Hard Coatings and Vapor Deposition Technologies
Room California - Session B2-1

CVD Coatings and Technologies

Moderators: Michel Pons, University Grenoble Alpes, SIMAP, CNRS, Makoto Kambara, The University of Tokyo

8:00am **B2-1-1 Microstructure Investigation on CVD $Ti_{1-x}Al_xN$ Hard Coatings***, **Ren Qiu**, O Bäcke, M Hassine, M Halvarsson,* Chalmers University of Technology, Sweden*; D Stiens, T Manns, J Kümmel, V Janssen,* Walter AG, Germany

TiN with NaCl crystal structure has been widely used in hard coatings for cutting tool materials. By replacing the Ti atoms partially with Al, cubic $Ti_{1-x}Al_xN$ is formed which has attracted significant attention in the latest years due to its outstanding oxidation and wear resistances. In recent years, CVD (Chemical Vapour Deposition) has been used for the deposition of the $Ti_{1-x}Al_xN$ coatings which used to be produced by PVD (Physical Vapour Deposition). In this work, CVD $Ti_{1-x}Al_xN$ hard coating is grown on cemented carbide substrate pre-coated with TiN. Lift-out samples at different interesting areas are prepared by focused ion beam (FIB) microscopy. Local variation of the coating structures is studied by electron diffraction and high resolution (scanning) transmission electron microscopy (S)TEM imaging. Local variation of the chemical composition is investigated by the energy dispersive X-ray analysis (EDX) and electron energy loss spectroscopy (EELS). It is found that the content of the coatings varied periodically with high (~90 at.%) and low (~50 at.%) regions of Al. Both regions exhibit the fcc structure, which is the desired phase for hard coatings. The general microstructure appeared as a “fish-bone” structure with a 111 texture, with growth occurring on 001 faces, leading to a pyramidal surface morphology. The microstructural differences for varying growth conditions will be described.

8:20am **B2-1-2 Elaboration and Characterization of (TI,AL)N Coatings Deposited by Thermal CVD for Protection in Severe In-service Conditions***, **Florent Uny**, S Achache, S Lamri, G Raine,* Nogent International Center for CVD Innovation, LRC CEA-ICD LASMIS UMR6281, UTT, Antenne de Nogent, France*; Z Dong,* Nanyang Technological University, Singapore*; M Pons, E Blanquet,* Université Grenoble Alpes, CNRS, Grenoble INP, SIMaP, France*; F Schuster,* Commisariat à l'Energie Atomique et aux énergies alternatives (CEA) Saclay - Nogent International Center for CVD Innovation, France*; F Sanchette,* Nogent International Center for CVD Innovation, LRC CEA-ICD LASMIS UMR6281, UTT, Antenne de Nogent, France

Ceramic hard coatings, especially TiAlN thin films received a good interest for several decades for protection of cutting tools owing to their high hardness and oxidation resistance [1]. While PVD deposition was widely investigated, only few literature are available on thermal CVD deposition of TiAlN coatings. Recent advances in CVD deposition showed the formation of nanocomposite coatings in an industrial deposition unit at pressure below 30mbar. These coatings, consisting of an arrangement of TiN and AlN lamellae, combine high hardness and good oxidation resistance [2], [3].

In this work, TiAlN coatings with varied Al-contents were deposited in an industrial CVD scale unit by means of ammonia and aluminum and titanium chlorides. Morphological and microstructural evolutions were characterized regarding the Al-content in the coating. A change in morphology, from globular grains to “cubic” grains was observed by increasing the amount of Aluminum in the film. This modification seems to be related to the appearance of the hcp-AlN structure. The influence of these morphological and microstructural changes on the mechanical properties and oxidation resistance was also characterized.

References:

[1] L. Chen, J. Paulitsch, Y. Du, et P. H. Mayrhofer, « Thermal stability and oxidation resistance of Ti–Al–N coatings », *Surf. Coat. Technol.*, vol. 206, n° 11–12, p. 2954–2960, févr. 2012.

[2] J. Todt *et al.*, « Superior oxidation resistance, mechanical properties and residual stresses of an Al-rich nanolamellar Ti0.05Al0.95N coating prepared by CVD », *Surf. Coat. Technol.*, vol. 258, p. 1119–1127, nov. 2014.

[3] J. Todt *et al.*, « Al-rich cubic Al0.8Ti0.2N coating with self-organized nano-lamellar microstructure: Thermal and mechanical properties », *Surf. Coat. Technol.*, vol. 291, p. 89–93, avr. 2016.

