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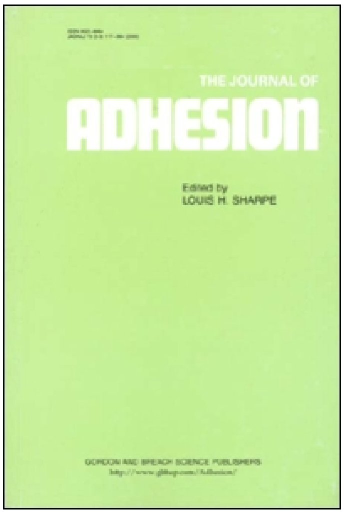

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Aerosol and Solution Modification of Particle-Polymer Interfaces

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Aerosol and Solution Modification of Particle-Polymer Interfaces *

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In recent years several investigators have focused on the synthesis of uniformly and continuously coated particles to impart improved chemical stability, mechanical strength, morphology and/or dispersibility to powders required for preparing next-generation composities. This paper reviews two *in situ* reaction methods employed at Clarkson University to selectively coat individual particles having widely different shape, size and chemical composition. The aerosol procedure allows core particles to become coated using room temperature liquid-gas reactions. Alternatively, coating particles dispersed in a solvent containing reactive precursors is more applicable to industrial processing. Uniform, well-adhering coatings of polyurea on titania powder, of polydivinylbenzene on silica beads, and of carbon and boron nitride on silicon carbide whiskers were made by selecting the correct precursors and reaction chemistries. Qualitative assessment of adhesion between the coatings and cores is given.

Keywords: Particle coating; silicon carbide whiskers; boron nitride coating; polymer coating; particle interfaces; coating adhesion

INTRODUCTION

The phenomenon called "adhesion" is defined as the energy of interaction between two surfaces in contact with each other. Such forces play huge roles in the practical world where manufactured goods must hold together to just the right degree for product function.

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As a result, numerous studies have focused on adhesion using at least one macroscopic surface, and on understanding at the molecular level how chemically similar and dissimilar substrates stick together. Coating of large surfaces to improve their aesthetic value or biological, chemical or physical functions are examples.

Adhesion technology is also important in the field of fine particle processing and this review paper discusses how scientists in the author's laboratory have employed two divergent techniques to prepare new particle composites having excellent adhesion of the coating to the core. It is axiomatic that only through surface modification of particles can next-generation composites become a reality. Core surfaces must be altered through deposition of a material to improve such characteristics as dispersibility, stability, electrical or thermal conductivity, and mechanical strength. Once altered, the adhesion between the surface of a particle and the coating material becomes the critical issue and can only be evaluated after a variety of chemical compositions and morphologies become available. Presented are data on coated particles prepared by an aerosol flow reaction process or by batchwise reactions of powders dispersed in liquids. The prepared composites are polyurea on titania, polydivinylbenzene on silica and carbon and boron nitride on silicon carbide. The bulk of this paper is on the latter system.

REACTIONS OF AEROSOLS

The experimental conditions pioneered at Clarkson University to convert droplets of a reactive substance into their corresponding product powders are well known [1–6]. Evaporation-condensation or nozzle spray methods can be employed to generate droplets of controlled size and distribution. When passed under laminar conditions through a manifold containing a coreactant vapor, the droplets react to produce discrete spherical solids as product. Oxides of aluminium, titanium and zirconium and addition and condensation organic polymers have been generated by this method.

Interfacial and adhesion issues between core and coating must be considered when particles composed of more that one chemical species are prepared by the aerosol procedure. Their morphology depends on the relative reactivity of the individual components in the droplets and the sequence in which they are admitted into the carrier gas stream. Examples are mixed metal oxides enriched in one component at the surface [7, 8] and metal oxide particles coated with organic polymer [9]. For the latter, titanium ethoxide droplets were reacted with water vapor in the first section of the flow apparatus. The thus-formed amorphous hydrous titanium dioxide particles carried in the gas stream then entered a vessel saturated with the vapor of an organic diisocyanate. The wetted titania was then exposed to ethylene diamine vapor which caused a polyurea coating to form on the cores. In order to estimate the adhesion of the coating to the core surface it is necessary to consider the chemical reactivity of the species as they are introduced into the system. Isocyanate functional groups are known to react slowly with hydroxyl groups and it is possible that, upon exposure of the diisocyanate to the hydrous titania particles, some reaction takes place with physisorbed water to produce molecules of $R(NH_2)(NCO)$ or $R(NH_2)_2$. These reactions are known to be catalyzed by acids and bases and the isoelectric point of pH 4.5 – 5.5 for titanium dioxide may serve to activate the process. The hydrolysis products are highly polar and relatively nonvolatile at the room temperature conditions employed and, if formed, would remain at the core-diisocyanate interface and could be a factor in promoting the excellent coating results observed (Fig. 1). Experiments have yet to be carried out to determine how much hydrolysis of isocyanate groups takes place in the time before ethylene diamine vapor is introduced downstream.

