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A Novel Combinatorial Approach for the Realization of Advanced cBN Composite Coating

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Summary:

The paper reports a novel coating process for the synthesis of hard material composite coatings. It consists of electrostatic spray coating (ESC) of powder particles (of micron-nanometer size) followed by chemical vapor infiltration (CVI) of a suitable binder phase. This novel approach enables fabrication of unique compositions such as cubic boron nitride (cBN) and titanium nitride (TiN) in a coating form. Recently, we have demonstrated the success of this technology by first coating a uniform over-layer (in excess of ~ 10 μm) of cBN particles on carbide cutting tool inserts using ESC, followed by infiltration of particulate cBN matrix with TiN from its vapor phase using CVI to synthesize cBN-TiN a composite coating. The composite has shown excellent cBN-to-TiN and composite coating-to-carbide substrate adhesion. One of the main emphases of the paper is to discuss optimization and scale up of the ESC technology to achieve the desired microstructure and tailor the thickness across the cutting tool for better performance. Further, the cutting tools have been successfully tested for advanced machining applications.

Keywords:

Cubic boron nitride, composite coating, cBN-TiN, ESC, CVI, particulate coating

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Introduction:

Thin film and coating technology has observed many phases of progress in engineering coating and deposition processes. It has resulted in a variety of novel micro-structural coatings and processes for thin film synthesis of a wide variety of materials. The techniques have evolved with concurrent progress of supporting infrastructure and applications. Even so, the state-of-the-art coating technology is challenged by materials like cubic boron nitride (cBN), where it is practically difficult to coat homogenous cBN on technologically important substrates like tungsten carbide, e.g. for cutting tool applications. Cubic boron nitride is of great interest for a multitude of applications. It combines extreme material properties, like high hardness and rigidity, high thermal conductivity and chemical resistance. This article is a direct result of the development of a novel hybrid technique designed to realize novel engineered a cBN-TiN composite for cutting tools for advanced machining applications, and the related research focused in targeting the challenge.

Cubic boron nitride hard coatings – Need & Challenges:

Cubic boron nitride is a man-made material and is listed as the second known hardest material next only to diamond (refer Table 1 for their property comparison). Diamond has been used in tool industry for a long time. However, due to its aggressive reaction with iron during the cutting process, it cannot be effectively used for machining ferrous alloys. CBN, on the other hand, has outstanding thermal stability and chemical inertness toward iron.

Table 1: Important property comparison of pure cBN and diamond in bulk form.

Property	CBN	Diamond
Density	3.48	3.52
Hardness (kg/mm^2)	4500	9000
Stability against Oxidation (^{o}C)	1200	600
Chemical reactivity with Ferrous alloys	No reaction With Ferrous alloys	Reacts with Ferrous alloys at high temperature (>900 ^{o}C)
Thermal conductivity (W/cm-^{o}C at 25 ^{o}C)	8 (polycrystalline) 13 (calculated)	20
Bonding	Covalent + Ionic (22-27%)	Covalent

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Currently, cBN is being used in its bulk form, polycrystalline cubic boron nitride (PCBN), in limited applications as a cutting tool for machining ferrous alloys. Thus, diamond and boron nitride based tools compliment each other in their application fields. Diamond can cut only non-ferrous materials (volume of 20-25% of the total world machining market), whereas, cBN can be used for machining ferrous alloys (volume of 75-80% of the total world machining market.

Several efforts are in progress for obtaining cBN thin films on a variety of substrate materials (1). However, such cBN films exhibit limited thickness and poor adhesion. The films have been found to be accompanied by a high amount of film stress. Presently, the research is concentrated on eliminating the limitations in coating thickness. The cBN-coated tools, if available, could be used for the surface finishing applications in the ferrous metal machining industry.

