Hard Coatings and Vapor Deposition Technologies
Room Town & Country C - Session B1-2-ThA

PVD Coatings and Technologies II

Moderators: Dr. Christian Kalscheuer, RWTH Aachen University, Germany, **Dr. Vladimir Pankov**, National Research Council of Canada

1:20pm **B1-2-ThA-1 Contemporary Trends in the Decorative Coatings*, Ivan Kolev,*** *A. Fuchs, P. Immich, H. Vercoulen, D. Barnholt,* IHI Hauzer Techno Coating B.V., Netherlands

Decorative coatings have been increasingly used since 1990's in various applications and end products. Originally applied to door handles and sanitary hardware from the premier segment, their use has expanded towards mobile appliances and automotive interior and exterior parts. Nowadays, decorative PVD and PECVD finishes are widely spread in a broad range of consumer products covering almost the whole price range. This spread comes with continuously growing demand for wider range of colors from one side and improved or new functional properties from other side. Originally limited to variations of golden and metal colors, today's market demands deep black, rose gold, purple, brown, blue and other colors. Next to the appearance, properties like scratch, corrosion and fingerprint resistance become a must. For many applications, which are in direct contact with the human body, antimicrobial properties are highly desired. In the automotive industry, aesthetics often needs to be combined to the possibility of back lighting or radar transparency. To meet all this, the individual benefits of different PVD and PECVD technologies need to be combined in a single process.

In this talk, we are presenting the current state of the contemporary decorative industrial coatings combining technologies such as UBM sputtering, HiPIMS, arc evaporation and (microwave) PECVD. The paper discusses color development, radar transparency, antibacterial properties and hydrophobic performance.

1:40pm **B1-2-ThA-2 Metallic Chromium Coatings with Different Thicknesses on Polycarbonate Surface*, Filipa Ponte,*** *P. Sharma, N. Figueiredo, S. Carvalho,* CEMMPRE, Department of Mechanical Engineering, University of Coimbra, Coimbra, Portugal

Over the years, polymer engineering comes out as a benefit for the automobile industry. Polymers are known for their good properties such as flexibility, durability, and lightweight material with low-cost production make them perfect for their various uses in automobiles, including for decorative purposes, and that is why they can be found almost everywhere from the dashboard, logos, and door panels to the exterior body and much more. To provide a decorative look on the polymer surface, in the present study, a metallic coating of Chromium (Cr) is deposited via magnetron sputtering on Polycarbonate (PC) polymer surface. Deposition of metallic coating directly onto the polymer surface is a challenge as the coatings are subjected to external thermal shocks or impact stresses and as a result, can easily crack. To overcome this challenge, the coating has been done after pre-treatment of the polymer surface i.e., plasma etching. The selection of plasma etching parameters has been carried out by changing bias voltage (400 V to 300 V, or without bias), etching time (450 sec to 150 sec), and pressure (0,4 Pa and 1 Pa). After analyzing the impact of these different etching parameters, the PC polymer surfaces were plasma treated at 300 voltage bias, 1 Pa pressure for 150 seconds, and then, coated with a Cr layer at ~0.74 nm/sec deposition rate. This plasma etching treatment, not only helps in saving from cracking of Cr coating, but it also provides good adhesion on the polymer surface. This study includes the optimization of the thickness of the Cr layer with lower defects (pinholes, cracking, reflectivity, hardness, and surface energy). The pretreated and untreated polymer surfaces were characterized for a wide range of thicknesses from ~400 nm to ~1600 nm. It has been observed that up to 1400 nm, we can achieve a shiny, noncracking, and adhesive Cr coating on this polymer surface.

Keywords: Plasma etching, Metallic coating, Magnetron sputtering, Polycarbonate

2:00pm **B1-2-ThA-3 Effect of O_2 Addition During Magnetron Sputtering Deposition on the Growth and Chemistry of Ag Thin Films*, Ramiro Zapata,*** Laboratoire Surface du Verre et Interfaces UMR 125 / Institut de Nanosciences de Paris UMR 7588, France*; R. Lazzari,* Institut des Nanosciences de Paris UMR 7588, France*; H. Montigaud, M. Balestrieri, I. Gozhyk,* Laboratoire Surface du Verre et Interfaces UMR 125, France

In the context of Ag-based low-emissive glazing developed by glass manufacturers, magnetron sputtering deposition is the industrially relevant technique to grow thin films of a wide range of materials, ranging from metals to dielectrics and semiconductors. Microstructural control of the active Ag layer used for infra-red reflection is a crucial issue, since its electrical conductivity ultimately drives the glazing thermal insulation efficiency. It is thus of great importance to better understand the link between deposition process parameters and the Ag film growth mechanism.

