Advanced Surface Engineering
Room 101C - Session SE+TR-WeM

Protective Coatings for Tribological Applications in Surface Engineering

Moderators: Andrey Voevodin, University of North Texas, Michael Stueber, Karlsruhe Institute of Technology, Germany

8:00am **SE+TR-WeM1 Correlative Theoretical and Experimental Investigation of the Formation of $AlYB_{14}$ and Competing Phases**, ***Oliver Hunold***, *Y.T. Chen, D. Music,* RWTH Aachen University, Germany; *P.O.A. Persson,* Linköping University, Sweden; *D. Primetzhofer,* Uppsala University, Sweden; *M. to Baben,* GTT-Technologies; *J. Achenbach, P. Keuter, J.M. Schneider,* RWTH Aachen University, Germany

The phase formation in the boron rich section of the Al-Y-B system has been explored by a correlative theoretical and experimental research approach. The structure of coatings deposited via high power pulsed magnetron sputtering from a compound target was studied using elastic recoil detection analysis, electron energy loss spectroscopy spectrum imaging, as well as X-ray and electron diffraction data. The formation of $AlYB_{14}$ together with the $(Y,Al)B_6$ impurity phase, containing 1.8 at. % less B than $AlYB_{14}$, was observed at a growth temperature of 800 °C and hence 600 °C below the bulk synthesis temperature. Based on quantum mechanical calculations we infer that minute compositional variations within the film may be responsible for the formation of both icosahedrally bonded $AlYB_{14}$ and cubic $(Y,Al)B_6$ phases. These findings are relevant for synthesis attempts of all boron rich icosahedrally bonded compounds with the space group: *Imma* that form ternary phases at similar compositions.

8:20am **SE+TR-WeM2 Investigation of Friction and Wear for the Oxide-Oxide Contact in the Piston Ring–liner System**, *P. Ernst, P. Luethy, Ch. Bohnheio,* Oerlikon Metco AG, Wohlen, Switzerland; *F. Seibert, B. Widrig,* ***Jürgen Ramm***, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein

The reduction of friction and wear are important issues in the development and optimization of internal combustion engines increasing their efficiency and reducing the service interval times. One possibility to increase the efficiency of an engine is an operation at higher temperature. Surface coating could help to keep the standard materials and extend their operation range to higher temperatures. In this work, the friction and wear of oxide coatings are investigated and compared with coatings which are standard for an engine like Nikasil and Fe- based liner coatings and CrN for piston rings. The oxide coating material was first tested in a SRV test and the coefficient of friction against steel and alumina was measured for dry and lubricated conditions. In addition, the wear of the coatings and the steel or alumina counter-part was inspected. The most promising coating combinations were tested in a motor-bike engine configuration and compared with standard material.

8:40am **SE+TR-WeM3 Local Characterization Tools as the Key for Optimized Performance of Hard Coatings**, ***Christian Mitterer***, Montanuniversität Leoben, Austria **INVITED**

Advanced tribological hard coatings providing multi-functional properties like wear and oxidation resistance combined with high toughness require sophisticated selection and design of materials and architectures. For a knowledge-based development of such coatings, advanced characterization techniques on the nano-scale are needed to establish the necessary link of their microstructure to their properties. Within this contribution, recent progress in coating characterization techniques is highlighted. The application of focused ion beam techniques, electron backscatter diffraction and synchrotron X-ray nanodiffraction enables previously unrevealed insights in microstructure evolution. For the determination of mechanical and tribological properties at elevated temperatures, high-temperature nanoindentation and high-temperature ball-on-disk tests in combination with in-situ measurement techniques and site-specific sample preparation for damage analysis are discussed. Utilization of micromechanical tests for coatings provides information about their fracture toughness and rupture strength. The available portfolio of characterization techniques enables the determination of a complementary microstructural and mechanical fingerprint of tribological hard coatings, which allows to understand the complex structure–property relations in these materials and subsequently to further improve their performance.

9:20am **SE+TR-WeM5 High Temperature Oxidation in Pure Steam Environment of HIPIMS Deposited CrN/NbN Nanostructured Coatings**, ***Papken Hovsepian***, *A.P. Ehiasarian, Y. Purandare,* Sheffield Hallam University, UK; *F.J. Perez, M.I. Lasanta, M.T. de Miguel, A. Illana,* Universidad Complutense de Madrid, Spain; *J. Juez-Lorenzo,* Fraunhofer Instititute fur Chemische Technologie ICT, Germany; *A. Aguero,* Instituto Nacional de Tecnica Aeroespecial (INTA), Spain

The demand for new materials to be used in supercritical steam power plants for efficient and clean coal utilization is ever growing. A significant reduction of CO_2 emissions is expected by increasing the efficiencies of the steam turbines to $\eta > 50\%$ which can be achieved by moving from subcritical low pressure/ low temperatures, (180 bar/540 °C) to high pressure/high temperature, (300 bar/600-620 °C) ultra-supercritical regime of operation. The main challenges faced by different steel components of the power plant with this approach however, consist of material failure due to high temperature oxidation, and phenomenon such as creep, erosion and descaling after a stipulated period of time. Over the years considerable research has been done in finding solution to the above problems in terms of protective surface layers with limited success.