Today, the major roadblocks in the realization of cBN coated cutting tools from vapor growth techniques can be summarized as: excess compressive stress, non-homogenous phase synthesis and stoichiometry control, limited coating thickness (< 1 μm), poor adhesion with substrates, and lattice mismatch with different substrates. These difficulties are more pronounced when considered from the viewpoint of the desired quality control at the manufacturing scale.

It is evident from the literature that the synthesis of cubic boron nitride coating from the vapor phase, using different state-of-the-art techniques, is still far from reality. In an endeavor to reach the goal, a novel combinatorial approach of integrating a non-traditional electrostatic spray coating (ESC) process with chemical vapor infiltration (CVI), a modification of classical CVD, has been invented. The details of the technique, approach and advantages are discussed in the following text.

Experimental Approach and Advantages:

The experimental combinatorial process relies on an infiltration assisted particulate matrix binding, as well as the bonding the coating to a suitable substrate. The potential of this approach is significant. The novel technology discussed herein refers to a two-step process including electrostatic spray coating (ESC), followed by chemical vapor infiltration (CVI) (2). The concept of the two-step process is shown in Figure 1. The details of the first step are

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described further, whereas, information on the second step is discussed separately (3). The first crucial step involves the electrostatic spray coating (hereafter referred to as ESC) of cBN particulates on the substrates. The electrostatic spray coating is a well-known process in the paint industry for applying paint coatings and related finishing applications. In the past few years, it continues to occupy an ever-increasing share of this market, with the powder coating technology proving to be more economical (4,5). This process has been tailored for applying the cBN particulate coating (2). In this process, a known amount of cBN powder of the required particle size is sprayed on electrically grounded substrates in a closed electrostatic spray setup housing (6,7). Flat geometry, as well as a chip breaker geometry, tungsten carbide tool inserts (WC-Co) were selected as the experimental substrates. A scanning electron microscope (SEM, Hitachi, S-2300) was used to analyze the non-infiltrated porous cBN coated carbide substrates for powder coating thickness, as well as the spatial morphology of the coating across the parts coated in a batch process.

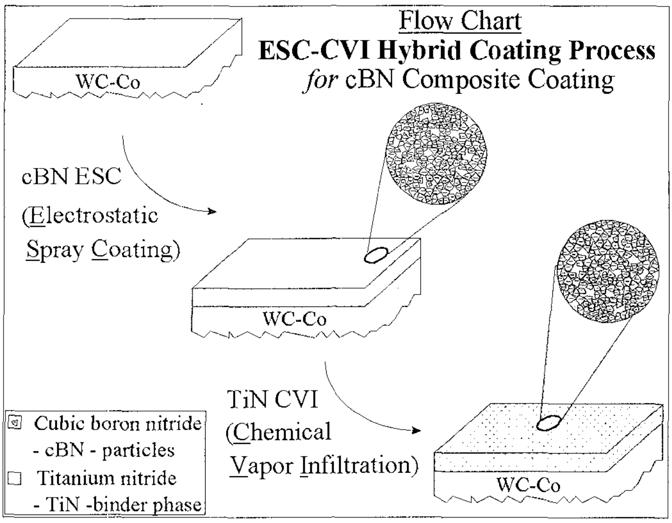

Figure 1: Schematic of the ESC-CVI hybrid technology.

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The setup of the electrostatic spray process consists of the following parts; powder delivery unit, powder feeder unit, spray gun with its controller, a

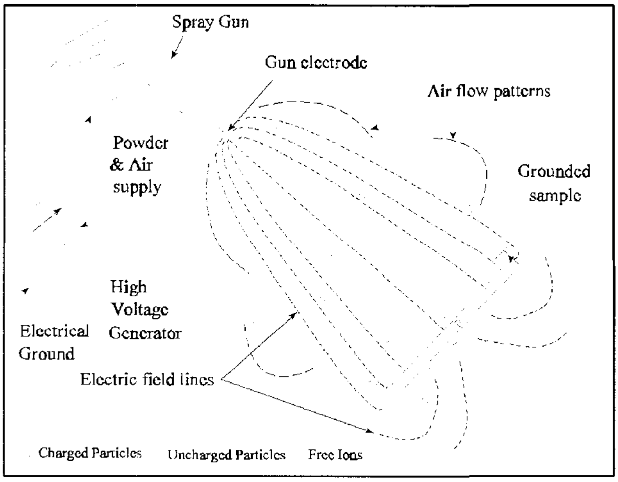

Figure 2: Schematic of the electrostatic spray coating (ESC) process.