The diisocyanate vapor condensed on the hydrous titania particles can also react with surface Ti—OH groups. This would result in covalent tethering of the isocyanate to the particle (Ti—O—CONHRNCO). With more diisocyanate plus ethylene diamine vapor, the observed polymer coating is formed.

Two levels of polyurea coating are shown in the TEM micrographs in Figures 1A – B. In 1A the relative mass of the coating is large enough so that the energy of the electron beam does not separate the polyurea from the surface of the titania core. In Figure 1B, however, the separation of the thinner polyurea coating during TEM examination is indicative of little or no covalent interaction between the surface of the titania core and the polymer. That is, the adhesion of the organic coating to the inorganic core does not appear to be very strong

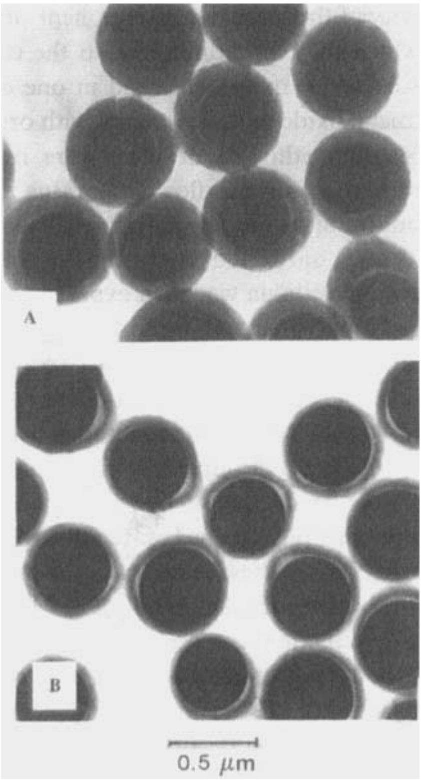

FIGURE 1 TEM micrographs of titania cores coated with different amounts of polyurea formed from toluene diisocyanate and ethylenediamine.

in Figure 1B and, therefore, probably also not in 1A, since the same chemicals were used in both preparations. Therefore, the above mentioned tethering of diisocyanate and then polymer to the core is probably not occurring. It is anticipated that by increasing the contact time of adsorbed diisocyanate on the hydrous titania cores before exposures to amine vapor, the covalent bonding of isocyanate groups, and thus coating adhesion, to the cores will be enhanced.

REACTIONS IN LIQUID DISPERSIONS

A more general technology for coating particles involves deposition of the surface material onto the cores dispersed in a condensed phase. A wider spectrum of core shapes and core and coating compositions can be accessed when reactions are carried out in the presence of a solvent. The technology of physically depositing a coating is mature and widely employed by industry. For example, ceramists apply binders to powders by dispersing the solids in a solution of polymers in a solvent, followed by evaporation of the solvent. Manufacture of ceramics, foods, pharamaceuticals and other products also take advantage of the Würster fluid-bed technique for coating particles. The factor that distinguishes these methods from the dispersion coating procedures being developed at Clarkson University is that in the latter the encapsulating material is being **chemically generated *in situ*** and selectively on the surfaces of the dispersed solids. As a result, the adhesion of the coating to the core is enhanced under specific conditions. This philosophy is not new [10–14] but the core-coating chemical combinations studied by the author are unique and designed for use in imaging, electronic and ceramic materials. Two examples of *in situ* coating where the degree of adhesion of the coating to the core has been visibly observed are described below.

Coating Milling Beads with Polymer

During wet milling, high density metal oxide beads ~ 400 μm in diameter are used to reduce the particle size of powders. In some cases, even slight contamination of the powders by metal oxide mechanically dislodged from the beads is unacceptable. To avoid this problem, experiments have been carried out to coat the beads with several different polymers so that the powders could be crushed while the metal oxide is retained inside the continuous polymer membrane.

