Hard Coatings and Vapor Deposition Technologies
Room California - Session B5-2

Hard and Multifunctional Nanostructured Coatings

Moderators: Jiri Capek, University of West Bohemia, Robert Franz, Montanuniversität Leoben

1:30pm **B5-2-1 B_4C and Mo Coatings Characterization regarding Stamping Dies Application***, F Silva,* ***Liliana Fernandes****, M Andrade,* ISEP - School of Engineering, Polytechnic of Porto, Portugal*; R Alexandre,* TeandM - Technology, Engineering and Materials, S.A., Portugal*; A Baptista,* INEGI - – Instituto de Ciência e Inovação em Eng. Mecânica e Eng. Industrial, Portugal*; C Rodrigues,* Colep Portugal, S.A., Portugal

Prestigious brands of cookies usually use metallic tins as package to distribute and sell their products, trying to impress the customer through the look and avoiding cookies' break and/or damage during logistics operations. These packages are made commonly in tin coated (2.8 g/m^2) thin steel sheet (electrolytic Tin plate), which originates severe wear problems on both die and punch tool components during the stamping process. The border of the package represents a non-considerable deformation, despite their almost perpendicular orientation to the top surface, but this top is usually patterned, also implying the flow of the sheet between the top and bottom die surfaces. Due to the softness of the Tin coating, it easily adheres to the die generating premature wear and several concerns in maintaining the required final shape of the tin lid. Lubrication would be an easy way to solve the problems above referred but lubrication operations should be avoided regarding that these kind of packages are for food purposes.

This study has been developed in order to find the best coatings which avoid Tin adhesion and wear on the stamping surfaces when deforming Tin coated steel plate. Two advanced PVD coatings (B_4C and Mo) were characterized and tested leading to improve the wear behavior of the punch and die under these work conditions. The transfer of Tin material from the metallic sheet to the punch and die was also studied, as well as the friction coefficient of this sheet against some selected coatings, also trying to minimize the Tin adherence to the tool surfaces. Tribological tests under medium loads were carried out in order to realize what kind of coating presents better wear behavior in those work conditions. Worn surfaces were studied by Scanning Electron Microscopy (SEM) and material transfer was analyzed by Energy Dispersive Spectroscopy (EDS).

Results obtained with some of the tested coatings allow to confirm that it is possible to minimize the Tin transfer from the covered steel sheet to the die and punch, ensuring a longer life of these parts, decreasing the tool maintenance operations and improving the Overall Equipment Efficiency (OEE) of that stamping process.

1:50pm **B5-2-2 Effect of Energy on Structure, Microstructure and Enhanced Resistance to Cracking of Hard Sputter Deposited Ti(Ni)N_x and Ti(Al,V)N_x Films***,* ***Martin Jaroš****, J Musil, R Čerstvý, S Haviar,* University of West Bohemia, Czech Republic

