TPCVD Synthesis of Si(-B)-C-N Coatings

Johannes Wilden, Andreas Wank

Inst. of Composite Materials, Chemnitz Univ. of Technology, 09107 Chemnitz, Germany

Abstract

Materials in the system Si-C-N feature excellent properties for wear and corrosion protection applications even at elevated temperatures and an excellent thermal shock resistance among the ceramics. Thermal Plasmajet CVD processes with single and triple DC torches and HF torches with supersonic nozzles have successfully been applied to produce Si-C(-N) coatings on different metal substrates, on graphite and C / SiC compounds. The application of liquid single precursors with suitable composition allows to coat areas up to 50 x 50 mm² with deposition rates up to 1.500 µm/h. The coatings are evaluated with regard to their morphology and structure and the processes are compared taking into account their characteristics concerning the injection modes, gas temperature and velocity profiles. Guidelines for the optimum production of Si-C(-N) coatings by Plasmajet CVD are deduced. Emission spectroscopic analyses show, that the precursors are completely dissociated in the thermal plasma. As the addition of boron is known to expand the range of applicable temperatures, adapted precursors are developed.

1. Introduction

Si-C-N coatings feature excellent properties for wear and oxidation protection applications, but conventional CVD and reactive PVD processes permit only low deposition rates and are therefore time demanding and expensive. Additionally partial coating is in most cases impossible. Therefore these processes often do not meet the logistical and economical demands of industrial production processes.

The diamond deposition rate of TPCVD is one order of magnitude higher than for any other process. A correlation of the boundary layer thickness with the chemical reactions on the substrate surface and the deposition rate has been deduced [1]. Yu et al. suggest, that processes with a high energy density and therefore strong dissociation of the precursors and small boundary layer thicknesses, achievable by high process gas velocities, are best suited for high synthesis rates. Furthermore, the application of liquid precursors has proven to increase the deposition rate in comparison to gaseous precursors [2]. Assuming, that Si-C-N coatings, which also have predominantly covalent bonds, grow by comparable mechanisms, the combination of liquid precursors and TPCVD processes with high gas velocities will result in high deposition rates. As the plasma jet acts only on a confined area, partial coating is possible. The TPCVD synthesis of diamond is restricted to small areas, because the different conditions outside the deposition centre favor sp² bonds. As for Si-C-N no graphite like structures are known, nearly constant coating properties can be expected.

Investigations on polymer derived silicon based ceramics show, that the addition of boron to the Si-C-N system expands the range of applicable temperatures significantly [3]. Both
single precursors and mixtures of different precursors may be used for the synthesis of Si-B-C-N coatings.

2. Experimental

Three different types of TPCVD processes are used for coating synthesis. A schematic is shown in Figure 1. For a conventional single DC torch process a Plasmatechnik A 3000 S vacuum plasma spraying system (Sulzer Metco Inc., Wohlen, Switzerland) with radial injection at a single position is used. Three modified DC torches AS - 103L (Tekna Plasma Systems Inc., Sherbrooke, Canada) with jets converging about 30 mm below the plane of the torch exits with central axial precursor feeding through a water cooled injection probe into the converging jet region are applied in the Triple DC Plasmajet CVD process. The characteristics concerning temperature and gas velocity profiles are published elsewhere [4]. Finally a HF plasma torch PL35 (Tekna Plasma Systems Inc., Sherbrooke, Canada) with a water cooled copper Mach 1 nozzle and axial precursor injection is used to investigate the High Velocity HF Plasmajet CVD (HVHF) process. Enthalpy probe studies of this fairly new process are also published elsewhere [5].

![Figure 1: Schematic of the TPCVD processes with liquid precursor injection](image)

The liquid precursors are atomized into the plasma jet with gas mixtures of Ar, H₂, N₂, He, CH₄ and C₂H₂; pure Ar and mixtures with H₂, N₂ or He are used as plasma gases. The chamber pressure and the substrate temperature are kept constant during the coating process.
Mild steel, austenitic stainless steel, aluminum and Al Mg 1.5, titanium, molybdenum and APS molybdenum, copper, brass Cu Zn 10, graphite and C / SiC substrates are coated. Chloromono- and -disilanes are applied to test the applicability of silicon industry waste for the production of high quality Si-C-N coatings. To reduce the chlorine content aminodisilanes are also synthesized and tested. In addition the chlorine free oxygen containing hexamethyldisiloxane and tetramethyldisiloxane and the oxygen free hexamethyldisilazane and hexamethylecloptolisilazane are applied.