coating chamber, and a powder recovery unit. The cBN powder, which is used as the starting material, is an expensive material. The recovery of the sprayed but unused powder *during* and *after* the coating process is extremely important for the cost effectiveness of the hybrid coating technology. The extensive investigation of the powder recovery from the setup has resulted in 95% recovery of the powder. The schematic of the ESC process is shown in Figure 2. CBN powder particles with a particle size varying from 0 to 2 μm (BORAZON®, General Electric Co., USA) were used in the experiment. CBN particles are electrically insulating and can carry a static charge over a distance of a few tens of centimeters. The electrostatic charge is generated on the powder particles by applying high voltage to the spray gun electrode (typically a few tens of kilo volts - kV) with respect to the electrically grounded substrate (8).

A typical scanning electron microscope (SEM) picture, shown as in Figure 3 (a), reveals a uniform cBN ESC coating layer (thickness ~ 15 μm) on a carbide tool substrate. A cBN coating thickness in excess of 10 μm can be achieved in a short period of few seconds. The particulate cBN coating, as seen in Figure 3 (a) & (b), is porous. A pore in the ESC coating is a void space between adjacent particles. The average pore size in the particulate

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coating is found to be a few microns and serves as the channels for the infiltrating reactants during the CVI process.
Some of the obvious advantages of this simple but significant process can be listed as follows: fast deposition rate, low capital investment, compatible to simple and complex geometries, offers wide selection of composite coatings, simple setup construction, easy to operate unlike CVD/PVD process, no requirement of vacuum reactors and hazardous gases, low maintenance and, more importantly, the combination of material phases is not limited with phase formation as allowed by the phase diagram of a particular system.

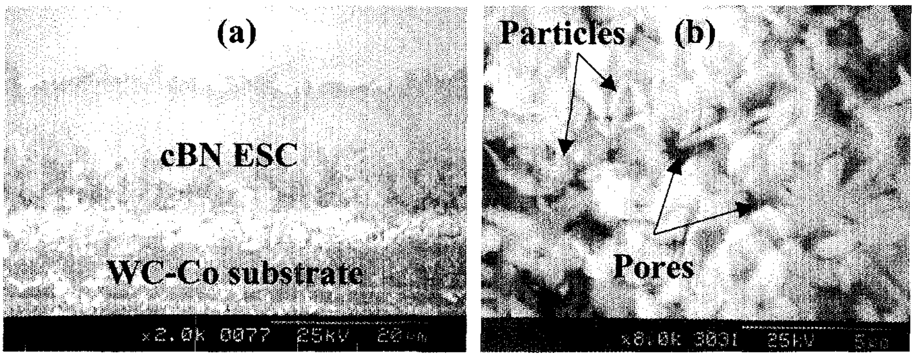

Figure 3: SEM micrographs, (a) cBN ESC layer on carbide substrate (2000x), and (b) ESC, cBN surface layer (8000x) showing cBN particles and porosity.

ESC *operating parameters:*

The ESC process can be controlled using various operating parameters to achieve the desired coating thickness and quality. In addition to the starting powder quality and quantity, a few other important operating parameters, which can alter the result of ESC, are listed in the Table 2, along with the operating range of the parameters for the cBN powder deposition. In the current investigation, the resultant particulate cBN coating can be graded by important quality factors like coating thickness, coating uniformity, porosity, and particle clusters.

Table 2: Operating Parameter range in ESC Process for cBN coating.

