

## The Surface Chemistry of Diamond Dispersions

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### Introduction

Ultrafine superabrasive particles in the 50nm -2mm range are currently used in the electronics market for texturing and lapping applications. At the lower end of this size range, only a few hundred carbon atoms span the length of the particle. Based on size alone, these particles may be categorized as "colloids." It is clearly evident under an optical microscope that Brownian motion of ultrafine particles does not follow a completely unrestricted random path. In a highly dispersed system, particles lower their energy by maximizing the space between nearest neighbors. When conditions favor flocculation, the particles are attracted to each other forming clusters of various sizes and shapes. An ultrafine particle dispersion is perhaps better characterized as a "colloidal state of matter", which includes not only the particle size and type, but also, of equal importance, its surface characteristics, the surrounding ionic matrix, and inter-particle forces (1) (figure 1).

For any two-component system, such as diamond in aqueous media, it can be shown that particles composed of the same substance always attract each other regardless of the nature of the fluid phase (2) (the deBoer-Hamaker theorem). The most likely mechanism responsible for long-range attractive forces is the stabilization of the zero point energy due to alignment of instantaneous electric moments with nearest neighbors. In the absence of any other forces, one might expect that particles in suspension should always agglomerate.

The surfaces of solids, particularly superabrasive materials, have characteristically high surface energies. Atoms at the solid-gas or solid-liquid interface are essentially cut off from the atoms in the bulk solid phase (figure 2). Both natural and synthetic diamond colloids are typically produced by fragmentation of larger diamond pieces. Since fragmentation occurs most readily from a defective plane, the surfaces of diamond colloids will be enriched in metallic contaminants. These high-energy surfaces readily adsorb both gases and liquids to reduce the solid-fluid surface energy.

In an aqueous environment, ions, together with their associated hydration spheres, preferentially adsorb into the interfacial region. The first layer or two, referred to as the Stern layer, is a tightly bound, relatively immobile layer. The outer layer, which is about three to ten ionic atmospheres thick, is more diffuse and mobile relative to the inner layer. The potential difference between the bulk solution and the diffuse outer layer is the zeta potential (figure 2). Most naturally occurring substances have a negative zeta potential. The magnitude of the net surface charge is often greater than the inter-particle attractive force. Such systems remain dispersed for long periods of time even though the particle density is 2-3 times that of water. The manufacture of stabilized sols and suspensions strongly depends on the delicate interplay between attractive and repulsive forces in the colloidal system.

A colloidal system with no net charge on the particle is defined by IUPAC as the isoelectric point (iep). For most colloidal systems, the instability region is coincident with the iep. In this study, the instability regions of three synthetic diamond sizes (0.25mm, 0.50mm, and 1.0mm) were identified by measuring Zeta potential as a function of ionic strength. The microelectronics community continuously demands lower amounts of ionic contaminants. We will also show

that ions are actually a pre-requisite for the production of diamond dispersions. If we theoretically wash all ions from the diamond surface, no charge buildup would be possible, and hence the dispersion would flocculate. Since ions are inherently present with all diamond dispersions, it would also be useful to study the effects of increasing cation charge on the zeta potential. Solutions of Sodium (+1), Calcium (+2), and Iron (+3), all chlorides, were studied to compare the effect of charge on surface penetration. As a functional test, the influence of zeta potential on grading parameters was investigated. Finally, the treatment of "difficult feeds" with dispersants will be discussed.

## Experimental

The diamond samples chosen represent approved 0-0.5mm, 0-1.0mm, and 0-2.0mm finished goods materials. The diamond samples were synthetic and monocrystalline. All abrasive concentrations were 2% or 25cts/250g. The water used was doubly deionized and filtered through a 0.5mm cartridge filter. The conductivity of the DI water was less than 0.06micromhos/cm. The salts used were Fisher certified grade. The concentration of all salt solutions used in the additions was 2.5g/100gDI water. The CBN used was a purchased feedstock, not finished goods inventory. The material used to disperse the CBN was a commercially available surfactant.

The zeta meter used was an ESA 9800 Zeta Potential Analyzer from Matec Applied Science combined with a Hamilton Microlab 500 auto diluter. All readings were based on a 20% Ludox TM-50 standard solution (-38mv). The stir rate was set to 3.5 for all runs. The temperature was room temperature 20oC, but the water used was 17oC± 2oC. The optical microscope pictures were taken with an Olympus BH2 microscope with a 20x objective. The slides were prepared by placing one drop onto the surface and observing the edge. A cover slip was not used to preserve the integrity of the dispersion. The particle size distributions were measured with a Horiba 920 Particle Size Analyzer. The ion types and concentrations were analyzed with a Dionex ion chromatography system. The system consisted of an EG40 eluent generator, an LC 25 chromatography oven, a CD20 conductivity detector, and a GP 50 gradient pump. Dionex A.S.T.M. standards were used to calibrate the instrument. The conductivity meter used was a Cole-Palmer 1500-00 that was calibrated with Fisher 10 micromho/cm conductivity standard. The centrifuge model and equipment is a trade secret.

