Hard Coatings and Vapor Deposition Technologies
Room Town & Country C - Session B2-MoA

CVD Coatings and Technologies

Moderators: Prof. Raphaël Boichot, Grenoble-INP/CNRS, France, **Dr. Hiroki Kondo**, Nagoya University, Japan

1:40pm **B2-MoA-1 Si and SiC-based CVD Coatings for High Temperature Structural Applications***, A. Le Doze, P. Drieux,* Laboratoire des Composites Thermostructuraux - CNRS, France*; S. Jacques,* Laboratoire de Composites Thermostructuraux - CNRS, France*; G. Couégnat, **Georges Chollon**,* Laboratoire des Composites Thermostructuraux - CNRS, France **INVITED**

Thermal chemical vapor deposition (CVD) is well suited to produce high-purity, high-crystallinity films compatible with high temperature structural applications. A good example of such structural coatings is the silicon carbide matrix of ceramic matrix composites (CMCs). However, in SiC/SiC composites, the role of the matrix in the overall mechanical behavior appears to be minor compared to that of the fibers or the interphase.Yet, intrinsically, the CVD coating can exhibit all these qualities. The key is to adjust the process parameters to obtain an appropriate composition and microstructure. The evaluation of the mechanical properties of the coating itself must also be performed using specific tests. These two aspects will be developed in the presentation through two examples.

The first one is a high-strength, gas-tight CVD SiC sheath, to complete the composite structure of a nuclear fuel claddings. Long, free standing SiC tubes were prepared at atmospheric pressure using $CH_3SiHCl_2/C_3H_6/H_2$ mixtures, in a fast, original, and near net shape process. Sliding the heating system along the tubular substrate allowed the continuous deposition of long and thick CVD SiC sheaths. Their composition, microstructure and surface morphology were analyzed in details. C-ring specimens were cut from the tubes and submitted to high temperature compressive tests. The deposition rate, Si/C atomic ratio, crystalline state and surface roughness of the CVD-SiC tubes are related to the gas phase reactions. Their thermomechanical properties can be improved by adjusting the through-thickness composition gradient using a proper precursor mixture.

The second example is a CVD silicon coating used as the bond coat (BC) of an environmental barrier coating on a CMC. In use, the BC may oxidize, which can cause local stresses and eventually damages. Centrifugal loads can also generate some creep deformation of the rotating parts. It is thus crucial to control the creep behavior of the BC, and hence its microstructure, through the CVD process. The deposition of polycrystalline silicon from $SiHCl_3/H_2$ was explored and a selection of coatings were prepared on fine carbon fiber substrates for testing. The morphology and microstructure of the deposits were investigated by SEM and EBSD, and the creep properties by 3-point bending. Several microstructures were obtained by various combinations of CVD conditions and thermal annealing. Different responses of the silicon coatings to mechanical stresses have been measured, illustrating different deformation mechanisms.

2:20pm **B2-MoA-3 Influence of Bilayer Periodicity on Microstructure, Residual Stress and Mechanical Properties of CVD TiN/TiB$_2$ Multilayer Coatings***, **Michael Tkadletz**,* Montanuniversität Leoben, Austria*; A. Lechner, B. Sartory,* Materials Center Leoben Forschung GmbH, Austria*; C. Czettl,* CERATIZIT Austria GmbH, Austria*; N. Schalk,* Montanuniversität Leoben, Austria

Chemical vapor deposited (CVD) TiN and TiB_2 are quite different materials, but both are frequently utilized as wear resistant hard coatings. CVD TiN exhibits a comparatively large grain size in the µm range, tensile residual stress and a moderate hardness. CVD TiB_2 in contrast is usually characterized by a nanocrystalline microstructure and high compressive residual stress accompanied by a high hardness. In order to investigate the interaction of such different materials, CVD TiN and TiB_2 were combined in two multilayer coatings with different bilayer periodicities of ~100 and ~200 nm. Subsequently, the influence of the multilayer architecture on the evolving microstructure and grain size was investigated by means of scanning transmission electron microscopy, energy dispersive X-ray spectroscopy and transmission Kikuchi diffraction. X-ray diffraction provided insight into the phase composition and evolution of residual stress state and magnitude of the individual layers. In addition, to clarify whether B diffusion between the different layers takes place during deposition, atom probe tomography was applied to the multilayer coating with lower bilayer periodicity. The microstructural and chemical investigations were accompanied by cross-sectional hardness mappings via nanoindentation with high lateral resolution and micromechanical bending tests. The study was complemented by experiments on reference single layers of both materials which allow a thorough conclusion about the effects and changes provoked by the implemented multilayer architecture at different length scales.