Operating Parameter	Control Window
Powder composition	Uncoated / coated cBN

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Powder size	0 – 12 μm
Powder feed rate	< 0.1 g / min.
High voltage at the electrode (V)	– 40 to – 90 kV
Substrate to gun electrode distance (D)	3.5" – 8"
Substrate size	Limited to the size of spray unit
Time of deposition	< 5 minutes
Air pressure (P)	20 – 40 psi

ESC process optimization and ESC cBN coating evaluation:

The electrostatic spray coating process has been successfully employed to obtain cBN powder coatings on tungsten carbide (cobalt binder) tool inserts. The powder coating was studied with respect to the important qualities of a particulate coating like adhesion, coating thickness, uniformity, porosity and particle clusters. The cBN particulates are held to the substrates with an electrostatic force. This force of attraction between the substrate and cBN particulate layer – generally defined as the adhesion - is strong enough to keep the over-layer intact until transferred to the CVI reactor and weak enough to be wiped off by improper handling. After processing the samples with the second step, i.e., CVI, the resultant composite cBN-TiN coating has excellent adhesion.

ESC operating parameters discussed earlier have an influential role on the process output. A number of experiments were carried out to optimize the ESC operating parameters, which are considered to be the process input, to evaluate the relation between the operating parameters and to obtain desired ESC coating specifications. The process output, in the present case, is defined as the coating quality and coating characteristics like edge-to-edge, part-to-part and batch-to-batch uniformity, coating thickness, porosity, distribution of particle clusters, etc. A statistical methodology, well known as the Taguchi method, was employed to find the optimum conditions which reliably produce the desired coating quality as required for efficient CVI infiltration for consistent performance in machining (9). The Taguchi approach of parametric design allowed us to converge on the best combination of process parameters using an orthogonal array table (OAT). The optimization experiments were designed and conducted as per the selected OAT. The data generated from such selected experiments was analyzed by the analysis of variance (ANOVA) technique using statistical software MINITAB (6).

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The ESC optimization was carried out to determine the operating parameters for obtaining a coating with a uniform coating thickness, a minimum number of clusters, and an average porosity. Based on the available experimental data and the potential application of the end product, a uniform ESC cBN coating thickness of about 21 µm was targeted with Taguchi methodology. The important parameters, which affect the result the most, referred as the control factors, are 1. distance between the substrate and spray electrode, 2.

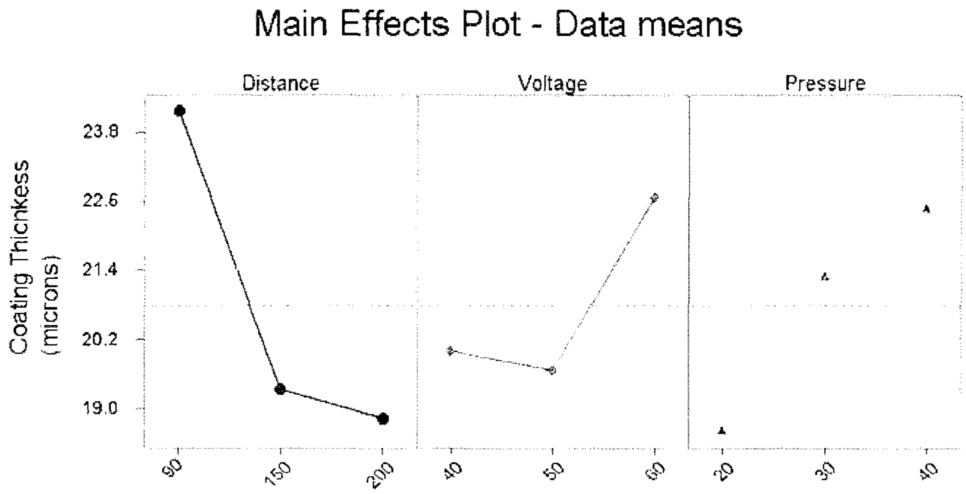

Figure 4: Optimization experiment main effect results from MINITAB software showing the effects of variation of substrate-electrode distance, spray gun voltage and air pressure on the ESC cBN coating thickness on carbide substrate.

spray electrode voltage, and 3. air pressure. The values of control factor were varied to see the effect on ESC cBN coating, while keeping the other parameters constant.

