reported particle size of 1–5 μm with an average diameter of 2.5 μm and a B_2O_3 content of $\leq$1%. Type HCP-BN[‡] powder has a plate-like morphology and a manufacturers reported diameter of 17 μm with a B_2O_3 content of 0.19%. The particle size was verified by Scanning Electron Microscopy (SEM) which confirmed the manufacturer's reported particle sizes of 2.5 μm for the HCV-BN and 17 μm for the HCP-BN. B_2O_3 contents were verified using transmission infrared spectroscopic analysis[§] [11].

3. Results and discussion

ζ-potentials for HCV-BN and HCP-BN at 10^{-3} N $NaNO_3$ are plotted as a function of pH and shown in Fig. 1. The HCV-BN powder possesses its maximum ζ-potential at pH 8–10, where $\zeta \approx -17$ mV. ζ-potentials of stable, dispersed suspensions are typically greater than $|\pm 25.7|$ mV. Thus, the ζ-potential results indicate suspensions of HCV-BN powder will not be stable throughout the range of pH 3–10. This conclusion was confirmed by visual observation. Experimentally, it was relatively easy to disperse and create a suspension using the HCV-BN powder, but the powder settled out of suspension within 15–20 s. This short time period is incompatible with most slip casting operations. While ESA measurements were made using 0.5 vol % powder concentrations, suspensions of 1.0 vol % HCV-BN were possible.

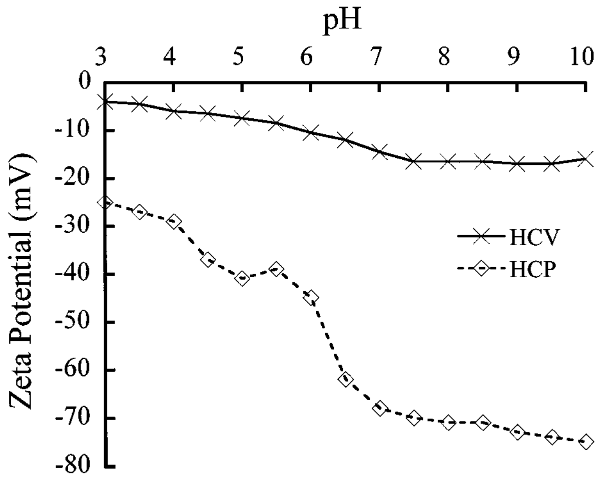

Figure 1 ζ-potential versus pH for HCV-BN and HCP-BN in 10^{-3} N $NaNO_3$ as determined by Electroacoustic Sonic Amplitude measurements (0.5 vol % solids).

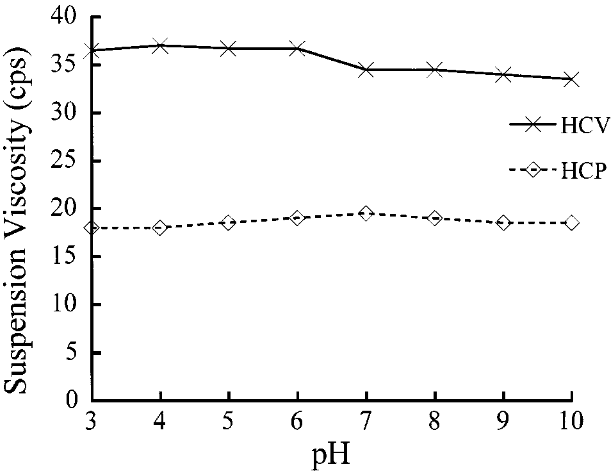

Figure 2 Viscosity (cps) versus pH for HCV-BN and HCP-BN in 10^{-3} N $NaNO_3$ electrolyte (0.5 vol % solids).

The ζ-potential curve for HCP-BN is markedly different from the ζ-potential curve for the HCV-BN. The HCP-BN powder shows a significant ζ-potential ($\zeta \approx -60$–80 mV) from pH 6–10, indicating a large region of stability where the HCP-BN powders will form stable suspensions. It should be noted that it was somewhat problematic to prepare suspensions of HCP-BN powder, even in the predicted stable pH range, because it was difficult to wet the powder. A thin film of HCP-BN powder formed on the surface of the electrolyte which acted as a barrier to dispersion, thereby preventing additional powder from contacting the electrolyte. This limited the amount of HCP-BN powder entering suspension to 0.5 vol % solids in contrast to the 1.0 vol % HCV-BN suspensions. Attempts to create 1.0 vol % HCP-BN suspensions resulted in clumps of non-dispersed HCP-BN powder which yielded inconsistent ζ-potential data. However, once the HCP-BN powder was successfully dispersed into the electrolyte, the powder remained suspended for up to 10 minutes, compatible with slip casting requirements.