In the current work, 4 µm thick CrN/NbN coating utilising nanoscale multilayer structure with bi-layer thickness of Δ = 3.4 nm has been used to protect low Cr content P92 steel widely used in steam power plants. The uniquely layered coatings have a combination of nitrides of chromium and niobium which are not only resistant to aqueous corrosion, corrosion erosion and excellent tribological properties, but also have oxidation resistant in dry air up to a temperature of 850 °C. The novel High Power Impulse Magnetron Sputtering (HIPIMS) deposition technology has been used to deposit CrN/NbN with enhanced adhesion (critical scratch adhesion value of Lc= 80N) and very dense microstructure as demonstrated by XTEM imaging. These superior coating properties are achieved due to the unique high metal ion content (up to 90%) in the HIPIMS plasma, which allows particle acceleration and trajectory control by external electrical and magnetic fields thus delivering highly energetic material flux on the condensing surface.

P92 bare and coated samples were oxidised at 650°C in 100% steam atmosphere up to 2000 h, in order to simulate the future operation conditions of steam turbines employed in power plants. The oxidation kinetics was evaluated by mass gain measurements in a five decimal balance. In these conditions CrN/NbN provided a reliable protection of the P92 steel and outperformed other coatings such as ceramic Al_2O_3 and intermetallic Fe44Cr5Al used for the same application. The paper also discusses the effect of the growth defects and high temperature crack formation analysed by SEM and FIB- SEM techniques on the high temperature corrosion resistance in pure steam atmosphere thus revealing the coatings failure mechanisms.

9:40am **SE+TR-WeM6 Improved Thermo-Mechanical Properties and Oxidation Resistance of Ti-Al-N Coatings by Alloying Ta and Modifying the Coating Architecture**, ***Christian Martin Koller***, *A. Kirnbauer,* Technische Universität Wien, Austria; *H. Bolvardi,* Oerlikon Balzers, Liechtenstein; *P. Polcik,* Plansee Composite Materials GmbH, Germany; *P.H. Mayrhofer,* Technische Universität Wien, Austria

In recent years, different approaches towards the enhancement of physical vapor deposited TiAlN hard coatings were made. Among these, the alloying of additional elements to form quaternary compounds proved to be extremely efficient. In addition to as-deposited film properties also the coatings' thermo-mechanical behaviour and the performance in oxidizing environments, both constitute fundamental requirements for cutting applications, can be significantly increased.

One example is the substitution of Ti or Al by Ta, which chemically strengthens the face-centred cubic cell, leading to higher hardness values and increased Young's moduli. Furthermore, Ta prevents the formation of anatase $TiO_2$by directly promoting rutile-structured TiO_2. Consequently, a thermal-induced phase transformation of anatase into rutile TiO_2 and its therewith associated generation of crack networks is avoided.

In the present study two subsets of multilayers based on TiAlN/TaAlN and TiAlTaN/TaAlN were investigated. The coatings were synthesised using powder-metallurgically manufactured $Ti_{0.5}Al_{0.5}$, $Ta_{0.9}Al_{0.1}$, $Ta_{0.75}Al_{0.25}$, $Ta_{0.5}Al_{0.5}$, $Ti_{0.475}Al_{0.475}Ta_{0.05}$, and $Ti_{0.45}Al_{0.45}Ta_{0.10}$ targets. The TiAlN and TiAlTaN-base layers were arc evaporated (arc), whereas the TaAlN layers were either arc evaporated or reactively sputtered (rsd) [1][2]. The multilayer architecture was realised by the use of a shutter system or through the continuous two-fold rotation of the substrate holder, resulting in sharp and slightly burred layer interfaces. The overall Ta-content and

TaAlN–layer thickness was varied by different power settings of the $Ta_{0.75}Al_{0.25}$ cathode and shutter-open times, respectively.

We can show that a coating architecture of $TiAlN^{arc}$ and $TaAlN^{arc}$ allows for thermo-mechanical properties comparable to TiAlTaN, whereas superior oxidation resistance only can be achieved by a $TiAlN^{arc}/TaAlN^{rsd}$ arrangement. For both rsd-multilayer arrangements the critical factor in terms of thermo-mechanical performance and oxidation resistance is the TaAlN layer thickness as well as the overall interface volume. Results are discussed based on X-ray diffraction and electron microscopy studies.