In this work, the effect of O_2 addition on the microstructure and the electrical and chemical properties of Ag nanometre-thick films grown on SiO_2 was explored using a custom sputtering deposition setup, by means of *in situ* X-ray photoelectron spectroscopy (XPS) and real-time measurements of electrical film resistance and Surface Differential Reflectance Spectroscopy (SDRS).

The impact of O_2 addition turned out to be divided into three regimes, depending on its relative amount in the incoming gas flux into the deposition chamber. *In situ* XPS analysis showed that mixtures of metallic Ag and Ag oxides (both surface oxides and bulk-like Ag_2O) were obtained in varying proportions depending on the O_2 flux used during deposition. In parallel, real-time electrical resistance measurements allowed for the detection of the percolation threshold thickness, in which a conductive Ag network is formed on the surface of the substrate. Such a threshold was lowered by increasing O_2 flux (Fig-A), but at the expense of final film resistivity. Finally, SDRS measurements were used to characterize the Ag nanoparticles formed during the initial stages of the 3D "Völmer-Weber" growth mechanism, namely nucleation, growth and coalescence. Information on the film morphology evolution were inferred from the plasmonic response using simulations from the *Granfilm* software, with the conclusion that O_2 addition leads to changes in nanoparticle aspect ratio, surface oxidation state and density (Fig-B). The latter was also confirmed by a statistical analysis of Transmission Electron Microscopy images for each condition.

2:20pm **B1-2-ThA-4 Effect of Molybdenum Interlayer on Mechanical and Elevated Temperature Tribological Properties of Molybdenum Nitride-Coated D2 Steel*, Te-Hsin Liu,*** *J. Huang,* National Tsing Hua University, Taiwan

Hard coatings are commonly used in industrial applications to prolong the service lifetime of cutting tools. Tribological property is one of the important properties that could be enhanced by hard and protective coatings, by which wear rate can be decreased and better protection to the tools is provided. For environmental protection, dry cutting is becoming a requirement in the manufacturing processes, in which high-speed cutting at elevated temperature will increase the wear rate of hard coating and the underlying tool. Molybdenum nitride (Mo_2N) is regarded as one of the promising coating materials for the tools applied at elevated temperature, because Mo_2N will form a Magnèli phase with self-lubricating property at high temperature such that the coating can maintain good wear resistance. However, our previous study found that the Mo_2N coatings deposited on D2 steel by the high-power pulsed magnetron sputtering (HPPMS) was with insufficient adhesion strength that induced delamination during wear test. In this study, Mo interlayer with various thicknesses was introduced to enhance the adhesion of the Mo_2N coating. The objective of this study was to investigate the influence of Mo interlayer on the adhesion and tribological properties of Mo_2N coatings on D2 steel substrate. Mo_2N coatings with different thicknesses of Mo interlayer were respectively deposited by HPPMS and DC magnetron sputtering on D2 steel substrate. Compared with the traditional DC magnetron sputtering, HPPMS can achieve higher ionization rate and plasma density due to the high instantaneous peak power, where the adatoms can obtain higher energy and thereby producing coatings with better crystallinity. After deposition, X-ray diffraction was used to identify the crystal structure. The cross-sectional and surface morphology were determined using field emission scanning electron microscope microscopy. The compositions of the specimens were measured by an electron probe microanalyzer. The residual stress of both coating and interlayer was separately measured using the average X-ray strain method. The hardness of specimens was determined by nanoindentation. The adhesion strength of the coatings was evaluated by scratch test, and the wear rate was measured by pin-on-disk test at temperature ranging from room temperature to 600 °C. From the experimental results, the effects of Mo interlayer on the adhesion strength and the tribological properties of Mo_2N coatings on D2 steel will be discussed.

2:40pm **B1-2-ThA-5 Enhanced Adhesion and Thermal Stability of Thick $(Al,Cr)_2O_3$ Coatings on Hot Work Steel***, K. Bobzin, C. Kalscheuer,* ***Parisa Hassanzadegan Aghdam,*** RWTH Aachen University, Germany