Figure 2 shows the fluid-flow apparatus especially designed to coat the dense beads with polystyrene derivatives.

Compartments 1 and 2 were filled with a solution of solvent (~ 1.0 l), monomer (10 ml) and azo or peroxo initiator (1.0 g) up to the bypass tube 3. Beads (100 g) were added to compartment 2, the pump started, and the circulating fluid heated to 100°C. The rate of flow of the solution was adjusted so the beads gently "bobbled" in the stream in compartment 2. After 10 hours the reaction mixture was cooled and the coated particles plus less dense latex were collected and separated. SEM micrographs in Figures 3A–B show the continuity and external

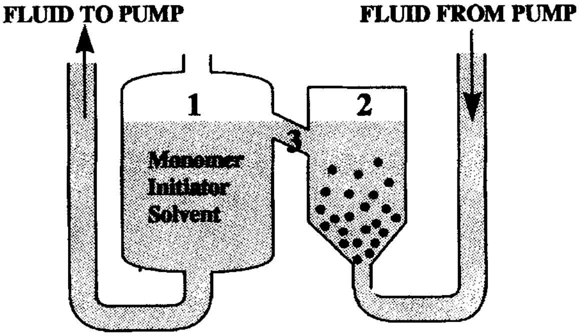

FIGURE 2 Continuous flow reactor for coating dense particles larger than 100 μm diameter with polymer.

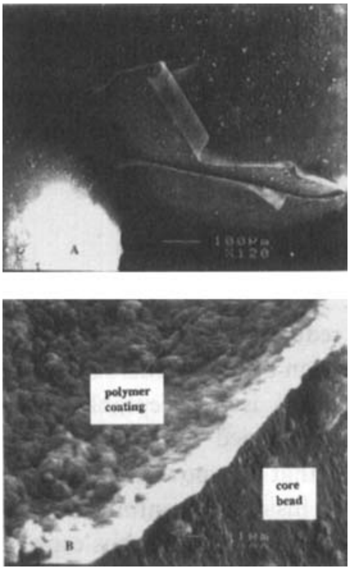

FIGURE 3 SEM micrographs of (A) partial surface of a ~ 400 μm diameter silica bead coated with polystyrene derivative, and (B) portion of a bead surface showing ruptured area of polymer coating.

uniformity of the polymer coating and the thickness of the coating (~ 1.0 μm) at a location where it ruptured during analysis, respectively. As in the case shown in Figure 1B, it is evident from Figure 3B that very little adhesion exists between the surface of a metal oxide bead and the polystyrene film. This is probably due to formation of oligomers in the solvent medium which then physisorb to the surface of the particle and continue to polymerize and to the lack of functional groups on polystyrene to interact with the metal oxide surface.

Coating Silicon Carbide Whiskers with Boron Nitride

Boron nitride (BN) is ideal for use in electronic and ceramic composite applications [15–17]. Recently, BN thin film coatings have been investigated as an interfacial layer to control or alter the bonding in fiber-reinforced ceramic matrix composites [18–25]. However, there is little information on BN film coatings on silicon carbide whiskers (SiCw) to improve chemical stability and enhance whisker/matrix interaction [26].

To take advantage of the reinforcing properties SiCw offers in metal and ceramic matrices, a commercially viable method for producing BN thin films on silicon carbide whiskers using inexpensive borate precursors has been developed. A polymer coating of polydivinylbenzene is first formed on the whisker which is subsequently thermally degraded creating a highly porous carbon layer. The carbonized polymer coating serves to embed precursors to the final BN coating. Three different BN precursors, sodium borate, ammonium borate and boric oxide have been examined. The thickness of the nitride coating can be controlled by varying the thickness of the carbonized polymer layer. The resulting ceramic coatings are uniform, continuous and free of carbon. The method described is an inexpensive, commercially viable alternative to CVD methods.

MATERIALS AND EXPERIMENTAL CONDITIONS

Commercial grade silicon carbide whiskers were obtained from Advanced Refractory Technologies, Buffalo, NY, USA. The average length and diameter of the whiskers was approximately 20 μm by 1–2 μm, respectively. All chemicals were reagent grade from J. T. Baker.