From the results of the MINITAB software, it was found that all the control factors mentioned above have a significant influence on the coating results. For a given control factor with two or more values, referred to as factor levels, it is possible that one level increases the data mean more compared to the other level. This change in the mean outcome is called a main effect. Figure 4 is a plot of characteristic averages from the MINITAB software for important control factor levels. Figure 4 illustrates that the main effect exists for all three

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control factors, i.e., different levels of the factor affecting the coating characteristics differently. As can be seen from the figure, with an increase in the substrate-electrode distance from 90 mm to 200 mm, the coating thickness decreases from about 24 μm to less than 19 μm. The decrease in thickness is caused by the increase in spread of the spray envelope and particle path distance. When the magnitude of the gun voltage was increased from 40 kV to 60 kV, the coating thickness showed an increase from 20 μm to close to 22 μm. The coating thickness increases with an increase in the spray electrode potential since there is an increase in effective charging of the cBN particles sprayed and the formation of a denser particle cloud at the spray electrode. In the case of air pressure, the cBN coating thickness increased from about 18 μm to close to 23 μm in response to the air pressure increase from 20 psi to 40 psi. The air pressure increase influences the efficiency of the powder fluidization process, thereby enhancing the effective charging of particles and terminating a higher number of cBN particles on the substrates.

In addition to the main effects, it is also important to study the interactions that exist between the control factors. An interaction, as defined in statistical terms, is said to occur when two or more factors acting together have a different effect on the quality characteristic than the effects of each factor acting individually. Failure to recognize the presence of an interaction can lead to misinterpretation of the experimental data and failure to include important considerations in optimizing the process. The strength of interaction can be studied with the help of interaction plots. The interaction plots obtained from the MINITAB software output are shown in Figure 5.

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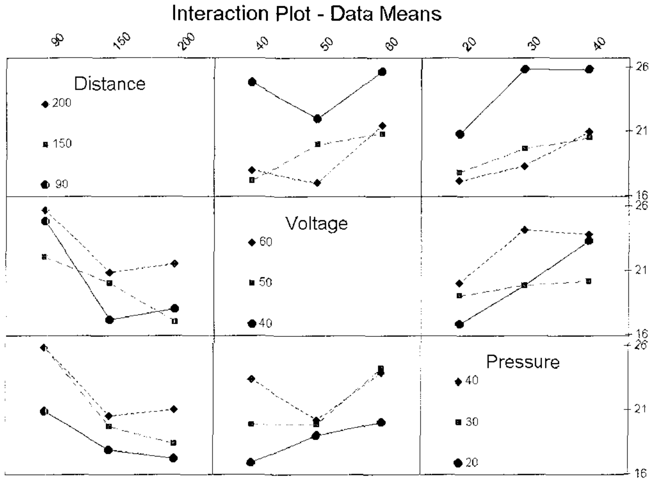

Figure 5: Optimization experiment interaction effect results from MINITAB software showing inter-parameter variation of control factors on the ESC cBN coating thickness on carbide substrate.

Some of the inferences drawn from Figure 5 are as follows. The interaction between the substrate-spray electrode distance and charging voltage is significant, whereas, it is insignificant between the distance and air pressure. The main effects for the distance and air pressure play a major role on the process output, even with insignificant interaction between them. At a given pressure, an increase in the substrate-electrode distance results in a decrease in the coating thickness. Similar is the case when the pressure is varied for a given substrate-electrode distance. The coating thickness increases with an increase in pressure and, depending on the distance, there is a variation in the coating thickness. Hence, considering the main effect of pressure on the coating thickness, the optimum pressure was set to 30 psi to obtain a targeted coating thickness of 21 µm.