Crystalline aluminium oxide coatings deposited by chemical vapor deposition (CVD) at temperatures T > 1,000 °C are state of the art for wear and oxidation protection in manufacturing processes such as cutting and die casting applications. In recent years physical vapor deposition (PVD) gained great interest to synthesize crystalline aluminium oxide phases at lower process temperatures T ≤ 700 °C by modification of the binary Al-O system using Cr. Thereby, High Speed PVD showed a high potential to synthesize crystalline $(Al,Cr)_2O_3$ with high thickness s > 15 µm. However, previous studies showed that increasing adhesion between substrate and coating is required concerning the targeted applications. Therefore, various interlayer systems were taken into account in this study to enhance the compound adhesion between $(Al,Cr)_2O_3$ and hot-work steel 1.2344. Hereby, AlCrN interlayers with different thicknesses, architectures and bias voltage were deposited on steel 1.2344. Three AlCrN interlayers were produced with varying thicknesses 5 µm < d < 11 µm at constant bias voltage. Moreover, two graded $AlCrN_g$ interlayers were deposited at different bias voltages. Deposition of the functional $(Al,Cr)_2O_3$ layer is initially omitted to analyze the adhesion strength between substrate and interlayer. In a next step, compounds of 1.2344 and $AlCrN/(Al,Cr)_2O_3$ with total thickness of 21 µm < s < 30 µm were produced. Hereby, the thickness of functional layer s_f is varied between 16 µm < s_f < 25 µm in order to analyze the effect of functional layer thickness. Moreover, the thermal stability of the $AlCrN/(Al,Cr)_2O_3$ coatings was investigated by annealing tests in vacuum at T = 1,000 °C and T = 1,200 °C, with regard to the application on cutting and casting tools. Thereby, the diffusion behavior of the interlayer was the focus of investigations. In comparision to $(Al,Cr)_2O_3$ coated substrate, the $AlCrN_g/(Al,Cr)_2O_3$ coated steel compounds show no spallation at the edge of the Rockwell imprints and scratches at higher normal forces. The results thus show that the application of graded $AlCrN_g$ interlayer increases the adhesion of thick $(Al,Cr)_2O_3$ coating on 1.2344. Moreover, no diffusion processes leading to chemical and structural changes was obtained after annealing processes. This confirmed the thermal stability of the $AlCrN_g/(Al,Cr)_2O_3$ coatings during annealing up to a temperature of T = 1,200 °C. Therefore, thick $(Al,Cr)_2O_3$ coatings, s ≈ 30 µm, deposited by HS-PVD in combination with a graded $AlCrN_g$ interlayer provide a high potential for the protection of hot-work steel against thermal loading up to T = 1,200 °C.

3:00pm **B1-2-ThA-6 Combinatorial Synthesis of Novel Compositionally, Mechanically, and Structurally Heterogenous CuWCrTi Alloys with Unique Properties***,* ***Michal Zítek,*** Montanuniversität Leoben, Austria*; E. Rossi,* Università degli Studi Roma Tre, Italy*; G. Konstantopoulos,* National Technical University of Athens, Greece*; M. Sebastiani,* Università degli Studi Roma Tre, Italy*; J. Keckes, R. Daniel,* Montanuniversität Leoben, Austria

Complex coatings with compositional, mechanical, and structural gradients over a wide area are powerful in seeking perspective materials with specific combination of properties. Multielement CuWCrTi alloy is an auspicious candidate for such aim as it contains elements, which well differ in their mechanical properties and tend to form various phases with unique microstructure and properties, depending on the total amount of each element.

We have selected 13 different CuWCrTi alloy compositions in total as they formed on a static 3" Si wafer during magnetron co-sputtering deposition from Cu, W, Cr and Ti targets operated at an optimized discharge power ensuring homogenous thickness of the alloy over the entire wafer area and nearly equiatomic composition of the alloy at its center. Due to large compositional variations and limited miscibility of the elements, solid solutions, nanocomposites, and metallic glasses have been found to form, having unexpected combinations of hardness and elastic modulus. Even alloys composed primarily of elements exhibiting low hardness and elastic modulus such as Ti and Cu (e.g., $Cu_{51}W_{25}Cr_8Ti_{16}$)achieved high values of hardness ranging between 7 and 8.5 GPa.

This work demonstrated a potential of combinatorial synthesis approaches for rapid development of multielement alloys with a wide range of elemental and phase compositions, microstructures, and unique mechanical properties, proving, at the same time, the importance of multi-technique characterization tools with 2D (XRD, EDX) and 3D (nano-XRD, nanoindenation)mapping capabilities for a fast determination of processing-structure-property relations in new nanostructured materials.

