Thermal plasma deposition of nanophase hard coatings

J. Heberlein\textsuperscript{a,}\textsuperscript{*}, O. Postel\textsuperscript{b}, S. Girshick\textsuperscript{a}, P. McMurry\textsuperscript{a}, W. Gerberich\textsuperscript{c}, D. Iordanoglou\textsuperscript{a}, F. Di Fonzo\textsuperscript{a}, D. Neumann\textsuperscript{a}, A. Gidwani\textsuperscript{a}, M. Fan\textsuperscript{a}, N. Tymiak\textsuperscript{c}

\textsuperscript{a}High Temperature and Plasma Laboratory, Department of Mechanical Engineering, University of Minnesota, 111 Church Street SE, Minneapolis, MN 55455, USA
\textsuperscript{b}Mechanical Engineering Department, Stanford University, Stanford, CA 94305, USA
\textsuperscript{c}Department of Chemical Engineering and Materials Science, University of Minnesota, 421 Washington Avenue SE, Minneapolis, MN 55455, USA

Abstract

Thermal plasmas offer several specific advantages for the generation of hard coatings. In particular, the high energy density of the thermal plasma allows higher precursor flow rates and a wider choice of precursors. Expansion of the plasma into a low pressure chamber offers the additional advantages that improved control over the chemistry can be achieved or that nanosize particles can be generated. In this contribution, two experiments are described and the results reviewed in which supersonic plasma jets have been used to deposit nanophase hard coatings. In one of them, hard boron carbide coatings have been deposited using a supersonic plasma jet and a secondary discharge between the nozzle and the substrate. Spectroscopic analysis has been used to determine the reaction processes responsible for the deposition. In the other experiment, a plasma-containing silicon or titanium and carbon vapor has been expanded through a supersonic nozzle to form nanosize silicon or titanium carbide particles which are subsequently deposited on a substrate. Addition of a system of aerodynamic lenses allows the formation of a beam of nanosized particles which are deposited with high spatial definition. Narrow lines of a hard coating can thus be produced. In both processes, the deposition occurs rapidly, a fact which makes the processes attractive for a variety of potential applications. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Thermal plasma; Hard coatings; Boron carbide; Silicon carbide; Supersonic jet

1. Introduction

Hard and wear resistant coatings have increased in importance recently for a variety of reasons, among others due to a push for dry machining as a consequence of the increase in cost for disposal of cooling fluids. In particular, the extreme hardness that can be obtained with materials with grain sizes of a few nanometers to a few tens of nanometers has led to a significant effort in developing methods for producing coatings consisting of such materials. A recent review article [1] presents several ways of generating superhard nanophase coatings. In particular, the formation of nanocomposites during the film formation has led to hardness values which rival or even surpass those of diamond. However, most of these methods produce the coatings at very low deposition rates, limiting somewhat their attractiveness.

Thermal plasmas offer several specific advantages for the generation of hard coatings. The high energy density of the thermal plasma allows higher precursor flow rates and a wider choice of precursors. Even solid particles can be vaporized. Consequently, higher depo-
solution rates can be obtained. Furthermore, the high quench rates which are associated with the high energy densities facilitate formation of nanosize particles or structures. The drawbacks of using thermal plasmas are also a consequence of the high energy density, namely strong gradients between the medium carrying the deposition precursor and the surroundings, including the substrate. The thermal plasma coating process requires, therefore, special efforts to deal with coating non-uniformities and with control of the boundary layer in front of the substrate. For example, a plasma jet containing vapors of the deposition precursors directed towards the substrate may cool sufficiently in the boundary layer to allow nucleation and formation of nanosize particles which may or may not be deposited on the substrate. However, if the boundary layer thickness is sufficiently small, the chemical reactions in the boundary layer may be at least partially frozen and homogeneous nucleation may be avoided, allowing the thermal plasma vapor deposition process to proceed.

Both design challenges, that of deposit non-uniformity and that of boundary layer chemistry control, are alleviated by the use of supersonic plasma jets emanating into a low pressure environment. This effect has been used in the development of several coating processes in particular for the deposition of diamond films and more recently for the deposition of boron nitride with a high fraction of the cubic phase.