8:40am **B2-1-3 Investigation of CVD-AlTiN Films with High Al Content***, **Kenichi Sato**, S Tatsuoka, K Yanagisawa, T Ishigaki, K Yamaguchi,* Mitsubishi Materials Corporation, Japan **INVITED**

Recently, Aluminum Titanium Nitride (AlTiN) films deposited by thermal CVD method (CVD-AlTiN) has attracted cutting tools suppliers because some research groups have reported their good results in milling tests of alloy steels and cast irons. In this deposition method, ammonia gas is used as nitrogen source. One of the most interesting characteristics of CVD-AlTiN films is the amount of Al. It is higher than that of AlTiN films deposited by PVD method. It is well-known that conventional AlTiN films deposited by PVD method have cubic structure in the range of Al content lower than about 0.7, while they obtain hexagonal structure in the range of Al content higher than 0.7. However, CVD-AlTiN films keep cubic structure in Al content higher than 0.7, which prevents their cutting properties from getting worse. The amount of Al of AlTiN films is one of the most important factors which determine cutting properties, because it affects mechanical properties. For the last several years, the research on CVD-AlTiN films has made some progress, and some cutting tools suppliers have launched CVD-AlTiN films inserts which showed good cutting performance.

In this presentation, our works on CVD-AlTiN films with high Al content will be shown. We have focused on the influence of Al content on the characteristics of CVD-AlTiN films and the change of their structure and characteristics. As a result, we obtained CVD-AlTiN films with high Al content, about 0.85, which showed high hardness and interesting structure. From the result of Electron Backscattering Scanning Microscopy (EBSD), mis-orientation in grains was observed and the average value of Grain Orientation Spread (GOS) is bigger than that of conventional hard coatings. Also, nano-lamellae structure was observed by Scanning Electron Microscopy. We are going to discuss the growth mechanism of CVD-AlTiN films from our results. CVD-AlTiN films with these interesting characteristics showed better cutting performance than conventional CVD-inserts and PVD-inserts in our milling tests of ductile cast irons.

9:20am **B2-1-5 Microstructural Investigation of CVD Titanium Aluminium Nitride – Kappa Alumina Coatings***, **Olof Bäcke**, M Halvarsson, H Petersson,* Chalmers University of Technology, Sweden*; D Stiens, T Manns, J Kümmel,* Walter AG, Germany

TiAlN is today a common choice for wear-resistant coatings on cutting tools used for metal machining due to its high hardness and excellent oxidation resistance. For long, physical vapour deposition (PVD) has been the standard method for producing commercial available TiAlN coatings. Using PVD it has been impossible to reach $Ti_{(1-x)}Al_xN$ coatings with a higher Al content than x = 0.65. A few years ago however a new low pressure chemical vapour deposition (CVD) technique was developed that makes it possible to deposit $Ti_{(1-x)}Al_xN$ coatings with a very high Al content, x = 0.9. These high Al content TiAlN coatings show improved hardness compared to other TiAlN coatings and commercially available CVD grown TiAlN coatings are just reaching the market. However, wear-resistant coatings often combine layers of different materials to improve properties, where one common candidate is alumina. It is thus of interest to investigate if CVD grown TiAlN can be combined with other materials in multilayered coatings. In this work, the focus has been on investigating the possibility of growing kappa alumina on CVD grown TiAlN. TiAlN multilayer coatings were produced on standard WC/Co cemented carbide substrates, where kappa alumina layers were grown on top of TiAlN layers with different texture. The coatings were characterized by X-ray diffraction (XRD), scanning and transmission electron microscopy (STEM and TEM), and energy dispersive X-ray analysis (EDX). Focus were on how the microstructure of the different textured TiAlN layers, which are metastable, changed when exposed to temperatures necessary for growing kappa alumina, and the texture of the grown kappa alumina. The results show that hexagonal AlN and cubic TiN can be found precipitated along grain boundaries in the TiAlN layers. The orientation relationships between TiAlN and kappa alumina layers were also described and a model for how the kappa alumina grains are growing on the TiAlN grains suggested.

9:40am **B2-1-6 Deep Electron Microscopy Investigation of $Ti_{1-x}Al_xN$/TiCN Multilayer CVD Coatings***, **Mohamed Ben Hassine**, O Bäcke,* Chalmers University of Technology, Sweden*; D Stiens, T Manns, J Kümmel, W Janssen,* Walter AG, Germany*; M Halvarsson,* Chalmers University of Technology, Sweden

$Ti_{1-x}Al_xN$ is a well-established material for cutting tool applications exhibiting high hardness and excellent oxidation resistance. Recently, CVD has been used for the deposition of TiAlN coatings. The desired fcc phase of TiAlN is metastable and can be produced by CVD processes using ammonia

(NH_3) as a precursor. The Al/Al+Ti ratio in TiAlN is around 0.9 by CVD. This is thought to be beneficial for the oxidation resistance and performance of such coatings in metal cutting applications. Moreover, the combination of $Ti_{1-x}Al_xN$ with TiCN has attracted significant attention in the latest years due to its outstanding oxidation and wear resistances.