It is evident from the interaction between the voltage and distance that, for a targeted cBN coating thickness of 21 µm, gun voltage of 60 kV is an optimum, irrespective of the substrate-electrode distance. There is no significant change in the coating thickness when the distance is increased from 150 mm to 200 mm. In addition, it can be inferred that the substrate-electrode distance has to be maintained at 150 mm. If the interaction between the spray gun voltage and air pressure is considered from Figure 5, it can be seen that the spray gun voltage has to be set at 60 kV for a desired coating thickness of 21 µm with an air pressure of 30 psi.

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By considering the main effects plot (Figure 4) and interaction (Figure 5) between the control factors, it was concluded that the optimum control factor levels are 150 mm, 60 kV, 30 psi for the respective factors, namely substrate-gun electrode distance (D), spray gun voltage (V) and air pressure (P). ANOVA analysis thus resulted in an optimum set of conditions, which provided the targeted cBN coating thickness of 21 μm. A set of two confirmation experiments was conducted under these optimized conditions. Analysis of the cBN ESC coated samples was done using SEM to find the resulting coating thickness of about 22 μm.

As shown in Figure 3 (a), a uniform cBN coating can be deposited on a carbide substrate using the ESC. The coating thickness was measured on all edges of the carbide substrate to estimate the thickness variation. The observations for the coating thickness variations are tabulated in Table 3. The table lists the results of two experiments conducted, along with the optimum conditions obtained from the design of experiments (DOE). It can be seen

Table 3: ESC cBN coating thickness variation in a given insert and from inser to insert. (D: Substrate-electrode distance, V-Electrode Voltage, P-Air pressure Δ_1 &...Δ_2 : Variation in thickness on four edges within samples 1 & 2, respectively Δ_3: Variation in coating thickness on four edges between samples 1 & 2)

Sr. No.	D	V	P	Coating thickness (microns)										
	mm	kV	psi	Sample 1				Δ_1	Sample 2				Δ_2	Δ_3
1	150	60	30	23	25	25	24	2	25	27	24	27	3	4
2				24	22	24	24	2	23	24	24	24	1	2

that there is a variation (Δ) in the coating thickness of about 3 μm on a given insert, under the optimized conditions, compared to a coating variation of 4 μm between two different inserts from the same experiment. The variation in the coating uniformity can be attributed to the noise factors (factors which are uncontrollable or too expensive to control) or the inherent variations in the process conditions. A confirmation experiment was conducted to check the variation in coating uniformity and was found to be less than 3 μm.

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Pore size analysis was performed on the samples prepared under the optimized set of conditions (refer to Table 4 for the conditions). The pores have special significance in chemical vapor infiltration. SEM micrographs of the ESC cBN coatings obtained at a magnification of 8000x (describing an area of 15 μm x 12 μm) were used for the pore size measurements. The void space sizes were measured at four different regions of the cBN coating and are given in Table 4. The average pore size is about 2 μm.

Table 4: Porosity in the ESC cBN coating.

D	**V**	**P**	***Pore size measured on an area of ~ 15 um x 12 um***						
mm	**kV**	**psi**	**Pore size at 4 different locations**				**Min.**	**Max.**	**Avg.**
150	60	30	1.15	2.56	2.56	1.54	1.15	2.56	1.95

The ESC cBN coating is a particulate coating. Consequently, the particles tend to cluster, contributing to non-uniformity. The clustering is a result of non-uniformity in the particulate size, as well as the surface energy of the particles. Due to the variation in particle size and the subsequent variation in the effective charging of the particles, the particles tend to form big chucks. Employing optimum values of air pressure and substrate-electrode distance can minimize the cluster density. It was seen that higher values of air pressure and substrate-electrode distance tends to reduce clustering. The particle clusters were measured on the cBN coating obtained using optimum conditions. By employing similar method as used for pore analysis, the average cluster size was determined to be about 15 microns over an area of 100 μm x 75 μm.