The paper reports on the preferred orientation, structure and mechanical properties of magnetron sputtered Ti(Ni)N_x and Ti(Al,V)N_x films and their resistance to cracking in bending. The films were reactively sputtered on Si(111) plate and Mo strips in a mixture of Ar+N_2 gases using a DC magnetron equipped with a TiAlV alloy target (6 at.% Al, 4 at. % V), or a TiNi alloy target (5 at. % Ni) respectively. The preferred orientation, structure, macrostress, mechanical properties (the hardness H, effective Young's modulus E^*, elastic recovery W_e), of Ti(Ni)N_x and Ti(Al,V)N_x films and theirs resistance to cracking in bending were characterized by (i) the X-ray diffraction (XRD), (ii) Scanning Electron Microscope (SEM), (iii) the bending of Si(111) plate using the Stoney`s formula, (iv) the diamond indentation test and (v) the bending of coated Mo strip around a fixed cylinder of small radius (down to 5 mm), respectively. It was found that: (1) the preferred orientation of sputtered Ti(Ni)N_x and Ti(Al,V)N_x nitride films depends on energy $E_{bi} \approx U_s \times i_s / a_D$ delivered to the film during its growth, here is U_s the substrate bias, i_s the substrate current density and a_D the deposition rate. The texture continuously changes from (i) TiN(220) -> TiN(111)+TiN(200) -> TiN(220) for Ti(Ni)N_x films and (ii) TiN(200) -> TiN(220) -> TiN(111)+TiN(220) for Ti(Al,V)N_x nitride films with increasing E_{bi}. (2) The Ti(Al,V)N_x and Ti(Ni)N_x nitride films with low resistance to cracking are prepared at lower value of E_{bi} < 1.5 MJ/cm^3 exhibit (i) low ratio $H/E^* \leq 0.1$, low elastic recovery $W_e \leq 65$ %, compressive macrostress ($\sigma < 0$ GPa) and (ii) are composed of grains contain TiN(200) and show a columnar structure. (3) The Ti(Al,V)N_x and Ti(Ni)N_x nitride films with enhanced resistance to cracking are prepared at higher value of E_{bi} > 3.7 MJ/cm^3 exhibit (i) high ratio H/E^*> 0.1, high elastic recovery W_e > 65 %, compressive macrostress ($\sigma < 0$ GPa) and (ii) are composed of grains witch do not contain TiN(200) and show a dense structure.

2:10pm **B5-2-3 Ultra-thick, Superhard Nanocomposite Coatings Deposited using Plasma Enhanced Magnetron Sputtering (PEMS) and their Practical Applications***,* ***Ronghua Wei****,* Southwest Research Institute, USA **INVITED**

In this presentation, the research on thick TiSiCN-based nanocomposite coatings (up to 560 µm) conducted at Southwest Research Institute (SwRI®) will be reviewed. These coatings have been developed using a plasma enhanced magnetron sputtering (PEMS) process via sputtering of Ti from all targets in a gas mixture of Ar, N_2 and TMS (trimethylsilane). In the PEMS process, in addition to the magnetron plasma, a global plasma is generated by W filament thermionic emission for the enhanced ion bombardment. The coatings thus produced have a dense structure, good adhesion to the substrate, low internal stress and superior mechanical properties compared to those obtained with the conventional magnetron sputtering. The coatings formed have a microstructure composed of nanocrystalline TiC_xN_{1-x} (x=0, 0.3 or 0.7) with the grain size of 4-10 nm in a matrix of amorphous SiC_yN_z, or nc-TiC_xN_{1-x}/a-SiC_yN_z. The microstructure of the coatings results in the super-hardness (up to 4600HV). However, the internal stress was found to be less than 1 GPa, thereby allowing the deposition of ultra-thick coatings of over 500 µm. The coatings also have high toughness characterized by high values of H^3/E^{*2} and H/E^*. The nanocomposite coatings have been developed specifically for severe environments including sand erosion, sand abrasion, water droplet erosion, and heavy load sliding wear on various alloy substrates including Ti-6Al-4V, Inconel 718, Al alloys, synthetic diamond inserts, WC-Co and various steels. These coatings have a few specific industrial applications including compressor blades or vanes for aero engines; piston rings, cylinder liners and stamping dies for automotive; and ball valves, valve stems, valve seats and plungers the for oil and gas industry. In this paper we review the method for preparing these coatings, discuss their microstructural, mechanical and tribological properties, and present examples for practical applications.

2:50pm **B5-2-5 Role of Interfaces in Determining the Fracture Resistance of Nanocomposite/Metal Nitride Multilayers***,* ***Naureen Ghafoor****,* Linköping University, IFM, Thin Film Physics Division, Sweden

Role of interfaces in determining the fracture resistance of nanocomposite/metal nitride multilayers

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We present mechanical response of TiN/ZrAlN multilayers and monolithic ZrAlN nano-composite coatings investigated through nano indentation and micropillar compression tests. The study highlights effect of interface structure on pre yield and post yield behavior of nano scale multilayer deformation in compression.