In this work, hard CVD coating of multilayer of $Ti_{1-x}Al_xN$ and TiCN is grown on cemented carbide substrate pre-coated with TiN. The microstructural development of $Ti_{1-x}Al_xN$ growing on TiCN is compared with TiCN growing on $Ti_{1-x}Al_xN$. A suite of electron microscopy and spectroscopy techniques was used to carefully examine the structure and chemical composition of the multilayer at different scales including grain size, texture and atomic resolution imaging. Aberration corrected scanning transmission electron microscopy (STEM) revels the presence of interfacial dislocations, twins, stacking faults and the formation of new interfacial phases. These results explain the different growth modes observed in the two multilayer systems.

10:00am **B2-1-7 Some Guidelines for the Determination of Texture Coefficients in CVD α-Al_2O_3 Coatings***, **Rafael Stylianou**, M Tkadletz,* Montanuniversität Leoben, Austria*; M Penoy,* CERATIZIT Luxembourg S.à r.l., Luxembourg*; C Czettl,* CERATIZIT Austria GmbH, Austria*; C Mitterer,* Montanuniversität Leoben, Austria

α-Al_2O_3 coatings deposited onto cemented carbide tools by chemical vapor deposition (CVD) are widely employed in cutting applications due to their excellent wear resistance, thermal stability and chemical inertness. Recent advances have allowed the control of their crystallographic texture, enabling α-Al_2O_3 coatings to benefit from the anisotropy in wear resistance across various orientations. Within this study, a comprehensive microstructure characterization of CVD α-Al_2O_3 coatings is presented, with the goal to provide useful guidelines for the determination of their crystallographic texture in the growth direction using texture coefficients determined by X-ray diffraction, as well as pole figures derived from X-ray diffraction and electron back-scatter diffraction. Texture coefficient calculations require the X-ray diffraction intensities from a θ/2θ scan of texturized coatings and non-texturized powder standards. Within this work, texturized coating intensities were determined for a representative sample (i.e. a CVD α-Al_2O_3 coating). Non-texturized intensities were retrieved, firstly from an equivalent coating turned into powder by chemically etching the substrate with HNO_3, and secondly from a corundum standard sample provided by NIST. Synchrotron intensity measurements have been performed for the non-texturized powder samples, and are used as a reference. In a next step, intensity data has been collected from four different X-ray diffractometers in parallel beam and Bragg-Brentano configurations, for both coating and powder samples. The calculated texture coefficients indicate a (001) growth texture, which was confirmed by pole figure measurements of the α-Al_2O_3 coating surface. Based on the results obtained, a simple set of guidelines is advised for the determination of texture coefficients: (a) X-ray intensity acquisition only for symmetric θ/2θ scans, (b) removal of X-ray background intensity, (c) introduce intensity corrections, that take into account the irradiated α-Al_2O_3 volume, corresponding to each diffraction angle value, (d) use of reflections that have a high peak to background X-ray intensity ratio, (e) exclusion of second order reflections at the presence of first order reflections, (f) texture coefficients provided should be accompanied by the respective coating thickness due to its dependency, and (g) use of appropriate powder standards.

10:20am **B2-1-8 Hot Filament CVD Diamond and HIPIMS-Diamond Coating Technology on Cemented Carbide Substrates for Cutting Tool Applications***, **Michael Woda**, W Puetz, M Frank, S Bolz, W Koelker, O Lemmer, T Leyendecker,* CemeCon AG, Germany

Polycrystalline CVD diamond thin films are mainly deposited by means of either microwave or hot filament assisted CVD coating techniques. The later one being discussed here is a suitable coating method for cutting tools with complex geometries and is well established on an industrial scale. Besides addressing the basics of the coating equipment and deposition technology, this presentation discusses the results of case studies dealing with cutting applications on machining of various classes of highly abrasive materials with pure CVD Diamond thin films. These case studies include applications with Carbon fiber reinforced plastics (CFRP) systems for aerospace industry, zirconium oxides systems for dental applications up to direct milling of cemented carbide. In addition a novel class of coating materials which combines thin film HIPIMS and CVD Diamond is introduced. This merging of ultra-hard CVD diamond coatings and extremely dense and extraordinary smooth HIPIMS coatings creates the possibility of completely new cutting tool performance. The extreme hardness and excellent thermal properties of diamond is a clear benefit for the overall tool performance. The HIPIMS contribution provides excellent heat flow properties into the chips, serves as a well-suited protection mechanism at high cutting temperatures and improves the reduction of friction. Coating technology, film properties and application results for HIPIMS-Diamond coatings will be discussed in the scope of this work.

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