In the High Temperature and Plasma Laboratory, two variants of the supersonic plasma jet deposition technique have been used to deposit nanophase coatings. In one of these, the reactants have been injected into the plasma jet in the diverging part of the supersonic nozzle, and reaction chemistry has been enhanced through the use of a secondary discharge between the nozzle and the substrate. However, it is clear that the chemistry is determined by both dissociation and recombination kinetics. In this case, super-hard boron carbide coatings have been deposited in a vapor phase deposition process. In the other process, the reactants are injected into the plasma before the acceleration of the plasma in the nozzle, and full dissociation of the reactants is expected. Acceleration of the gas in the nozzle leads to quenching of the vapor stream and the nucleation of nanosized particles. These particles are accelerated to hypersonic velocities and deposited inertially on a substrate in front of the nozzle exit. This hypersonic plasma particle deposition (HPPPD) process has been used for the deposition of silicon carbide and titanium carbide coatings.

In the following, the two supersonic plasma jet deposition processes are described and some of the results obtained are reviewed. Details of the experiments and the coating analysis have been presented previously. Here, the emphasis is on the process analysis. A new variant of the hypersonic plasma particle deposition process which has been recently developed, the focused particle beam deposition, is also presented. The paper will end with some brief conclusions about these processes.

2. Boron carbide deposition with supersonic plasma jet and auxiliary discharge

2.1. Description of the experiment

Boron carbide has a number of attractive properties as a hard, wear resistant material. Compared to diamond, it is more stable at higher temperatures and also exhibits better chemical stability when in contact with ferrous materials. Compared to cubic boron nitride, it can be deposited with lower intrinsic stresses and has better adhesion to substrates of interest. Traditional boron carbide deposition processes, e.g. sputtering, are relatively slow, and availability of a high rate deposition process would make boron carbide an attractive coating material for wear resistance applications.

For the thermal plasma vapor deposition process, a medium power (3 kW) arcjet thruster developed by NASA and a Robicon 80-kW d.c. rectifier have been used to generate the thermal plasma and accelerate it to supersonic velocities. A mixture of argon (15 slpm) and various amounts of hydrogen (0–150 sccm) has been used as plasma gas, and the arc current has been 90 A. The reactants, boron trichloride and methane, are injected into the plasma jet through refractory tubes inserted into the diverging section of the nozzle. The BCl flow rate has been 20 sccm (standard cm$^3$/min), and the CH$_4$ flow rate 5 sccm. The arcjet thruster is mounted inside a chamber the pressure of which is kept at 260 Pa by a large mechanical pumping system. The substrate is mounted 10 cm from the nozzle exit and is oriented perpendicularly to the plasma jet axis. The substrate is water-cooled, and a flow of He between the substrate and the substrate holder allows precise temperature control within the range desired (500–650°C). The temperature is measured at the back face of the substrate using an optical fiber transmitting the radiation to a pyrometer. Most results have been obtained at 550°C substrate temperature. A detailed description of the experimental apparatus has been presented previously.

A set of two bipolar pulse power supplies connected to the nozzle and the substrate allow biasing of the substrate either in the pulse mode with a range of frequencies and duty cycles, or with a d.c. voltage, and d.c. currents up to 3.5 A can be drawn from this power supply for the auxiliary discharge superimposed onto the supersonic plasma jet. The applied voltage is usually limited by the current which can be drawn from the
power supplies. Most experiments have been conducted with a pulse frequency of 1 kHz, a duty cycle between 25 and 100% and maximum applied voltages of 55 V.

The characteristics of the plasma jet and the auxiliary discharge have been determined using an optical spectrometer together with a photomultiplier or a CCD array. The photomultiplier system has been used to determine the temperature distribution, while the CCD array has been used for measuring the relative line intensities from specific plasma components. For measurements with a pulsed bias, the detection system has been operated at a frequency considerably higher than the pulse frequency, and data analysis has been performed at constant phase to account for the variation in power. The entire optical system can be moved to take measurements at different axial locations. Details of this system have been presented by Postel [12].

Most of the experiments have been performed with single crystal silicon wafers as substrates, although other substrate materials have been used as well. The films have been characterized using micro X-ray diffraction (Siemens GADDS), XPS (Physical Electronics PH15400) and FTIR (Nicolet Series II Magna-IR 750), and by nanoindentation. Details of the film characterization are presented by Postel [12] and Postel and Heberlein [8].