To understand stress-strain response in a uniaxial micropillar compression tests the pillars of height of 1 mm and diameter of 300 nm were compressed using in situ SEM nanoindenter equipped with a flat punch (diameter 5mm)[Ref 2]. The pillars were milled using focused ion beam. The interface structure of the multilayers is tuned by varying growth parameters during magnetron sputter deposition on MgO (001) substrates. The growth temperatures above 700 °C facilitated in situ segregation of ZrN-and AlN- rich domains within ZrAlN layer during growth [Ref 1]. The growth conditions and multilayer design are varied to tailor crystal structure of AlN rich domains from cubic to wurtzite and consequently to obtain coherent, semicoherent, and incoherent interfaces.

The degree of plastic deformation and work hardening is found to be dependent on the bilayer periodicity as well as on the nature of internal interfaces inside ZrAlN nano-composite layers. Micropillar compression tests revealed higher yield stresses and larger post yield displacements in 2 and 5 nm thin ZrAlN layers consisting of cubic phases of ZrN and AlN- rich domains forming coherent interfaces. For 15 and 30 nm thick ZrAlN layers, involving incoherent interfaces, the dominant crack propagation occur through layer interfaces. Nanoindentation measurements of the multilayers display a systematic variation of hardness with a value between 34 ± 1 to 22 ± 0.8 GPa as a function of layer thickness and interface structure. The dominant deformation mechanisms in connection with interface coherency and multilayer periodicity will be presented.

1: K. Yalamanchili,....N. Ghafoor, et al., Acta Materialia 89 (0) -2015, K. Yalamanchili,....N. Ghafoor, et al., Acta Materialia, [http://dx.doi.org/10.1016/j.actamat.2016.07.006]

2: S. Korte, W.J. Clegg, Scr. Mater. 60 (2009) 807–810.

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3:10pm **B5-2-6 Novel CrVN/TIN Nanoscale Multilayer Coatings Deposited by DC Magnetron Sputtering**, ***Elbert Contreras**, Y Galindez, G Bejarano, M Rodas, M Gómez,* Universidad de Antioquia, Colombia

The constant search by development coatings with higher properties opened the doors to the research and development of nanoscale multilayer coatings, hardness higher than 40 GPa, friction coefficients lower 0.3, improved adhesion and increased heat and corrosion resistance are some of the most interesting properties of these multilayer coatings compared to monolayers. In this research novel CrVN/TiN nanoscale multilayer coatings were deposited onto H13 steel substrates by DC unbalanced magnetron sputtering. Prior to the coatings deposition an ionic cleaning was carried out to clean the surface of the substrates with a 40 sccm flow of Ar and a pressure of 2-3x10^{-2} mbar during 30 minutes. The deposition of multilayer coatings was using two targets opposite each other, Cr-V (70-30 %wt) and Ti, with a power density of 2.4 W/cm^2 at both, a nitrogen gas flow of 20% in the gas mixture (N_2/(Ar+N_2)) obtaining a working pressure of 6-7x10^{-3} mbar, deposition temperature was 250°C and a BIAS voltage of -70V. In order to varying the bilayer period a microcontroller was used to control the rotation and residence time of the substrates against each target in 15, 30 and 40 seconds, looking for some different bilayer periods, CrVN and TiN monolayer coatings were also deposited. Microstructural analysis by X-ray diffraction (XRD) showed a FCC crystal structure to the monolayer coatings CrVN and TiN with preferential orientation (111); multilayer coatings showed a preferred orientation (200); the roughness and grain size was characterized using an AFM technique, CrVN monolayer coating showed less roughness and the multilayer coatings showed a decrease of the grain size while decreasing the bilayer period. SEM images revealed columnar structure for CrVN and globular structure for TiN, similar structure was found in the multilayer coatings. Tribological properties of the coatings were investigated using Pin-on-disk, all the multilayer coatings showed lower friction coefficients and wear rates compared with the monolayer coatings.

