Hard Coatings and Vapor Deposition Technologies
Room Pacific D - Session B3-ThA

Deposition Technologies and Applications for Carbon-based Coatings

Moderators: Konrad Fadenberger, Robert Bosch GmbH, Germany, **Frank Papa**, GP Plasma, USA

1:20pm **B3-ThA-1 Smooth and Wear-resistant Carbon Coatings Deposited by S3p™**, ***Julien Kéraudy (julien.keraudy@oerlikon.com)***, *K. Siegfried, D. Martin, S. Guimond,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein

Diamond-like carbon (DLC) coatings, namely hydrogenated amorphous carbon (a-C:H) coatings deposited by a PECVD process emerged years ago as the ideal solution for applications where component parts are under high loads or subject to extreme friction, wear and contact pressures with other parts. However, there are nowadays many tribological systems, in which the abrasion resistance of a-C:H coatings is at the limit or even insufficient. With its higher hardness, tetrahedral amorphous carbon (ta-C) would provide more abrasion resistance, a longer lifetime and enable a better performance for the related components. However, the state-of-the-art arc-deposited ta-C coatings (filtered or not) are simply too rough for many applications. Possible solutions to improve surface quality are post-finishing methods such as brushing or polishing, which however have a significant impact on the processing costs.

Recently, high power impulse magnetron sputtering (HiPIMS) was reported to be a suitable method to deposit dense hydrogen-free amorphous carbon (a-C) coatings. In this work, we report on the coating growth and properties of smooth and hard carbon coatings produced by the S3p™ (Scalable Pulsed Power Plasma) method in an industrial deposition plant. S3p™ technology enables scalability of the pulse power density and pulse length in a wide range and expands significantly the choice of the deposition parameters and process stability as compared to conventional HiPIMS technology. Smooth and hard hydrogen-free carbon layers were produced using graphite targets in Ar ambient. The thermal stability of the coatings in air and their tribological behavior in dry and lubricated environments were investigated and compared to the results of standard a-C:H and ta-C coatings. Furthermore, the influence of adding a C_2H_2 precursor in an Ar ambient atmosphere on the film properties and S3p™ reactive process was investigated.

Finally, selected applications where carbon coatings deposited by S3p™ outperformed common DLC coatings will be presented.

1:40pm **B3-ThA-2 New Developments on Hydrogen Free Carbon Coatings for Automotive, Industrial and Tool Applications**, ***Philipp Immich (pimmich@hauzer.nl)***, *L. Tegelaers, G. Negrea, R. Jacobs, G. Fransen,* IHI Hauzer Techno Coating B.V., Netherlands

Nanostructured and amorphous coatings play an important role in today's automotive, industrial and tool applications. There are huge areas for application for these kinds of coatings – first of all the automotive market, but also traditional applications like cutting or forming tools.

Today the focus is on the growing customer demand for coating properties like higher temperature stability and increased wear resistance in combination with low viscosity lubricants and fuels. In the last years therefore development work shifted to the group of hydrogen free DLC coatings like a-C and ta-C coatings.

To industrialize these coatings different developments routs were carried out in the last years, to ensure an economic and reliable way of deposition. The equipment design and even the selection of most suitable process technology are however also strongly determined by the productivity and the coating properties. In this regard we will demonstrate by using the different Hauzer high energetic pulsed technologies HIPIMS as well as new developed pulsed arc, that coatings can be more tuned and tailormade towards dedicated properties. We will also show that these technologies can be easy upscaled on different machine sizes and deliver here reliable industrial processes with a good ratio of coating cost per coated part and performance.

2:00pm **B3-ThA-3** ***Carbon-Based Coatings for Forming and Protection of Stainless Steel Sheets***, ***Marcus Morstein (marcus.morstein@hightechzentrum.ch)***, Hightech Zentrum Aargau AG, Switzerland **INVITED**

Carbon-based coatings, because of their unique combination of low friction, low wear and chemical inertness, have a long-proven potential as coating materials. Both cutting and forming tools are coated with diamond-like carbon (DLC) coatings, as are components in the automotive sector, both for combustions engines and xEV components. Besides, its appealing dark black color renders DLC useful for decorative purposes.

For different applications different types of DLC coatings have been established, where hydrogen-stabilized DLC, despite its relatively low hardness, is the material of choice for components such as sliding or rolling bearings, or decorative coatings. On the high-performance end, tetrahedral amorphous carbon (*ta*-C) withstands tough conditions and provides superior hardness of up to about 60 GPa.