2:40pm **B2-MoA-4 Effect of the Substrate Treatment on the Microstructure of CVD Ti(C,N)/Al$_2$O$_3$ Hard Coatings***, **Christiane Wächtler**, C. Wüstefeld,* TU Bergakademie Freiberg, Germany*; M. Šíma, J. Pikner,* Dormer Pramet, Czechia*; D. Rafaja,* TU Bergakademie Freiberg, Germany

Although the use of protective $Ti(C,N)/Al_2O_3$ coatings produced by chemical vapour deposition (CVD) on cemented carbide (WC-Co) substrates is the state of the art in the high-speed metal cutting, the effect of the substrate treatment on the microstructure and properties of such coatings is not fully understood yet. In this contribution, the role of the size of the tungsten carbide grains (1.9 µm and 0.7 µm, respectively) and the substrate treatment (as-sintered, wet blasted, ground or polished) was systematically investigated for a constant amount of the cobalt binder (10 wt.%) in the cemented carbide. The hard coatings with different architectures, i.e., the $TiC_{0.6}N_{0.4}$ monolayers and complete $TiC_{0.6}N_{0.4}/Al_2O_3$ stacks, were deposited using the same parameters of the CVD process.

The microstructure analyses carried out using scanning electron microscopy with electron backscatter diffraction, transmission electron microscopy, laboratory X-ray diffraction and nanobeam synchrotron diffraction revealed that the kind of the substrate treatment strongly influences the preferred orientation and the lateral size of the grains in the coatings, as well as the residual stress in both phases (fcc-Ti(C,N) and α-Al_2O_3). Finally, the adhesion of the coatings to the substrate was quantified using scratch tests. The strongest preferred orientation of crystallites, which was {211} in fcc-Ti(C,N) and {001} in α-Al_2O_3, developed in coatings with consistently narrow grains. The texture was always weakened, when coarse Ti(C,N) and/or Al_2O_3 grains grew in the coatings in addition to the narrow grains. The dependence of the texture degree and the grain size on the substrate treatment was also observed for the α-Al_2O_3 layer, although the bonding layer between fcc-Ti(C,N) and α-Al_2O_3 consisted of very small crystallites having no pronounced preferred orientation. The comparison of the single-layer Ti(C,N) coatings with the $Ti(C,N)/Al_2O_3$ stacks helped us to understand the effect of the additional thermal exposure of the samples during the Al_2O_3 deposition on the microstructure of the Ti(C,N) layer.

The results of this study emphasize that the surface condition of cemented carbide substrates needs to be considered as it has a clear impact on the microstructure formation of the $Ti(C,N)/Al_2O_3$ coatings produced in CVD processes.

3:00pm **B2-MoA-5 Novel ZrB$_2$ and HfB$_2$ Metaldiboride Coatings by LPCVD***, **Mandy Höhn**, M. Krug, B. Matthey,* Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Germany

The synthesis of metal diboride thin films is recently attracting large interest. Boron forms binary compounds with most metals.These materials in general are high-melting, extremely hard solids with high degrees of thermal stability and chemical inertness.

In this work the preparation of metal diboride coatings of ZrB_2 and HfB_2 by CVD is described. A LPCVD process using $MeCl_4$ (Me = Zr or Hf), BCl_3, H_2 and Ar is applied. At deposition temperatures between 800°C and 1000°C diboride layers were prepared. The coatings were characterized with respect to phase composition, crystal structure, hardness and wear behaviour. The deposited diboride layers show well defined crystallites with a high hardness up to 32 GPa for ZrB_2 and 38 GPa for HfB_2. In dependence of substrate temperature and precursor ratio layers with different textured crystalline structure were obtained with different deposition rates. Phase composition and structure were examined using SEM and EDX-analysis. The measured tensile stress in the obtained coatings depends on the deposition conditions and varies between 350 MPa and 600 MPa.