3:20pm **B1-2-ThA-7 Deposition Aspects of High Entropy Alloy Nitride Coatings with Arc-PVD***,* ***Tim Krülle,*** *M. Kuczyk,* TU Dresden, Germany*; M. Leonhardt, O. Zimmer, J. Kaspar,* Fraunhofer Institute for Material and Beam Technology (IWS), Germany*; C. Leyens,* TU Dresden, Germany

High Entropy Alloy (HEA) Nitrides are an interesting material system intended for sophisticated wear and high temperature applications, due to its core effects, such as entropic stabilization of solid solutions, severe lattice distortion, sluggish diffusion kinetics and the cocktail effect. Such materials could be easily synthesized by means of Cathodic Arc Evaporation (CAE) in various gas atmospheres, leading to metallic or ceramic HEAs. In previous works high hardnesses up to 37 GPa could be obtained [1-3]. In this contribution new results on different HEA nitride coatings (HfNbTaTiVZr-N and AlCrTaTiZr-N) will be presented, deposited by means of DC Cathodic Arc Evaporation from compound metal targets. The presentation will give an overview on the dependency of the deposition parameters, such as the nitrogen partial pressures, nitrogen flow and bias potential on the evaporation behaviour of the targets and the (spatial) chemical composition, mechanical properties and the coating structure as well. Analysis were carried out by different methods, for instance SEM, EDS, nanoindentation, XRD or TEM. Furthermore, peculiarities of the evaporation process, such as the evaporation behaviour of the metal compound targets will be discussed.

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3:40pm **B1-2-ThA-8 Compositional Modulations in Coatings Synthesized by Cathodic Arc Deposition from a Multi-Element Target with Substrate Rotation***,* ***Nicholas Bandiera,*** *S. Veldhuis,* McMaster University, Canada

Compositional modulations through the thickness are reported in a near-equimolar AlCrTaTiZr high-entropy nitride (HEN) and a $Al_{57}Ti_{35}Ta_8$ nitride coating. The coatings were synthesized by reactive cathodic arc deposition with two-fold substrate rotation from single powder metallurgical targets. High Angle Angular Dark Field (HAADF) Transmission Electron Microscopy (TEM) images of a Focused Ion Beam (FIB) lamella show a repeating, layer-like pattern with nanometer-scale periodicity. While evident as Z-contrast, Energy-dispersive X-ray spectroscopy (EDX) was used to quantify the pronounced, off-nominal fluctuations of the metallic element concentrations through the thickness. The periodicity and pattern of the modulations are governed by the combination of two known effects: the substrate's hypotrochoidal motion, and the non-homogeneous distribution of the film-forming species in the plasma. Using a widely accepted model for the cathodic arc plasma plume, the radial and angular flux distributions for the light and heavy elements from the target were determined experimentally by depositing on stationary substrates, followed by EDX and ball-cratering. A general line-of-sight, flux-tracking program was developed to model a substrate undergoing two-fold or three-fold rotation from one or more multi-element sources. The experimental average deposition rate was used to scale the simulated flux to coating thickness and secondary effects such as occlusion, re-sputtering and sticking probabilities were considered. The simulated line intensity profiles of the coatings are compared to those extracted from the HAADF lamella with excellent agreement and the relative concentrations match the EDX data. In the HEN, changing the table rotational speed decreased coating hardness and toughness, implying these modulations may enhance properties not unlike the engineered nano-multilayer coatings synthesized with multiple targets. A coating designer should consider the phenomena described herein when employing substrate rotation when the target contains elements with a large disparity in atomic masses.

4:00pm **B1-2-ThA-9 Modifications of Structure Tuning and Mechanical Properties on CoCrNi Medium-Entropy Alloys Films by Multiple Strengthening Mechanism*, Chia-lin Li,*** National Taiwan University, Taiwan

To modify the microstructures and enhance the mechanical properties of CoCrNi medium-entropy alloys films (MEAFs), multiple strengthening will be multiple strengthening methods will be introduced in this study. We will add rare-earth, neodymium, and metalloid, boron, elements into the MEAFs system to introduce precipitation and solid solution strengthening. $CoCrNiNd_xB_y$MEAFs will be deposited onto silicon wafers using DC/RF magnetron three-target co-sputtering of CoCrNi, B and Nd targets. Nd and B concentrations in CoCrNi-based films were controlled by various DC/RF sputtering powers. The effects of multiple dopants on the phases, microstructures, and mechanical properties on these MEAFs will be investigated systematically. The influences of Nd and B contents on the microstructure of MEAFs were studied by means of scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Meanwhile, mechanical properties were examined by a nanoindentation. Based on present results, when Nd and B concentrations was increased to approximately 0.5 and 1.0 at.%, respectively, hardness increased to 10.8 GPa from 9.0 GPa of CoCrNi MEAFs. A discussion on the phase structure and strengthening mechanisms will be given further in this study based on the experimental results.

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