2.2. Results of boron carbide deposition experiments

Boron carbide films have been deposited with typical thicknesses between 3 and 5 μm and average growth rates of 3.5 μm/h. The cross-sections of these films show no identifiable microstructure, but atomic force microscopy and micro X-ray analysis indicate grain sizes of hundred to a few hundred nanometers. Indentation measurements indicate maximum hardness values exceeding 40 GPa. A positive substrate bias leads to a strong increase in the deposition rate. Fig. 1 shows the dramatic, approximately 10-fold increase of the deposition rate with bias voltage. The instantaneous growth rate is shown during the time the voltage is applied, as well as the average growth rate for duty cycles between 25 and 100%. Pulsing the bias has the advantage that higher currents can be drawn from the amplifier used in our experiment and that discharge instabilities due to local substrate heating can be avoided. Other effects of the positive bias pale in comparison. Surface contamination with oxygen increased with bias by approximately 50% and boron to carbon ratios in the film increase by approximately 30% when the bias is increased from 0 to 55 V [8]. A negative bias has much less effect on the growth rate leading to a doubling of the deposition rate at −55 V. However, the increased ion bombardment with increasing negative bias results in stresses in the film which lead to easy delamination.

In order to understand the details of the deposition process, spectroscopic investigations of the plasma jet have been conducted. For the determination of the heavy particle temperature, the band spectra of the rotational band of the CH molecule has been analyzed [12]. A temperature profile along the jet axis is shown in Fig. 2 for a pure argon jet and for an argon jet with a 1% hydrogen addition. It is clear that the hydrogen addition leads only to a small increase in the temperature in the supersonic part of the jet, however, the significant increase of the temperature in the bow shock region in front of the substrate indicates a much higher velocity with the hydrogen addition. It is interesting to note that the temperature does not increase during the pulsing of the auxiliary discharge, although the emission from the plasma jet increases strongly indicating a higher number density of excited states. Comparing the increase in intensity of the emission lines of specific species, it is clear that some show a stronger response to the increase in bias voltage. In particular the atomic boron line intensity increases more than those of other species [13]. Furthermore, if the boron line intensity is plotted vs. the deposition rate as shown in Fig. 3 [8], it can be seen that there is a linear relationship between the growth rate and the integrated boron line intensity, both strongly increasing with bias voltage. In contrast, the intensities of lines emitted by other potential deposition precursor species, e.g. boron chloride and borane, show a lesser increase with bias voltage and reach a plateau at approximately 25 V. One may conclude that: (1) atomic boron is the dominant precursor species for the boron carbide films; and that (2) an auxiliary discharge leads to a higher production of boron atoms via increased dissociation reactions while it has little effect on the gas temperature.

![Fig. 1. Increase of boron carbide deposition rate with substrate bias voltage [8].](image-url)
3. Hypersonic plasma particle deposition of silicon carbide and titanium carbide

3.1. Description of the experiment

The second example of a supersonic plasma jet deposition process illustrates the formation of a coating after the homogeneous nucleation of the coating material before it is deposited [9]. In this project the concentration has been on silicon carbide because of its widespread use in many applications. But this choice of deposition material has been reinforced by the further development of this process into a focussed particle beam deposition process with potential application for hardening micro electro-mechanical devices (MEMS) consisting of silicon. Besides silicon carbide, titanium carbide and titanium–titanium carbide composites have been deposited.

The experimental apparatus has been discussed previously [14]. A d.c. plasma torch is mounted onto the stainless steel flange of a water-cooled chamber. The plasma jet enters a cylindrical section confined by a hot ceramic wall. Into this section, the reactants, SiCl₄ and CH₄, are injected, mixed with the plasma and dissociated. The plasma–vapor mixture is then accelerated through a converging hot wall ceramic nozzle by the pressure differential between the mixing section (approx. 80 kPa) and the chamber (330 Pa). The acceleration in the converging nozzle leads to a quenching of the plasma–vapor mixture and the formation of nano-size particles. The substrate is positioned 20 mm in front of the nozzle exit, and the plasma gas with the particles is accelerated to hypersonic velocities until the bow shock in front of the substrate leads to a pressure and temperature increase. Typical operating parameters are:

- Arc current: 225 A
- Plasma gas flow rate: 35 slm argon + 7.5 slm hydrogen
- SiCl₄ flow rate (vapor phase): 0.02–0.2 slm
- CH₄ flow rate: 0.1–1.0 slm (slm = standard liters per min).

The process has been characterized by a model describing the compressible flow in the system, the reaction kinetics and the nucleation in the nozzle, and the trajectories of the particles [15]. Further characterization has included the measurement of the particle size distribution using a scanning electrical mobility spectrometer (SEMS), and measurements of the deposit characteristics.

For the focussed particle beam experiments, the substrate has been replaced by a series of aerodynamic lenses which allow focussing of a flux of particles of a narrow size range [16,17]. The focussed particle beam will then go through a nozzle into the deposition cham-

---

Fig. 2. Axial temperature distribution in the plasma jet between nozzle and substrate [12].