3. Results

Three different types of coating morphologies are observed. At high precursor feed rates coatings consisting of nanoscaled particles are synthesized. Depending on the process parameters the diameters range from 20 - 400 μm. At lower precursor feed rates coatings with columnar or dense morphology are manufactured (Figure 2). For most columnar coatings there is a complete coverage at the interface to the substrate. This initial layer usually contains some cracks, if the thermal expansion coefficient of the substrate differs significantly from that of Si-C-N. During the Triple DC Plasmajet CVD synthesis secondary nucleation is observed in some coatings. The columns of the secondary nuclei grow much faster and form a microporous morphology with a smooth surface.

![Figure 2: SEM images of hexamethyldisiloxane coatings with columnar morphology and secondary nucleation (left) and dense morphology (right)]

In general a low chamber pressure is beneficial to synthesize coatings with a homogeneous microstructure, as the cross section of nearly constant plasma conditions increases with decreasing chamber pressure. The vacuum pumps of conventional plasma spraying equipment permit minimum pressure of about 3 kPa. Because of the large cross section of the HF plasma jet areas of 50 x 50 mm² are coated at a chamber pressure of 12 kPa without motion between substrate and torch. A single DC plasma torch has to be moved along a square with a side length of 10 mm to achieve a comparable coated area.

Columnar morphologies are synthesized at a rate of 400 μm/h in the conventional DC Plasmajet CVD process, while in the Triple Torch DC and HVHF Plasmajet CVD process 800 μm/h are achieved. If secondary nucleation occurs, the deposition rate increases to
1,500 μm/h. Dense morphologies are synthesized at 600 μm/h in the HVHF Plasmajet CVD process.

The coating composition depends strongly on the applied precursor and the chamber pressure. In all coatings synthesized with chlorine containing precursors chlorine with a minimum content of 1.5 at-% is detected by EDX. The chlorine causes a strong corrosive attack at the interface to the substrate, which results in complete delamination of the coating from mild steel substrates within a single day. The lower the oxygen partial pressure in the chamber, the lower the oxygen content in the synthesized coating. A high oxygen partial pressure also favors the formation of oxide layers on top of the substrates during heating before the synthesis, which worsens the coating adhesion. The application of H₂ as secondary plasma gas prevents oxidation, but causes damage to grain boundaries due to etching, if the H₂ content is too high.

The best adhesion is observed on molybdenum substrates, but mild steel, copper, brass Cu Zn 10, graphite and C / SiC compounds can also be coated without spallation or burst of small areas due to residual stresses. Oxide free and smooth surfaces are also beneficial to prevent coating failure. Though the thermal expansion coefficient of copper and austenitic stainless steel are comparable, coatings on copper tend to spall off much less. Aluminum has to be heated close to its melting point to achieve good coating adhesion. Graphite substrates must not be heated to red glow in order to deposit coatings. Otherwise even erosion is observed.

The plasma gas composition also takes influence on the coating composition. When N₂ is applied as secondary plasma gas or as atomizing gas, the coatings contain nitrogen. In some cases nitrogen can also be detected, if pure Ar or Ar / H₂ plasmas and the hexamethyldisilazane precursor are used.

In pure Ar plasmas usually amorphous coatings are synthesized. The use of H₂ or N₂ as secondary plasma gas increases the plasma enthalpy and the heat transfer to the substrate significantly. This favors crystalline structures. When N₂ is applied, β-Si₃N₄ and at high substrate temperatures additionally α-Si₃N₄ can be detected by XRD. H₂ addition also results in increased crystallinity. In most cases the diffraction pattern matches β-SiC, but in some cases peaks, that can be attributed to a silicon high pressure phase, are found as well. The same observation has been made in the HPPD synthesis of SiC coatings [6]. In one single case the formation of graphite is observed, when the trimethylchlorosilane precursor is applied to the DC Plasmajet CVD process.