CVI and composite coating:

The second important processing step involves chemical vapor infiltration (CVI) of the cBN coating with a titanium nitride binding phase. The chemical vapor infiltration is a modification of its widely known counterpart, chemical vapor deposition (CVD) (10). In the case of CVD, a uniform coating is precipitated, whereas, in the case of CVI, a porous matrix is "filled". The core chemistry of both processes is the same although the deposition or growth rates are controlled differently. In CVI, the rate of deposition must be slowed down to allow more time for surface diffusion so that the pores can be filled before the growing phase seals the openings. This can be assured if the rate

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of diffusion of the reactants within the porous body, either in the gas phase or as surface species, is greater than the rate of growth of the film. Diffusion rates and growth rates are both a function of temperature, so simply reducing temperature is not adequate for achieving CVI process conditions. It is more appropriate to control the rate of the reaction chemically so that heat can still be a driving force of the diffusion processes. The details of the process and operating parameters for CVI are discussed in a separate report (3).

Figure 6 shows a representative cross-sectional view of the cBN-TiN composite coating on a tungsten carbide (Co binder) cutting tool substrate. As is evident in Figure 6, the cBN particulate matter has been infiltrated by the TiN phase. The TiN phase is continuous between both the cBN particulates and, the particulates and the carbide substrate.

The composite coating of cBN-TiN on WC-Co tool insert was tested for the uniformity, and adhesion. Such coated tools were then tested in an actual machining environment. These results are discussed in detail in a separate

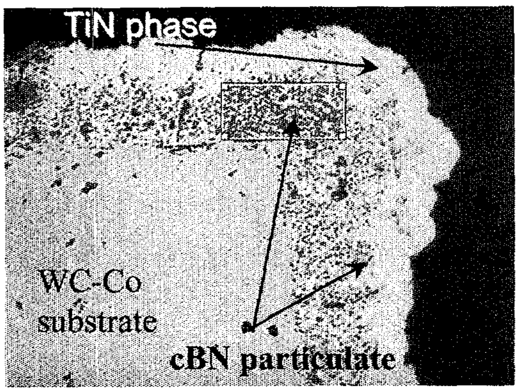

Figure 6: Cross-sectional view of ESC-CVI composite coating.

report in this conference (3).

Scaling up:

Based on the findings of ESC coating analysis, CVI, and machining results, it was determined that the cBN-TiN composite coating of cutting tools formed by the combinatorial technology results in functional cBN coated cutting tools. In order to adapt the ESC process for manufacturing a large number of tools,

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a scaled up prototype system is being developed at the MRL, University of Arkansas.

In summary, the ultimate success of the above discussed fundamental research and technological development was not only instrumental in the development of the cBN composite coated tool products, but will also allow the development of numerous versatile coating and products for applications such as wear parts, electronics, etc. The technology development is underway for other technologically important coatings.

Conclusion:

A novel combinatorial approach has been reported as an alternative for the synthesis of cubic boron nitride (cBN) in coating form. It comprised of electrostatic spray coating (ESC) of cBN powder particles followed by chemical vapor infiltration (CVI) of a TiN binder phase to synthesize a cBN-TiN composite. The composite shows excellent cBN-to-TiN and composite coating-to-carbide substrate adhesion. The electrostatic spray coating (ESC) process was optimized using a statistical methodology developed by Taguchi. A design of experiments method provided an optimized set of operating parameters, namely substrate-electrode distance, spray gun voltage, and air pressure. The ESC cBN coating was examined with respect to coating uniformity, porosity and particle clusters. Using the ESC optimization results, a scaled up system, which will handle a larger number of samples in a manufacturing unit, is being developed at the MRL, University of Arkansas, USA.

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