While the temperature- respectively, oxidation sensitivity limits the application range of carbon-based coatings, new applications keep being added and progress in deposition technology allows for (relatively) low-cost coating even of large-area parts with DLCs.

A recent example for the successful use of amorphous carbon as protective coating for stainless steel are metallic bipolar plates for proton-exchange membrane (PEM) fuel cells. These thin sheets of below 100 µm, often made from 316L (1.4404) steel, need to be protected from corrosion in order to achieve the desired stack lifetimes. For this purpose, chemically passive carbon-based coatings have been used with success.

Recently, precision forming processes have been developed for the economical mass production of these bipolar plates. In production-near tests, DLC coatings combined with an advanced surface treatment process for the steel tools have been shown to perform very well, compared to alternative PVD coatings

DLC coatings are also commonly applied as black color layer for e.g. household appliances. However, because of the imminent exposure to abrasive wear of those surfaces, the supporting properties of the otherwise soft stainless steel substrate need to be enhanced by mechanical of diffusion treatment.

Progress has been made in deposition technology, too. A novel hybrid deposition technique combining a microwave plasma with sputtering allows for the fabrication of high-hardness, non-hydrogenated diamond-like carbon coatings. The properties and morphology of the fabricated DLC films are comparedto those from pulsed-direct current magnetron sputtering (DCMS) or high-power impulse magnetron sputtering (HiPIMS), using techniques such as Raman spectroscopy, nanoindentation, X-ray reflectometry and scanning electron microscopy.

2:40pm **B3-ThA-5 DLC Coatings: Diamond Hardness & Graphite Lubrication Combined to Meet Industrial Application Requirements**, ***Hamid Bolvardi (h.bolvardi@platit.com)***, PLATIT AG, Switzerland; *J. Kluson, M. Jilek,* PLATIT a.s., Czechia; *R. Zemlicka, A. Lümkemann,* PLATIT AG, Switzerland

Dimond-like Carbon (DLC) coatings have unceasingly absorbed overwhelming interest from industry as well as academic research institutions within last years. High hardness and elastic modulus, chemical inertness, superior tribological properties and good corrosion resistance as well as high biocompatibility and resistance to bacterial colonization make DLC an engrossing coating system. Owed to the unique and broad range of properties, DLC coatings are constantly employed in new applications from cutting and forming tools to components; saw blades, end mills, micro-tools, punches, injection and extrusion molds and dies, automotive, decorative, medical applications are just some raised examples here. DLC coatings consist of a mixture of sp^3 (diamond) and sp^2 (graphite)bonds. The higher sp^3 bond fraction results in a higher density, hardness (at ambient and elevated temperature), thermal stability, oxidation resistance, higher residual stress and lower thermal conductivity. Hence, comprehending the correlation between DLC coating properties and industrial application requirements is a crucial prerequisite to a performance increase in industry. An attempt is made here to cover the range from DLC synthesis to its implementation in industrial applications and the obtained performance results thereof.

3:00pm **B3-ThA-6 Modeling of High Power Impulse Magnetron Sputtering Discharges With Graphite Target***, H. Eliasson,* Linkoping University, Sweden*; M. Rudolph,* Leibniz Institute of Surface Engineering (IOM), Germany*; N. Brenning,* KTH Royal Institute of Technology, Sweden*; H. Hajihoseini,* University of Twente, Netherlands*; M. Zanaska,* Linkoping University, Sweden*; M. Adriaans,* Eindhoven University of Technology, Netherlands*; M. Raadu,* KTH Royal Institute of Technology, Sweden*; **Tiberiu Minea (tiberiu.minea@universite-paris-saclay.fr),*** Universite Paris-Saclay, France*; J. Gudmundsson,* University of Iceland*; D. Lundin,* Linkoping University, Sweden

By using high power impulse magnetron sputtering (HiPIMS) to deposit tetrahedral amorphous carbon (ta-C) or diamond like carbon (DLC) thin films the aim is to increase the ionization fraction of the carbon atoms sputtered off the target, as it is known that energetic ion bombardment of the substrate is essential to deposit ta-C or DLC films with high sp^3 content. In fact the deposition of DLC films by HiPIMS has been explored extensively for deposition of DLC films. Here, the ionization region model (IRM) is applied to model a high power impulse magnetron sputtering (HiPIMS) discharge in argon with a graphite target. The model gives the temporal variation of the various species and the average electron energy, as well as internal discharge parameters such as the ionization probability, back-attraction probability, and the ionized flux fraction of the sputtered species. It is found that the discharge develops into working gas recycling and most of the discharge current at the cathode target surface is composed of Ar^+ ions, which constitute over 90 % of the discharge current, while the contribution of the C^+ ions is always small (<5 %), even for peak current densities close to 3 A/cm^2. For the target species, the time-averaged ionization probability $< \alpha_{t,pulse}>$ is low, or 13 - 27 %, the ion back-attraction probability during the pulse $\beta_{t,pulse}$ is high (> 92 %), and the ionized flux fraction is about 2 %. It is concluded that in the operation range studied here it is a challenge to ionize carbon atoms, that are sputtered off of a graphite target in a magnetron sputtering discharge, when depositing amorphous carbon films. It is concluded that it is a challenge to provide a high flux of ionized carbon from the HiPIMS process investigated here. This is due to a combination of a high ionization energy, a small ionization cross section and a low residence time of sputtered carbon in the ionization region. This requires fine-tuning of the process, for which the work suggests promising handles.