Investigations concerning the plasma chemistry of the single torch DC Plasmajet CVD process have been published elsewhere [7]. These prove the complete dissociation of the precursors within the first 20 mm behind the injection point even at flow rates of 0.01 l/min HMDSO.

4. Discussion

The dependence of the coating morphology and structure of Si-C(-N) coatings on the boundary conditions of the applied TPCVD process is summarized in Figure 3. High gas velocities and therefore short process times lead to a low crystallinity of the synthesized coatings. The crystallinity of SiC is easier suppressed in comparison to Si₃N₄. For increasing process temperatures and velocities the coating morphology turns from nanosized particles to columnar. At high gas velocities and moderate process temperatures dense coating morphologies are synthesized.

Axial injection results in a more homogeneous distribution of species in the plasma jet compared to radial injection and is therefore beneficial with regard to a constant coating thickness, morphology and structure. The torch can be moved relative to the substrate to
increase the coated area with simultaneous improvement of the coating homogeneity. The preparation of the substrate surface before the coating process takes significant influence on the coating properties. Polished surfaces without oxide layers achieve the best coating adhesion.

![Graph showing coating morphology and structure depending on the boundary conditions of the TPCVD process](image)

**Figure 3:** Coating morphology and structure depending on the boundary conditions of the TPCVD process

The application of chlorosilane precursors results in chlorine incorporation in the coatings and can cause severe damage in the interface between substrate and coating. Therefore chlorosilanes cannot be used to coat chloride sensitive substrates. As the precursors are completely dissociated on a very short way in the plasma jet, the bond structure of the precursor is less important compared to its composition. Therefore Si-B-C-N coatings with tailored composition may be synthesized from mixtures of different liquid Si-C(-N) and B(-C)-N precursors, e.g. hexamethylycyclotrisilazane and (methylized) borazine. On the other hand the application of single precursors can be expected to improve the homogeneity of the species distribution in the plasma jet. As even a significant carbon excess in the stoichiometry of the precursor usually does not cause the formation of graphite phases, a preferential growth of silicon based structures can be assumed.

5. Summary and Conclusions

TPCVD processes show high potential for the synthesis of silicon based ceramic coatings at high deposition rates. By optimization of the process parameters coating morphology and structure can be tailored. The application of liquid single precursors allows the synthesis of Si-C(-N) coatings with deposition rates up to 1,500 μm/h for columnar and up to 600 μm/h for dense morphologies. Amorphous or nanocrystalline structures can be synthesized.

Both DC and HF plasmas can be applied. To achieve constant coating microstructure and therefore constant properties plasmas with a large volume of quite constant plasma temperatures are beneficial. Relative movement of plasma torch and substrate allows improvement of the homogeneity of the coating microstructure and extends the coated area. Because of the local interaction of plasma jet and substrate partial coating is possible.
TPCVD processes can be applied to coat various metallic and ceramic materials with Si-C(-N). Because of the comparable thermal expansion and as oxides can easily be abstracted from the surface, molybdenum is an advantageous substrate material. The surface preparation takes significant influence on the coating properties, especially on the adhesion.

Further work will be carried out on the TPCVD synthesis of Si-B-C-N coatings from suitable, chlorine free precursors, as these materials are known to feature improved thermal stability and oxidation resistance compared to SiC and Si-C-N materials. Additionally the TPCVD synthesis of B-C-N coatings, that feature a high hardness, a low friction coefficient and improved oxidation resistance compared to DLC, will be investigated.

6. Acknowledgements

The presented results are partially funded by the Deutsche Forschungsgemeinschaft in the limits of the compound project "Precursor based plasma synthesis of multi component hard coatings for high temperature applications".

The authors want to thank Wacker Chemie, Germany, for providing precursors. Special thanks applies to Prof. Pfender and Prof. Heberlein from the University of Minnesota for the possibility to carry out investigations on the Triple Torch DC Plasmajet CVD process and to Prof. Boulos and Prof. Gitzhofer from the University of Sherbrooke for the possibility to carry out investigations on the HVHF Plasmajet CVD process.

References