Polydivinylbenzene/Carbon Precoating

The polydivinylbenzene precoat on the whiskers was produced by the following manner. Stock silicon carbide whiskers, 3.125 g, were sonically washed in 200 proof ethanol and dried in a muffle furnace at 200 C for at least 4 hours. The whiskers were placed in a dried 250 ml three-neck round bottom flask equipped with a stir paddle connected to a motor. Next, 100 ml of mineral spirits (boiling pt: 180 – 210 C) dried with magnesium sulfate was added to the flask. The assembled unit was placed in an oil bath maintained at 100 C ± 1 C and the mineral spirits and SiCw allowed to reach thermal equilibrium while stirring before adding 1.25 μl of divinylbenzene monomer. Benzoyl peroxide (0.125 g) was added to the flask within 5 minutes after the addition of the monomer. The reaction was allowed to take place for 1.5, 3, 6, 12, 18 and 24 hours.

Once the reaction had completed, the flask was removed from the hot oil bath and the contents immediately filtered using Millipore® filtration apparatus equipped with nylon filter (pore size approximately 0.5 μm). The polymer-coated whiskers were washed with 200 proof ethanol and allowed to dry under vacuum in the filtration apparatus. The sample was placed in a large alumina boat and inserted into a tube furnace for 10 minutes at 600 C in argon flowing at 10 ml/min to produce silicon carbide whiskers coated with carbon (SiCwC).

Boron Nitride Coating

Sodium borate decahydrate ($Na_2B_4O_7 \cdot 10\,H_2O$), ammonium borate tetrahydrate ($(NH_4)_2B_4O_7 \cdot 4\,H_2O$), and boric oxide ($B_2O_3$) were examined as precursors to BN film formation. The sodium borate decahydrate was dehydrated at 350 C for 12 hours, then ground with a mortar and pestle to break any agglomerates and to reduce the particle size further. The powder was sieved to provide particles with an average diameter less than 20 μm. Boric oxide and ammonium borate were ground and sieved in the same manner as the sodium borate. To compare the ability of each precursor to produce a suitable BN coating, each was mixed with SiCwC, formed by pyrolysis of whiskers coated with 22.5 wt% PDVB, in the following ratios: 0.90 g $Na_2B_4O_7$ or 1.17 g $(NH_4)_2B_4O_7 \cdot 4\,H_2O$ or 0.621 gm B_2O_3 per 1.0 g SiCwC. The SiCwC and borate precursor were mixed by hand with a spatula until the mixture appeared uniform in color, indicating that the borate was uniformly distributed. Each precursor/SiCwC mixture was placed in a large alumina boat and heated according to the following three schedules. After the reactions the furnace was cooled to 300 C before stopping the NH_3 flow.

1. Sodium borate: The $Na_2B_4O_7$/SiCwC mixture was inserted into the tube furnace at 300 C. The NH_3 flow was set at 10 ml/min and allowed to flow over the sample while heating at 20 C/min. The final furnace temperature was set at 1100, 1200, or 1300 C. Once the desired final temperature was attained, dwell times were set at 10, 30, 60, 150 and 480 minutes.
2. Boric oxide: The B_2O_3/SiCwC mixture was inserted into the tube furnace at 300 C and heated to 1200 C at 20 C/min under argon. Fifteen minutes after the sample had reached 1200 C, NH_3 gas was introduced at 10 ml/min as the argon flow was stopped. The furnace was ramped to 1300 C at 20 C/min and allowed to dwell for 150 minutes.
3. Ammonium borate: The $(NH_4)_2B_4O_7 \cdot 4H_2O$/SiCwC mixture was placed in the tube furnace at 80 C. The sample was heated to 105 C at 10 C/min with a 15-minute dwell at 105 C under NH_3 flow at 10 ml/min. Once the dwell period was complete, the sample was heated to 1300 C at 20 C/min. and allowed to react for 150 minutes.

The ability of the carbon precoating to facilitate control of the BN film thickness was examined using SiCwC, formed from SiCw coated with 7.8, 16.5 and 22.5 wt% PDVB, mixed with 0.312 g, 0.66 g, and 0.90 g $Na_2B_4O_7$, respectively. The mixtures were processed according to the above procedure for 150 minutes.