![Axial temperature distribution](image)

Fig. 3. Linear correlation between the boron line intensity and the growth rate for a range of bias voltages [8].

![Linear correlation](image)
ber in which the substrate is located on a traversing mechanism to allow deposition of a select pattern.

3.2. Hypersonic plasma particle deposition results

Modeling results have been obtained for the flow velocity and temperature distributions in the nozzle and in the free jet region between the nozzle exit and the substrate. At the nozzle inlet, the gas has been assumed to have a uniform temperature of 4000 K, a value derived from calorimetric measurements, the substrate temperature has been assumed to be at 600 K, and the experimental values for the flow rates and the geometrical dimensions have been used. The isocontours of the axial velocity indicate peak velocities of approximately 2400 m/s. The temperature at this location is calculated to be 193 K. The deceleration in the bow shock leads to a temperature recovery to almost 4000 K approximately 2.5 mm in front of the substrate, with a subsequent drop to the substrate temperature. Particle trajectories have been calculated for different particle sizes [15]. The particles are assumed to leave the nozzle exit at a location halfway between the centerline and the nozzle wall, and they are assumed to have the same velocity and the same temperature as the gas. It also has been assumed that the fluid flow is not affected by the presence of particles. The calculations indicate that particles as small as 5 nm are deposited by inertial impaction.

Particle size distributions obtained with a sampling probe positioned at the nozzle axis 20 mm from the nozzle exit are shown in Fig. 4 [9]. For these measurements, a small capillary probe is used to sample the gas stream with the particles, the sample is diluted by a factor of more than 1000, and the particle size distribution determined with the SEMS. Three different size distributions are shown each obtained at a different chamber pressure. The narrowing of the size distribution with lower pressures is noticeable. It should be mentioned that the pressure during film deposition has been 2.5 torr, a value too low for the design of our sampling system.

High resolution scanning electron microscope (SEM) images of the top and the bottom surface of a delaminated deposit indicate that both surfaces have grain sizes in the order of 20 nm diameter. The 60-μm thick film has been deposited in 75 s giving a growth rate of 0.8 μm/s.

The substrate temperature has a strong influence on the film characteristics. In particular adhesion to the substrate is improved when the substrate temperature is 700°C or above. Micro X-ray diffraction showed that films deposited below 500°C are largely amorphous, whereas films deposited at 700°C show the peak associated with β-SiC. Rutherford backscattering analysis has shown that most films are close to stoichiometric, but that films deposited at the lower substrate temperatures have more chlorine contamination. Film density values have also been derived from the Rutherford backscattering data, and it has been found that the density appears to increase from approximately 65% of theoretical obtained at substrate temperatures of 250°C to over 90% of theoretical for films deposited at 700°C.

A similarly strong effect has been observed in the hardness measurements using nanoindentation. Fig. 5 shows the hardness values as a function of the penetration depth for several films obtained at two different temperatures [9]. It is apparent that the films deposited

![Fig. 4. Measured particle size distributions in the supersonic plasma jet [9].](image)

![Fig. 5. Measured hardness values for two different silicon carbide films deposited at different temperatures [15].](image)
rapid deposition of material over a small area of typically 30–50 μm in diameter. Fig. 6 shows a tower composed of SiC and deposited with a growth rate of 1–2 μm/s [15]. Fig. 7 shows a pattern which can be deposited when the substrate is moved [18]. These kinds of deposits have also been obtained with TiC and Ti particles.

4. Conclusions

It is evident that coatings with nanophase structures can be deposited at rapid rates using supersonic plasma jet deposition techniques. While the films deposited from the vapor phase show higher densities, they also exhibit larger grain sizes. The use of an auxiliary discharge between the nozzle and the substrate does present an attractive way to increase the growth rate. For the case when the substrate is biased positively, this discharge provides an additional means to control the chemical reactions between the precursor injection location and the substrate. It should also be possible to deposit with this deposition method different film materials including composites.

The hypersonic plasma particle deposition process has demonstrated the deposition of several hard ceramic materials at very high rates and with a nanosize grain structure. The fact that the formation of the nanosize particles can be separated from the deposition process offers a range of interesting possibilities, including that of particle beam deposition and of producing deposits of composite materials. The development of a post-treatment method for further densification will permit this process to reach its full potential with respect to providing rapid deposition of hard coatings.

Acknowledgements

This work was supported in part by the NASA Lewis Research Center, by the Engineering Research Program of the Basic Energy Science Division, US Department of Energy, and by the National Science Foundation grant DMI-9871863.

References