3:20pm **B3-ThA-7 Time Resolved Determination of Plasma Parameters, Ionization and Macroparticles in an Industrial Scale Ta-C Laser-Arc Coating System***, **Mathis Klette (klette@physik.uni-kiel.de),*** Kiel University, Germany*; M. Kopte, W. Fukarek,* VTD Vakuumtechnik Dresden GmbH, Germany*; H. Kersten,* Kiel University, Germany

The early 1990s marked the beginning of carbon laserarcs being used to deposit tetrahedral amorphous carbon (ta-C). Since then, many improvements to the process have been made [1,2]. Ta-C coatings provide the treated object with improved tribological and hardcoating properties, lowering friction and improving wear resistance. These properties make them ideal for automotive powertrain components, drill bits, cutting tools and other applications. While ta-C can be deposited using various techniques, the laserarc technology allows for a strong temporal and spatial control of the deposition process while providing high deposition rate and enabling up-scaling for industrial applications.

However, the up-scaling of deposition rate and process geometry has a profound impact on the physical process. In this contribution, we present measurements of a 100 µs pulsed 1-2 kA up-scaled carbon laserarc using various diagnostics to analyze this effect. A custom-tailored diagnostic setup enables Langmuir probe and Faraday cup measurements for electron and ion energy distribution functions, while spatially and time resolved optical emission spectroscopy yields ion species and densities. Of special interest is the characterization of C2+ ions which have been rarely observed so far.

The energy influx on the substrate is monitored by using calorimetric probes [3], while a force probe [4] and a high-speed camera analyze the neutral contributions and macro particles. This information can be used to estimate the individual contributions to the total energy influx and allows to optimize the particle filter.

Additionally, a second high-speed camera monitors the arc discharge at the cathode itself.

References

[1] H.-J. Scheibe, “Laser-arc: A new method for preparation of diamond-like carbon films”, Surf. Coat. Technol. 47 (1991), 455-465.

[2] A. Anders, Cathodic Arcs: From Fractal Spots to Energetic Condensation, Springer-Verlag New York (2008)

[3] J. Benedikt, H. Kersten, A. Piel, “Foundations of measurement of electrons, ions and species fluxes towards surfaces in low-temperature plasmas”, Plasma Sources Sci. Technol. 30 (2021), 033001.

[4] T. Trottenberg, A. Spethmann, H. Kersten “An interferometric force probe for beam diagnostics and the study of sputtering“, EPJ Techniques and Instrumentation 5 (2018)

3:40pm **B3-ThA-8 Fabrication of Hot Magnetron Carbon Targets for a High-Rate Films Deposition by Using Magnetron Sputtering Technique Under the Injection of Neon-Helium Gas Mixture***, **Bartosz Wicher (Bartosz.Wicher.dokt@pw.edu.pl),** R. Chodun,* Warsaw University of Technology, Poland*; Ł. Skowroński, M. Trzcinski,* Bydgoszcz University of Science and Technology, Poland*; K. Król,* Institute of Microelectronics and Optoelectronics, Warsaw University of Technology, Poland*; A. Lachowski,* Institute of High Pressure Physics, Polish Academy of Sciences, Poland*; K. Nowakowska-Langier,* National Centre for Nuclear Research (NCBJ), Poland*; K. Zdunek,* Warsaw University of Technology, Poland