Viscosity measurements[**] were collected at rotational speeds of 1.5 to 60 rpm using the HB series spindle set. Suspensions were prepared in 10^{-3} N $NaNO_3$ electrolyte in the same manner as for the ESA measurements. Measurements were made as a function of pH for both HCV-BN and HCP-BN powders, and are shown in Fig. 2. Viscosity values were calculated from the torque readings using the manufacturer-supplied spindle factors. Both the HCV-BN and the HCP-BN powder show little variation in viscosity with changing pH. Comparing the two powders, the HCV-BN powder suspension is twice as viscous as suspensions of HCP-BN powders. This is consistent with the ζ-potential results where the HCV-BN powders were predicted to form agglomerated suspensions which would be expected to have higher viscosities when compared to suspensions of

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[*] Model S8000, Matec, Inc., Hopkinton, MA.

[†] Advanced Ceramics Corp., Lakewood, OH.

[‡] Advanced Ceramics Corp., Lakewood, OH

[§] Nicolet 170SX, Nicolet Instrument Corp., Madison, WI.

[**] Model DV-II digital viscometer, Brookfield Engineering, Stoughton, MA.

TABLE II Qualitative comparison of suspension characteristics for HCV-BN and HCP-BN

Powder	B_2O_3 content	Particle diameter	ζ-potential	Viscosity	Dispersion quality
HCV	$\leq 1\%$	2.5 μm	Moderately negative ≈ -17 mV	More viscous	Disperses easily but settles in 15–20 s
HCP	0.19%	17 μm	Highly negative ≈ -60–80 mV	Less viscous	Harder to disperse; but remains in suspension for up to $\approx$10 min

single particles. A summary of the ζ-potential and viscosity measurements along with observations about the suspension quality are listed in Table II.

Particle size differences cannot account for the variations in suspension behavior between the HCV-BN and HCP-BN powders. Indeed, contrary to expectations if only gravitational forces were acting on the particles, the larger diameter HCP-BN powder (17 μm), with its higher ζ-potential, remains in suspension for longer times when compared to the smaller diameter HCV-BN powder (2.5 μm) having lower ζ-potentials. At 17 μm, the HCP-BN powder falls at the outer limits where colloidal interactions dominate gravitational forces. Instead of particle size differences, it is the difference in the amount of B_2O_3 present on the two powders which determines the degree to which the powders form stable, dispersed suspensions. It is known that B_2O_3 reacts in aqueous medium according to the following reaction.

$$B_2O_3 + 3H^+ + 3OH^- \Leftrightarrow 2H_3BO_3 \qquad (7)$$

Because the HCV-BN has more B_2O_3, it will undergo this reaction to a greater extent in both acidic (H^+) and basic (OH^-) suspensions forming greater amounts of H_3BO_3 (or $B(OH)_3$), a weak, monobasic acid in solution as shown in the schematic diagram of Fig. 3. H_3BO_3 forms a layered structure with extensive hydrogen bonding between adjacent H_3BO_3 molecules. This allows the H_3BO_3 molecules to slide over each other during mixing. Such a structure would account for the ease at which the HCV-BN is dispersed, while at the same time, its lower ζ-potential values would cause agglomeration, giving its higher viscosity measurements. In contrast, the HCP-BN powder, having less B_2O_3, formed less of the layered H_3BO_3, remaining unagglomerated because of its high ζ-potential values. These unagglomerated particles, having an increased suspension stability, account for the lower viscosity measurements.

In a similar study, by Williams and Hawn, B_2O_3 was linked to both the degree of dispersion and the green density of slip cast boron carbide components. They found that increasing amounts of B_2O_3 decreased the ζ-potential, resulting in agglomerated powders, higher viscosity suspensions and lower density green components [12].