## Results

### *Zeta Potential Measurements*

The Zeta potential of the following systems was measured a) three different diamond sizes of synthetic monocrystalline diamond with constant cation type b) a series of increasing cation valences with constant diamond size. The plots in figure 3 show the correlation between diamond size and sodium ion addition. The initial regions of the graphs are quite steep and may be expanded with more dilute additions. However, the current study focuses on a full range of concentrations in attempt to identify stability regions and the iep. The initial sodium concentrations increase the zeta potential of diamond in the following order: 0.25mm>0.50mm >1.0mm. The zeta potential does not approach the iep for the sodium series even though microscope observations clearly show the diamond is agglomerated. The calcium curves in figure 4 nearly overlap and are much closer to the iep than the sodium series with the same concentrations. The iron series curves intersect the iep and change sign at higher concentrations. Figures 6-8 all indicate that the order of increasing zeta potential in a positive direction follows Fe<sup>3+</sup>>Ca<sup>2+</sup>>Na<sup>+</sup>.

### *Optical Microscopy*

Figure 9 shows optical microscope pictures of the sodium addition to 0.25mm monocrystalline diamond. At 0.75mls of sodium solution (A), the suspension is dispersed. The inter-particle spacing diminishes and agglomeration appears after 2mls have been added (B). After 3.5mls, the diamond is visually agglomerated (C). In comparison, figure 10 shows pictures of the addition of sodium to diamond with a mean value of 0.50mm. The diamond is dispersed after the addition of 0.50mls (A), but is visually agglomerated after 2.5mls (B). Agglomeration of 1.0mm mv diamond is clearly evident after only 1.5mls of the sodium solution (B). At higher concentrations, the solution surrounding the agglomerated regions increases in clarity (C). The pictures of the calcium series in figures 12-14 are all very similar. Agglomeration is evident immediately after the first 0.25ml addition. The outlying solution from the agglomerate is very clear. The clarity is evident at much lower concentrations than the sodium series. The pictures of the iron series (figures 15-17) are all similar to the calcium series with the exception of the 1.0mm diamond. The magnitude of the positive zeta potential re-stabilized (B) the dispersion after agglomeration was evident at lower concentrations.

### *Functional Test*

Figure 9 and 10 represents the grading functional test corresponding to the zeta potential vs. sodium addition graphs. The tests labeled I through IV represent 0ml, 0.5ml, 1.0ml, and 8.0ml additions of the sodium solution to 90 carats of the 0.25mm and 0.50mm diamond respectively. The centrifuge experiments were designed to study the effects of sodium on yield and psd. For the 0.25mm diamond, the supernatant contained 81.5%, 78.6%, 77.5% and 75.8% of the initial concentration from bottle I through bottle IV. This corresponds to the plug increasing from 18.5% to 24.2%. The 0.50 diamond showed similar trends. The supernatant decreased from 86.3% to 79.6% while the plugs increased from 13.7% to 20.4%. Figures 20 and 21 both indicate that the most efficient cut (corresponding to finest supernatant and coarsest plug) occurred in II.

### *Troublesome Feeds*

Figure 22 represents the ionic species in the solutions of the four abrasives in this study. This represents a total conductivity of 6.0, 2.8, 1.8 and 7.6 micromhos/cm, respectively. The ionic levels decrease from 0.25mm to 1.0mm for the monocrystalline series. The CBN feed has a similar level of ionic impurities, however it is enriched in calcium. The addition of commercially available dispersing agent to CBN is shown in figure 23. The optical microscope pictures showing the conversion from the agglomerated state to a fully dispersed state are shown in figure 24. Figure 25 shows two 100ml graduated cylinders, one filled with untreated CBN and one filled with treated CBN. The cylinders were allowed to sediment for 24 hours. After 24 hours, the sediment measured 7.0 mls in the untreated cylinder, while the treated cylinder had only 2.0 mls of sediment. The solution above the untreated CBN contained only 0.33 carats and the solution above the treated CBN contained 2.73 carats. Both containers initially contained 100 carats.