The surface morphology of the BN coating and composition was examined by scanning electron microscopy (JEOL JSM-6300) in conjunction with energy dispersive X-ray spectroscopy (EDX). The thickness of the coatings was determined by transmission electron microscopy (JEOL JEM-1200). X-ray diffractometry (XRD Kristalloflex 710) was employed to determine the crystalline nature of all the coatings formed on the whiskers. Pore volumes and specific surface areas were determined by single point BET nitrogen adsorption using Quantasorb® instrumentation. The Perkin Elmer series 7 TGA apparatus was used to determine the weight percent polydivinylbenzene after polymerization and carbon after thermal decomposition. Compressed air was used as the oxidizing gas in all measurements.

RESULTS

The general scheme describing the reactions discussed in this work is:

SiCw → Polymer coating → Carbon coating
→ BN precursor → BN coating

The polymer coating is unique due to its dual role in the reaction scheme. Its primary function is as a carbon source to absorb the precursor melt which will further undergo nitridation with ammonia at elevated temperatures. However, according to thermodynamic calculations, the carbon also promotes the conversion of B_2O_3 to BN and forms carbon monoxide as a byproduct. As the reaction progresses and boron nitride is formed, the porous carbon layer is consumed resulting in a carbon-free coating. Control of the ceramic coating thickness depends on the quantity and the physical characteristics of the polymer precoating which forms the porous carbon layer on the surface of the whisker.

At 750 C the polydivinylbenzene coating thermally degrades to a pure carbon coating. The maximum coating of 22.5 wt% PDVB, formed at 100°C after about 18 hours, produces roughly 1.4 wt% carbon layer. The available pore volume of the carbonized polymer coating *versus* the wt% carbon is shown in Figure 4. The average pore size was 19–20 Å for all samples indicating that the decomposition of the polymer is independent of the coating thickness. The least squares correlation of the pore volume and the weight of the carbon in each

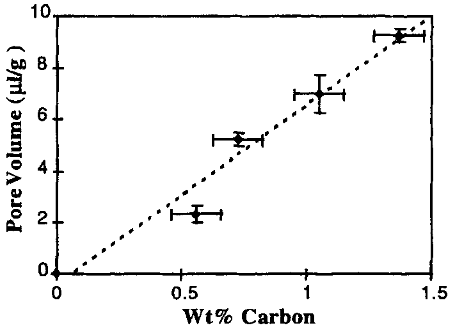

FIGURE 4 Pore volumes *versus* wt% cabon of carbonized PDVB coating on SiCw.

coating indicates the pore volume of the carbon layer is 697 μl/g while the specific surface area is 1380 m^2/g. The SEM micrographs in Figure 5 show the uncoated SiCw and polymer-coated SiCw, respectively.

The three borates employed in this study melt below 800 C and absorb into the carbon layer but the nitridation of B_2O_3 with NH_3 is not energetically favorable at this temperature. The physical properties of the borate precursors give insight into developing nitridation methods to produce thin films. Boron oxide and sodium borate will be discussed initially, ammonium borate will be addressed afterward.

Boron oxide melts at 450 C and penetrates the porous carbon layer before it reacts with NH_3. The viscosity of the melt [27, 28] is high

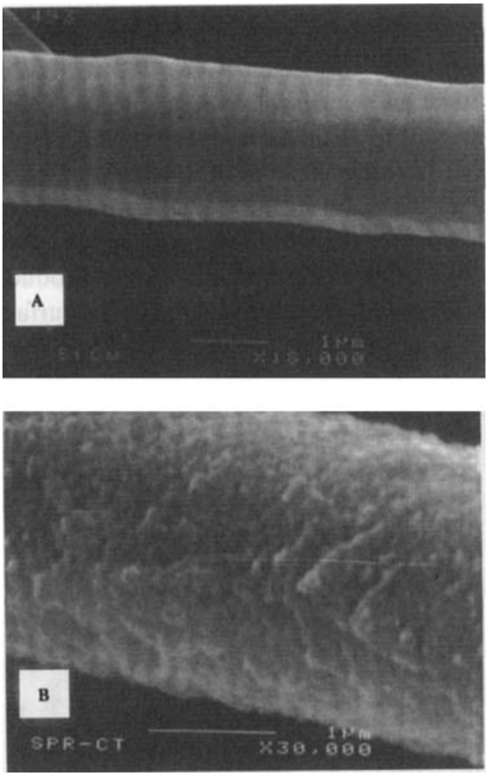

FIGURE 5 SEM micrographs of (A) uncoated SiCw, and (B) SiCw coated with 22.5 % PDVB.