4. Conclusions

ζ-potentials as a function of pH indicate significant stability ranges (pH 6–10) for HCP-BN powder suspensions in contrast to HCV-BN powder suspensions which do not display appreciable stability throughout the entire pH range tested (pH 3–10). The major differences between the two powder types are oxygen content and particle size. The greater oxygen content, in the form of B_2O_3, in the HCV-BN powder is believed to prevent suspension stability by forming B_2O_3, a weak, monobasic acid which does not readily ionize. This reduces the repulsive forces at the particle surface by creating only a small surface potential and therefore a thinner double layer. Having less of a double layer to repulse adjacent particles, the HCV-BN particles are overcome by the forces of attraction, forming agglomerates making the suspension unstable. This reduced double layer in combination with the "slippery" layered structure of the resultant H_3BO_3 accounts for both the higher viscosity and the ease of dispersion at lower ζ-potential values. HCP-BN powders have less B_2O_3 to depress the surface double layer and yield greater ζ-potentials and more stable, less viscous suspensions, more suitable for an industrial application such as slip casting.

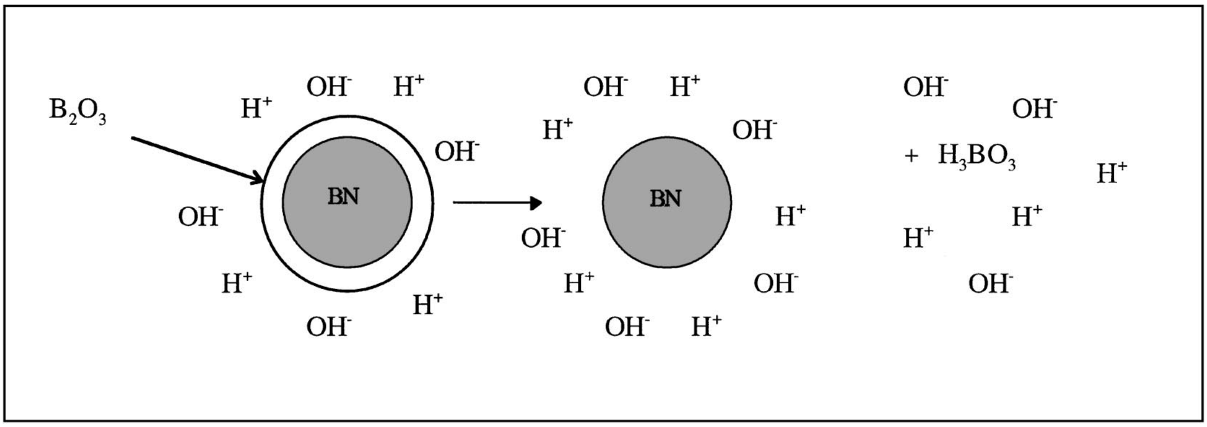

Figure 3 Schematic ionization reaction for B_2O_3.

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References

1. A. LIPP, K. A. SCHWETZ and K. HUNOLD, *J. Eur. Ceram. Soc.* **5**(1) (1989) 3.
2. T. ABRAHAM, *J. O. M.* **44**(8) (1993) 6.
3. L. VEL, G. DEMAZEAU and J. ETOURNEAU, *Mater. Sci. Eng. Biol.*, (1991).
4. D. A. LELONIS, *Ceram. Ind.* (1989) 57.
5. J. THOMAS, JR., N. E. WESTON and T. E. O'CONNOR, *J. Amer. Chem. Soc.* **84**(24) (1963) 4619.
6. D. J. SHAW, "Introduction to Colloid and Surface Chemistry," 4th ed. (Butterworth Publishing, Boston, 1992).
7. S. ROSS and I. D. MORRISON, "Colloidal Systems and Interfaces" (John Wiley & Sons, New York, 1988).
8. B. V. DERJAGUIN and L. D. LANDAU, *Acta Physicochim. URSS.* **14** (1941) 633.
9. E. J. W. VERWEY and J. Th.G. OVERBEEK, "Theory of the Stability of the Lyophobic Colloid" (Elsevier, Amsterdam, 1948).
10. A. BLEIER, *J. Amer. Ceram. Soc.* **66**(5) (1983) C-79.
11. K. KREHBIEL, B.S. thesis, Michigan State University, 1994.
12. P. D. WILLIAMS and D. D. HAWN, *J. Amer. Ceram. Soc.* **74**(7) (1991) 1614.

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