### **Discussion**

Since the first calcium addition agglomerated all three sizes, only the initial diamond dispersion was stable. The stability region for the sodium series is possible to characterize since the cation adsorption into the surface region was much less aggressive than the calcium series. The optical microscope images combined with the sodium addition graphs suggest that a stable

monocrystalline diamond dispersion must contain a zeta potential of at least -60, -70, and -80 for 0.25, 0.50, and 1.0 micron diamond respectively. The point, which corresponds to the abrupt change in slope, is a good indicator of the lower limits of the stability region. These results clearly indicate that the inter-particle attractive dispersion force, which may be treated as the sum of all atomic dispersion forces, increases with increasing mean value of the particle size distribution. It is also very important to note that the flocculation point for diamond is unrelated to the iep.

All things being equal, why does chloride, not sodium, show preferential adsorption in the surface region? Energetically, the sodium cation should stabilize the dispersion to the same degree by aligning the instantaneous diamond dipoles and charging the surface. If the energy terms are equal, the preferential adsorption of chloride ion must be due to the entropy component of the free energy. Most of the commonly occurring anions, particularly chloride and nitrate, are electrostatic structure breakers. These ions, when dissolved in water from a crystal, increase the disorder of water. Cations such as sodium, calcium and iron are associated with 13, 29, and > 40 water molecules, respectively (3). These ions are more structure making in nature than small, singly charged anions. The surface is essentially competing for a single negative charge or a single positive charge with increased structure and order. Considering the second law of thermodynamics, the latter should prevail. The diamond/sodium chloride system is consistent with nature in that the surface is negatively charged.

The addition of the sodium chloride solution compresses the double layer, essentially reducing the shielding effect of the charged surface. The calcium ion most likely begins to penetrate the double layer as evident from the near-zero surface potential. The +3 cation actually replaces the anion as the predominant species at the surface. The iron cation in the diffuse layer increases the order in this region, but this effect is certainly offset by the greater attraction of the particle for the +3 ion and loss of some waters of hydration in the first adsorption layer.

The sodium concentrations in the centrifuge functional test were targeted II) in the steep region, III) in the region with maximum slope change, and IV) in the visibly flocculated region. One might expect complete sedimentation in IV, since the particle masses in an agglomerated system are additive in a centripetal field. The results show a definitive increasing trend towards higher plug concentrations in both the 0.25mm and 0.50mm diamond samples. The diamond in bottle IV, however, did not migrate completely to the plug. To some extent, particles in an increased gravitational field flow independently. This can also be observed in a clear bottle of agglomerated diamond. If the bottle is quickly rotated by hand, the clusters disappear for a moment and then reappear. The plug size of IV was also out of proportion to the carat quantity in I-III (visual observation). This observation is typical in agglomerated systems since higher packing densities are offset by the dendritic structures of the agglomerated diamond.

Another subtle difference in the grading functional test is the psd trend from I to II. For both diamond sizes, this was the most efficient cut. The surface charge of the colloidal system in II was lower than I, however the magnitude is still sufficient for full dispersion. The movement of the larger particles in the system may be retarded somewhat by a very large repulsive force. For example, a larger particle, surrounded by 6 smaller ones, may be trapped momentarily in a repulsive cage. If this restriction is relaxed by decreasing the zeta potential slightly, the particle may travel more independently in the field. The efficiency of cuts as a function of zeta potential is well worth pursuing in future work.

The dispersion of feedstocks with only trace amounts of contamination is critical to the abra-

sive manufacturing industry. The CBN feed studied in this work had very similar ion concentrations as the diamond samples. The only difference is the calcium ion present in the ppm concentration range. It is evident that the ion is strongly associated with the surface region and aggregates the particles. The addition of small quantities of commercially available "dispersing" agent increased the zeta potential in the negative direction enough to visually stabilize the dispersion. About 28% remained in suspension after a one-day sedimentation experiment. The sediment in this case was visually close-packed, a good indicator that the system will run efficiently in an elutriation process. The stabilization mechanism is most likely a selective removal of the calcium ion from the interface, unlike the ionic adsorption of surfactant or highly charged cations. It is important to monitor the zeta potential as a function of dispersant concentration. The addition of too much dispersant will typically re-flocculate the dispersion by compressing the double layer with added electrolytes.

## References

1. Gushee, D.E. ED.(1965) Chemistry and Physics of Interfaces, American Chemical Society Publications, Washington, D.C.
2. Ross, S. and Morrison, I.D. (1988) Colloidal Systems and Interfaces, Wiley, New York
3. Wulfsberg, G. (1987) Principles of Descriptive Inorganic Chemistry, Brooks/Dole Publishing Company, Belmont California.