below 1200 C and may prevent it from thoroughly infiltrating into the porous carbon before BN formation commences at 900 C when NH_3 is present. To prevent premature conversion, argon was passed over the sample until the furnace temperature reached 1200 C. At that time, a 15-mintue dwell was initiated to allow sufficient time for the melt to penetrate all of the pores. The argon flow was then stopped and the ammonia flow started while the sample was heated to 1300 C and nitrided for 150 minutes. The vapor pressure of B_2O_3 is only 0.83 torr at 1200 C so little loss occurs during this procedure [29, 30]. The SEM micrograph in Figure 6 shows the results after thermal treatment at 1300 C for 150 minutes. The BN coating formed nodules on the surface of the whisker suggesting poor wetting of the melt on the SiCw surface even though the contact angle of the melt with the carbon layer is favorable.

We believe the poor wetting phenomenon is due to the energetically-unfavorable interaction of molten B_2O_3 with the molecular layer of SiO_2 native to most SiCw surfaces. The quantities of SiO_2 and B_2O_3 at the interface lie within the immiscibility region of the borosilicate phase diagram at the temperatures of nitridation [31]. The formation of BN nodules on the SiCw surface indicates the contact angle of the melt with the surface of the whisker is greater than 90 degrees.

Different from boron oxide, sodium borate produced continuous BN coatings as indicated in Figures 7A – C. The surface morphology

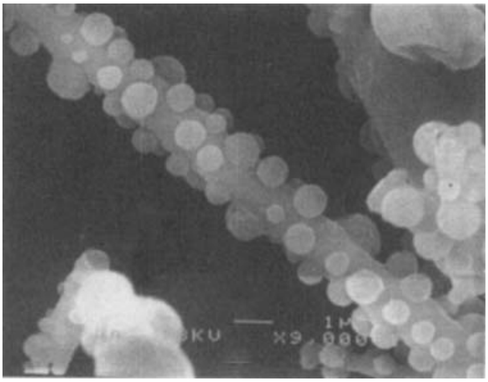

FIGURE 6 SEM micrograph of BN nodules on the surface of SiCw.

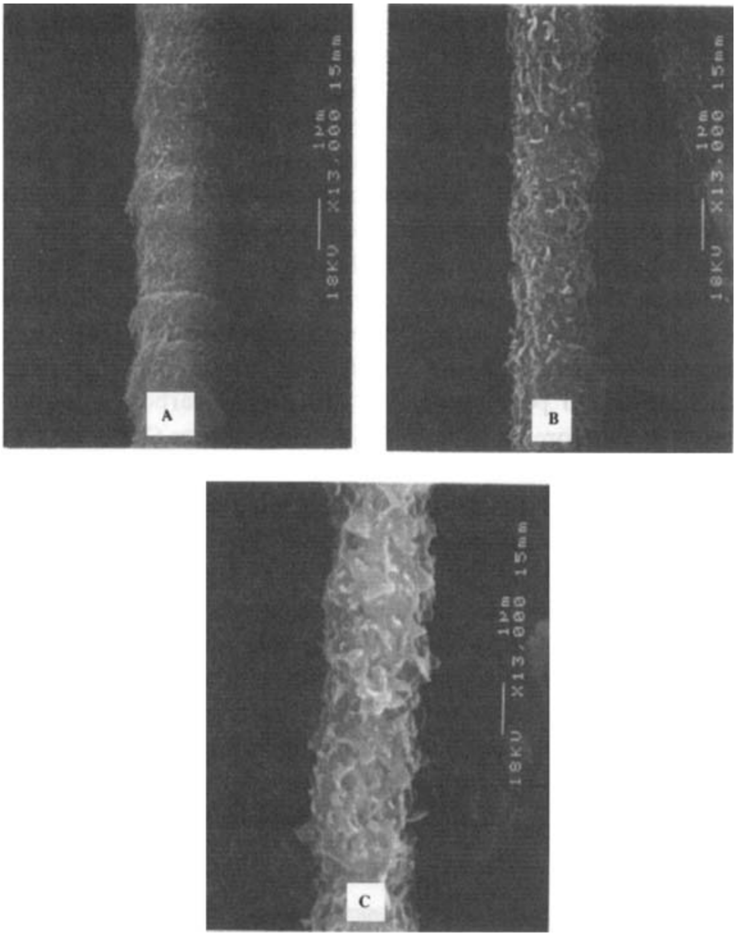

FIGURE 7 SEM micrographs of SiCw coated with three amounts of BN.