A study of temperature of magnetron glassy carbon targets was performed for the case of gas injection magnetron sputtering (GIMS) of diamond–like carbon (DLC) and amorphous C–SiC films, by using unique geometry of the cathode source with increased temperature (HT – hot target). Cathode material was hollowed out for this purpose, from the bottom to the max. depth of 5 mm, which allowed to achieve target temperatures ranging from 790 to 1350 °C during the deposition of h-free carbon films. For the latter, four sockets were drilled in carbon target and then filled up with silicon carbide powder. In the second experiment, temporal evolution and spatial distribution of C–SiC cathode surface temperature were controlled by initiation of discrete pulse plasma discharges with power energies (Ei) changing from 122 to 403 J, which resulted in the temperature range from 730 to 1200 °C. The role of sputtering, sublimation and thermalized electrons in the increase of atoms removal from targets with limited heat conduction was clarified on the basis of an almost 4–fold increase in film deposition rate (up to 74 nm/min), compared to the completely cold process. For both variants of film deposition, GIMS were operated by generating as short as 400–ms and 250–ms plasma pulses at the frequencies of 1 and 2 Hz, respectively, thereby limiting the capability to cool targets operation over the neon–helium gas mixture. By contributing through the heat dissipation effect of HT, GIMS regime proved therefore to be an accurate in terms of increasing optical bandgap within DLC films, from 2.3 to 3.1 eV, which is derived from ordering of sp^2–graphene domains. The chemical and phase state of C–SiC films deposited from HT, revealed in turn, ~ 15 % of Si–C bonds, terminated in the 30 %–rich sp^3 carbon matrix, which puts its positive attribution to enhanced mechanical response, by means of 30.1 GPa hardness result.

Fig. 1. IR-thermogram of the studied targets’ surface with its corresponding mean temperature; a, c) cold carbon and C–SiC targets, b, d) hot carbon and C–SiC targets, respectively.

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4:00pm **B3-ThA-9 Adjusting the Properties of ta-C by Doping with Metals and Non-metals***, **Frank Kaulfuss (frank.kaulfuss@iws.fraunhofer.de),** F. Hofmann, T. Kruelle, V. Weihnacht,* Fraunhofer Institute for Material and Beam Technology (IWS), Germany

Tetrahedral amorphous carbon coatings (ta-C) are characterized by their very high wear resistance and low friction under most conditions. However, the requirements in the various application areas differ significantly and there is a need for application-specific adaptations of the coatings in some cases.

Current investigations show that the Laser-Arc process can be used to produce doped carbon coatings via the evaporation of composite graphite cathodes. Cathodes with 5 at% dopant content were used for this purpose. Iron and molybdenum were investigated as metal dopants and boron and silicon as non-metal dopants. The processing conditions were kept identical for all doped cathodes, and an undoped ta-C reference was also prepared. It can be observed that the defect density of the resulting coatings are significantly lower than the reference, especially for boron and molybdenum doping. For example, a 5 µm thick boron-doped coating shows lower roughness than 1 µm ta-C. Significant differences are seen in the morphology of these coatings, with the defect density being significantly reduced. Excitation of boron in the plasma is similar to carbon, and amorphous coatings are formed with comparable hardness to the ta-C reference. In contrast, the very highly excited molybdenum reduces the hardness significantly. In the case of iron and molybdenum doping the coatings are then no longer completely amorphous, as crystalline clusters are formed. Under some lubricated tribological conditions, the ta-C:B and a-C:Mo show clear advantages over ta-C reference coatings with comparable hardnesses.

4:20pm **B3-ThA-10 Improved Tribological Properties of DLC Coatings by Pulsed Laser Hardening***, **Sylvain Le Coultre (sylvain.lecoultre@bfh.ch)**,* Berner Fachhochschule, Switzerland*; J. Matthey, C. Rieille,* HE-Arc, Switzerland*; B. Neuenschwander,* Berner Fachhochschule, Switzerland

For many applications in cutting tools or watchmaking industries, the need to develop new solutions in order to improve the lifetime and performances of the components requires new approaches and solutions. In a joint project between the (Berner Fachhochschule) BFH and the (Haute Ecole ARC) HE-ARC, promising results have been obtained with nanotextured graphite layers produced using a two step hybrid production technology. First, a graphite coating is deposited using magnetron sputtering technology. Second, the coating is treated at with high power pulsed laser at high repetition rate.

As pin-on-disc measurements show, laser nanotexturing not only lowers the friction coefficient of the graphite coating, but also eliminates the run-in phase and significantly reduces wear in dry conditions. In addition, the topography induced by the laser treatment generates an optical effect of iridescence which adds a decorative function.

These first result open possibilities to develop a new type of graphite coating modified by laser pulses for application on 2D or 3D products with sizes in the order of mm2 to a few cm2.

These are first results, further improvement are expected via appropriate texture patterns and doping of the carbon target. Under wet condition, microchannel with heights in the nanometer range between are expected to be beneficial for storing lubricant.

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