3:30pm **B5-2-7 Carbon Supersaturated Fe-Cr-Ni-C Thin Films with a Unique Nanocolumnar Structure - a Tough, Low Friction and Corrosion Resistant Coating**, ***Tomasz Suszko**, W Gulbinski, E Dobruchowska,* Koszalin University of Technology, Poland*; J Morgiel,* Institute of Metallurgy and Materials Science of Polish Academy of Sciences, Poland

Carbon supersaturated, amorphous FeCrNi:C coatings showing a unique nano-columnar structure have been deposited by pulsed magnetron sputtering of the 316L steel target in argon/acetylene atmosphere. HRTEM, EELS and XPS studies have shown that metallic cores of nano-columns oriented along the film growth direction are surrounded by amorphous carbon shells. The mechanism of growth of such a self-organized structure is discussed in terms of thermodynamically beneficial release of carbon from metastable metal carbides and from ternary phases formed during sputter deposition. The coatings are tough, have very good tribological behaviour in dry friction vs alumina and demonstrated excellent resistance to the formation and growth of pits in the corrosion environment containing chloride ions.

3:50pm **B5-2-8 Study of Wear Mechanism of Carbide and Ceramic Cutting Tools with Nano-structured Multi-layered Composite Functional Coatings**, ***Alexey Vereschaka**, A Vereschaka,* MSTU Stankin, Russian Federation*; A Batako,* Liverpool John Moores University, UK*; N Sitnikov,* Federal State Unitary Enterprise “Keldysh Research Center”, Russian Federation

The purpose of this study was to research wear mechanisms of carbide cutting tools with nano-structured multi-layered composite functional coatings under stationary cutting conditions. The study presents the results of extensive research of wear and failure mechanisms of carbide cutting tools with developed coatings on the basis of multi-component systems (for example, on the basis of systems Ti-TiN-(TiCrAl)N, Zr-ZrN-(ZrNbCrAl)N, and Ti-TiN-(NbZrTiAl)N) in longitudinal turning of steel of various compositions. The particular attention was paid to research of the kinetics and wear mechanisms of wear centres on contact areas of rake and flank faces of the tool with the use of a SEM equipped with microprobe analysis system. Chemical and phase compositions of developed coatings were studied by X-ray diffraction analysis. The objects of comparative analysis were represented by samples of carbides with wear-resistant coatings of traditional types (TiN, (TiAl)N). The particular attention was paid to the study of specifics of cracking mechanisms in coatings, as well as to interdiffusion processes taking place in the areas of contact between tool material and material being machined.

The following results were obtained:

- Tools with developed coatings provided the increase in tool life by 2-3.5 times as compared with uncoated tool and by 1.5-2 times - as compared with tool with tradition coatings .

- In the developed coatings deposited to carbide substrates, the mechanism of cracking is substantially different from the mechanism of cracking in the coatings of traditional type. In particular, the multi-layered architecture of developed coatings and the presence of sublayers of nano-meter thickness contribute to inhibition of initiation and development of cracks; nano-structured multi-layered composite coatings can be subjected to formation of rare longitudinal cracks less hazardous in context of failure of the coating in general with virtually no hazardous cross cracks, which are the major cause of premature complete failure of the coatings.

- The tests have detected active formation of oxides in areas adjacent to cracks and in the area of coating failure. Oxides of such metals as titanium and zirconium are formed very actively.

- Application of developed nano-structured multi-layered composite coatings contributes to the transformation of wear mechanisms of cutting tool. In particular, it almost completely excludes formation of cracks, microchipping and chipping of tool substrate (which is especially important for ceramic tools) and reduces the intensity of adhesion-fatigue wear; abrasive wear is mainly observed, and that results in increased tool life.

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