of the coating is expected due to the flake-like nature of *h*-BN. The samples were free flowing and non agglomerated. Figures 7A – C illustrate control over the ceramic coating thickness from mixing 1.0 g SiCwC, prepared by carbonizing SiCw coated with 7.8, 16.5, 22.5 wt% PDVB, with 0.31 g, 0.66 g and 0.90 g $Na_2B_4O_7$, respectively, and nitrided at 1300 C for 150 minutes. An energy-dispersive map indicates strong correlation of continuous boron and nitrogen over the whisker surfaces. The bright and dark field TEM micrographs in Figure 8 show that the thickness of the BN coating is continuous and about 0.2 μm thick on the ~ 1 μm diameter whisker.

The alkali borate is unique to the other BN precursors because the trigonal planar geometry of boron oxide can be distorted to tetrahedral geometry by the presence of an oxide, such as Na_2O [32]. The exact structure of the borate melt does not concern us here, only that its physical properties make $Na_2B_4O_7$ acceptable for generating continuous thin film coatings of BN on SiCw using the method described [33]. The viscosity of the sodium borate melt [34] is greatly reduced compared with the viscosity of boron oxide at elevated temperatures and penetration into the porous carbon layer on the whisker is, therefore, possible at lower temperatures (750–800 C) and before nitridation can occur. The unique effect of the Na_2O on the properties of the borate melt may be to act as a fluxing agent to reduce the contact angle of the melt on the SiCw, thus producing a continuous BN coating [33].

Ammonium borate was investigated as an alternative source of BN with less possibility of having sodium contamination. The result was the same as with boron oxide (Fig. 6) but with lower yield of BN due to the volatility of HBO_2 formed during heating [29, 30].

As stated in the experimental section, nitridation was examined over a range of temperatures for varying amounts of time-1100, 1200, 1300 C for 10, 30, 60, 150 and 480 minutes each. In each case, X-ray data

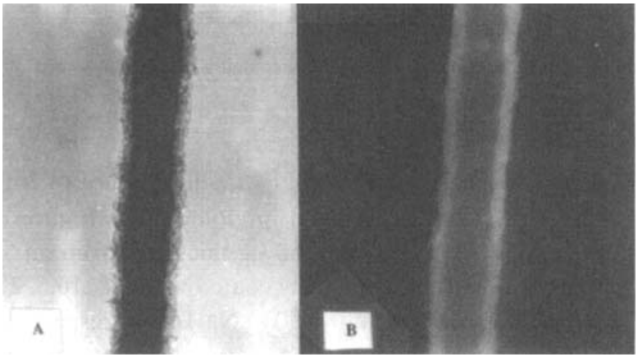

FIGURE 8 (A) Bright and (B) dark field TEM micrographs of BN coating on SiCw.

indicated all samples formed BN. The 10-minute reaction, in comparison with the 60-mintue reaction, had less crystalline *h*-BN and a smaller crystallite size, suggesting that longer reaction times and nitridation temperatures may improve the quantity of crystalline *h*-BN. About 20 % of BN is crystalline after thermal treatment at 1100 C for an hour. At longer reaction times, 150 and 480 minutes, silicon oxynitride (Si_2N_2O) was also formed as a sublayer below BN. The X-ray spectra in Figure 9 show BN formation for nitridation at 1100 C for 30 minutes, the onset of silicon oxynitride formation at 1100 C for 60 minutes, and significant Si_2N_2O formation at 1300 C for 150 minutes. A linear relationship exists between the amount of Si_2N_2O formed and the amount of Na_2O present prior to nitridation. The suboxide was not formed with any other BN precursor or when the bare whiskers were exposed to ammonia at 1300 C for extended periods of time (8 hours).