A strong adherence on hardmetal inserts is achieved by using a thin TiN bonding layer prior the diboride deposition. Scratch test measurements showed critical loads of about 90 N. In wear tests a high performance of the CVD diboride coatings was observed. HfB_2 coated inserts showed a higher lifetime in comparison with state-of-the-art CVD- and PVD-TiB_2 coatings in face-milling TiAl6V4.

3:20pm **B2-MoA-6 Diamond Coatings on Cutting Tools Applied to Super-Hard Workpiece Materials***, **Michael Woda,*** CemeCon AG, Germany*; J. Fuentes,* Hufschmied Zerspanungssysteme GmbH, Germany*; W. Puetz, M. Wegh, C. Schiffers, S. Bolz, O. Lemmer,* CemeCon AG, Germany

Thin film Diamond as pure sp3 bonded crystalline carbon is able to significantly improve cutting tool wear performance. Diamond coatings are typically deposited by the means of hot filament CVD processes on an industrial scale nowadays. The basic principle of the corresponding deposition technology and its resulting diamond coating properties are introduced in this presentation.

When applying these diamond thin films to cutting tools containing a cemented carbide substrate and possessing complex geometries, the machining of a large set of highly abrasive work piece materials can be enabled. These materials include Carbon Fiber Reinforced Plastics (CFRP), Ceramic Matrix Composites (CMC), zirconium oxide ceramics, hypereutectic aluminum silicon alloys, graphite or even cemented carbide. This work presents some of the latest results of selected case studies revealing the benefits of CVD diamond coatings at cutting operations on these very challenging and super-hard work piece materials.

3:40pm **B2-MoA-7 Study on Small-Volume and Flow-Type Hard DLC Film Process Using Substrate-Surrounding Microwave Plasma***, **Hiroyuki Kousaka,*** Gifu University, Japan **INVITED**

Recently, with increasing demands for energy saving by friction reduction and lifetime extension by wear reduction, the application of DLC (Diamond-Like Carbon) is spreading gradually and steadily. Plasma CVD is one of the promising manufacturing methods of DLC due to its excellent capability for coating 3-dimensional shapes; however, its coating speed is typically not so high, ~1 µm/h due to the use of low-density (n_e~10^8-10^{10} cm^{-3}) plasma with DC or RF discharge. At such a deposition rate, batch processing of a large number of parts (substrates) is essential for cost reduction. However, in the coating of machine parts, flow processing of a small number of parts may be desirable. To achieve this, it is necessary to coat one to several parts at a drastically increased coating speed.

For further increasing the coating speed of DLC, we have proposed an ultra-high-speed DLC coating at over 100 µm/h employing much higher-density plasma (n_e~10^{11}-10^{13} cm^{-3}), which is sustained by microwave propagation along plasma-sheath interface. In this work, we investigated the effect of atomic composition of DLC film on the deposition rate and hardness in such ultra-high-speed DLC coating. Si-containing a-C:H films (one type of DLC) were deposited on steel substrates by different 2 methods: DC plasma and microwave-excited high-density near plasma, or our newly proposed method, where the gas composition of Ar, CH_4, C_2H_2, and TMS, and the duty ratio of microwave and substrate bias were changed. Note that the substrate bias was fixed to be −500 V. For example, under the same condition except microwave injection, the deposition rate and hardness of the DLC deposited by DC plasma were 2.5 µm/h and 11.8 GPa, respectively; while the deposition rate and hardness of the DLC deposited by microwave-excited high-density near plasma were 156 µm/h and 20.8 GPa, respectively. The atomic composition of the films was evaluated by XPS for C, O, and Si, and RBS-ERDA for H/C ratio. Within the range of our results, the hardness films were almost linearly decreased from 6 to 22 GPa with decreasing hydrogen content from 45% to 22%, being independent from the composition of C and Si.

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