[1] C.M. Koller, R. Hollerweger, C. Sabitzer, R. Rachbauer, S. Kolozsvári, J. Paulitsch, P.H. Mayrhofer, *Surf. Coat. Technol.*259 (2014) 599–607.

[2] C.M. Koller, R. Hollerweger, R. Rachbauer, S. Kolozsvári, J. Paulitsch, P.H. Mayrhofer, *Surf. Coat. Technol.*283 (2015) 89–95.

11:00am **SE+TR-WeM10 Tribochemistry between Graphene and Fe, Fe_2O_3, and Fe_3C Surfaces**, ***J. David Schall,*** Oakland University **INVITED**

Tribosystems containing both iron and hydrocarbon-based lubricants are ubiquitous and an understanding of the chemistry that takes place in such systems is essential to the development of new lubricant additives designed to reduce friction and wear. Graphene nanoparticle additives have been proposed by numerous researchers due to the excellent friction and wear properties of graphene. Recent experiments have shown that even single layers of graphene in the absence of lubricants on steel components can greatly reduce wear (Berman, Carbon, 54, 2013, 454). Berman *et al* have hypothesized that graphene forms a conformal protective layer on the steel surface with or without additional lubrication. Simulations show vanishingly small friction when continuous sheets of graphene are sandwiched between Fe surfaces; however, real graphene has various functional groups including –carboxyls, -alkyls, -hydroxyls among others along the edges. Graphene can also be oxidized. In this talk simulations that illustrate the triboinitated mechanochemistry between graphene with various functional edge groups and Fe, Fe2O3 and Fe3C surfaces will be presented. These molecular dynamics simulations were conducted with a REAX-FF interatomic potential function for Fe, O, C and H (Zou, *JOM*, 64, 2012, 1426) that includes terms for chemical reactivity with charge transfer enabling investigation of tribochemistry in the sliding interface.

11:40am **SE+TR-WeM12 Tribological Testing of Leather Treated with Ag/TiO_2 Nanoparticles for Footwear Industry**, *M. Rebelo de Figueiredo,* Montanuniversität Leoben, Austria*; I. Carvalho, S. Carvalho,* Universidade do Minho, Portugal*; C. Gaidau,* Leather and Footwear Research Institute, Romania*;* ***Robert Franz,*** Montanuniversität Leoben, Austria

Ecologic and health effects of applying materials with advanced functions for leather surface finishing contribute to increasing the added value and durability of leather and fur articles. The innovative properties of Ag/TiO_2 nanoparticles on leather surface are due to their antimicrobial, self-cleaning and flame retardant characteristics. Furthermore, it leads to a reduction of chemicals with high pollutant potential, e.g. volatile organic biocides, organic solvents and halogenated flame retardants typically used during leather manufacturing.

The efficient anchoring of Ag/TiO_2 nanoparticles on leather surface ensures minimum risk of human skin penetration. To this aim, two different technologies for the functionalisation of the leather surfaces were explored: (1) physical mixing of Ag/TiO_2 nanoparticles with film forming polymers and leather surface covering by conventional technologies and (2) leather surface activation by cold plasma pre-treatment and magnetron sputter deposition of transparent Ag/TiO_2 nanoparticle layers.

In order to test the adhesion of the deposited Ag/TiO_2 nanoparticles to the leather substrates, a series of tribological tests in ball-on-disc configuration has been performed using different counterpart materials ranging from rubber (e.g. nitrile rubber) to polymers (e.g. PTFE, PUR or POM). The analysis of the coating wear by light optical and scanning electron microscopy as well as Raman spectroscopy revealed details regarding the adhesion of the Ag/TiO_2 nanoparticles depending on the deposition method and parameters applied. In a similar way, the sticking behaviour of the Ag/TiO_2 nanoparticles to the different counterpart materials was analysed to emulate the uptake of the released nanoparticles by the human skin. The conducted experiments represent a first step towards a systematic study of the mechanical performance of leathers treated with nanoparticles in order to evaluate their suitability for future applications in the footwear industry.