Production of Si_2N_2O on the surface of the whiskers was possible by reacting a mixture of SiCw and Na_2CO_3 with ammonia at 1300 C for 150 minutes but not at 1100 C for 30 minutes [35, 36]. It is believed that at 1300 C Na_2O oxidizes the SiCw surface which then reacts with ammonia to from Si_2N_2O. The surface shown in Figure 10 is markedly different from the surface morphology obtained when sodium borate

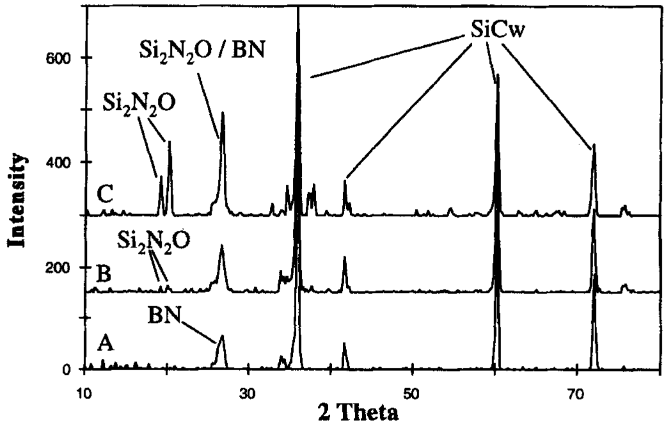

FIGURE 9 XRD spectra of (A) BN formation for nitridation at 1100 C for 30 minutes, (B) the onset of Si_2N_2O formation at 1100 C for 60 minutes, and (C) significant Si_2N_2O formed at 1300 C for 150 minutes.

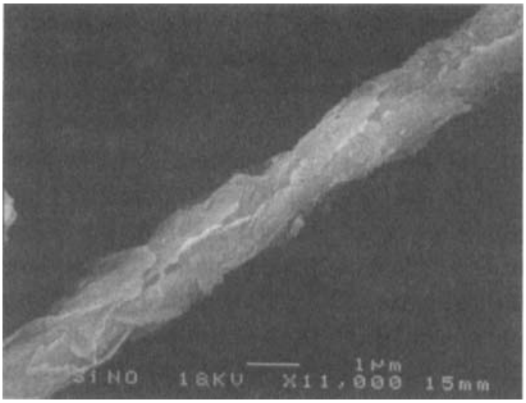

FIGURE 10 Si_2N_2O formation on SiCw using Na_2CO_3 at 1300 C for 8 hours.

was used, and the Si_2N_2O alone does not adhere to the SiCw when mechanically stressed.

The BN surface coatings adhere strongly to the core SiCw since grinding with a mortar and pestle did not dislodge them. It is not clear if the formation the Si_2N_2O offers any enhanced mechanical stability to the BN coatings and this requires further investigation. On the other hand, it is known that silicon oxynitride has good oxidation, corrosion, and thermal shock resistance [37].

CONCLUSION

The production of new core shell composite materials by aerosol and condensed-phase reactions was reviewed. Especially, preparation of titania particles with a polyurea coating, encapsulation of metal oxide milling beads with a chemically-generated coating, and boron nitride coatings on silicon carbide whiskers were used as examples to illustrate how reaction conditions affect core-coating properties.

Adhesion of polyurea coatings formed on titania by an aerosol-droplet technique was found to depend on the ability of coating precursors to bond covalently to the surface prior to polymerization. The use of diisocyanate in the presence of formed hydrated titania from titanium alkoxides appears to be useful in producing a polyurea coating upon exposure to ethylenediamine vapor in the aerosol apparatus.

Coating reactions were also studied in liquid media. Chemically-generated polydivinylbenzene coating on large metal oxide milling beads was investigated. As the monomer was polymerized in the presence of the beads, a thin polymer film was physisorbed to the surface. The unique technique allowed uniform coverage of the beads, but the weak adhesion of the coating to the cores resulted in coatings that easily ruptured. Lastly, the formation of BN coatings on silicon carbide whiskers by a disperse dry powder technique using sodium borate as a BN precursor was examined. Certain reaction conditions allowed formation of silicon oxynitride as a sublayer to BN. The BN coatings with and without Si_2N_2O robustly adhered to the core SiCw even under mechanical stress. The ability to tailor the interfacial adhesive properties in ceramic composites of the type investigated needs further study. Composite interfaces can then be fabricated to meet the specific needs for advanced material applications.

Acknowledgements

Many scientists contributed to the technology developed at Clarkson University, the most prominent being the author's close collaborator Egon Matijević. References [1 – 9] contain their names. Special appreciation is given to Todd Fountain who carried out the milling bead coating experiments. Generous financial support was received from Advanced Refractory Technologies, Inc., NanoSystems, Inc. and the New York State Science and Technology Foundation through a grant to the Clarkson University Center for Advanced Materials Processing.

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