12:00pm **SE+TR-WeM13 Phase Formation of Cathodic Arc Evaporated Al_xCr_{1-x} and $Al_xCr_{1-x}O_\delta$ Thin Films**, ***Valentin Dalbauer,*** CDL AOS TU Wien, Austria*; J. Ramm,* Oerlikon Balzers, Oerlikon Surface Solution AG, Liechtenstein*; S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; C.M. Koller,* CDL AOS TU Wien, Austria*; P.H. Mayrhofer,* Vienna University of Technology, Austria

Aluminium-based oxides and oxide scales are highly valued for various demanding applications due to their outstanding thermo-mechanical properties as well as their superior resistance in oxidising and chemically hazardous environments. However, the polymorphic character of Al_2O_3 (and consequentially also $(Al_xCr_{1-x})_2O_3$) synthesised at deposition temperatures lower than 800 °C is impeding its large-scale utilisation. Especially high Al–containing films, being dominated by transient oxides, are susceptible for thermally-induced phase transformations, which are associated with the formation of crack networks. Therefore, the growth of the thermodynamically stable α-Al_2O_3 at deposition temperatures ~ 400-600 °C has been in the focus of research for many years. Although considerable advances were made, none of them proved to be applicable to industrial utilisation. A comprehensive and in-depth understanding of mechanisms, leading to the growth of transient oxides within the quasi-binary system Al_2O_3–Cr_2O_3 synthesised by cathodic arc evaporation is therefore still of major interest, as this knowledge is crucial for being able to grow coatings with dedicated crystallography and microstructure.

In the present work, we approach this issue by investigating the structural evolution of intermetallic Al_xCr_{1-x} and $Al_xCr_{1-x}O_\delta$ films synthesised by arc evaporation. Depositions were carried out in non-reactive as well as reactive atmosphere, using low to intermediate O_2 flow rates to examine its impact on film morphology and phase composition. In order to correlate the chemical aspect and process conditions (i.e., Cr-content and O_2 partial pressure) with the accessible microstructure and crystallographic evolution, powder-metallurgically manufactured Al_xCr_{1-x} targets with different compositions were selected. By this, the significant phase regimes within the binary Al-Cr phase diagram are accessible.

In detail, arc evaporation of $Al_{0.9}Cr_{0.1}$, $Al_{0.7}Cr_{0.3}$, $Al_{0.5}Cr_{0.5}$, and $Al_{0.25}Cr_{0.75}$ targets leads to the formation of intermetallic films dominated by $Al_{13}Cr_2$, Al_8Cr_5 or $AlCr_2$ phases, which well–agrees with the equilibrium Al-Cr phase diagram. Chemical analyses demonstrate that differences in the Al/Cr-ratio between targets and films increase towards the Cr-rich side, which decrease by introducing O_2 to the deposition process. Furthermore, the simultaneous broadening and intensity reduction of dominant intermetallic XRD peaks is accompanied by the emergence of weak broad signals indicative for the development of X-ray amorphous areas. Between 70 and 90 at.% Al we find a compositional window, which is characterised by a maximum target evaporation and minimum film growth rate.

Author Index

Bold page numbers indicate presenter

— A —
Achenbach, J.: SE+TR-WeM1, 1
Aguero, A.: SE+TR-WeM5, 1
— B —
Bohnheio, Ch.: SE+TR-WeM2, 1
Bolvardi, H.: SE+TR-WeM6, 1
— C —
Carvalho, I.: SE+TR-WeM12, 2
Carvalho, S.: SE+TR-WeM12, 2
Chen, Y.T.: SE+TR-WeM1, 1
— D —
Dalbauer, V.: SE+TR-WeM13, **2**
de Miguel, M.T.: SE+TR-WeM5, 1
— E —
Ehiasarian, A.P.: SE+TR-WeM5, 1
Ernst, P.: SE+TR-WeM2, 1
— F —
Franz, R.: SE+TR-WeM12, **2**
— G —
Gaidau, C.: SE+TR-WeM12, 2
— H —
Hovsepian, P.Eh.: SE+TR-WeM5, **1**
Hunold, O.: SE+TR-WeM1, **1**
— I —
Illana, A.: SE+TR-WeM5, 1
— J —
Juez-Lorenzo, J.: SE+TR-WeM5, 1
— K —
Keuter, P.: SE+TR-WeM1, 1
Kirnbauer, A.: SE+TR-WeM6, 1
Koller, C.M.: SE+TR-WeM13, 2; SE+TR-WeM6, **1**
Kolozsvári, S.: SE+TR-WeM13, 2
— L —
Lasanta, M.I.: SE+TR-WeM5, 1
Luethy, P.: SE+TR-WeM2, 1
— M —
Mayrhofer, P.H.: SE+TR-WeM13, 2; SE+TR-WeM6, 1
Mitterer, C.: SE+TR-WeM3, **1**
Music, D.: SE+TR-WeM1, 1
— P —
Perez, F.J.: SE+TR-WeM5, 1
Persson, P.O.A.: SE+TR-WeM1, 1
Polcik, P.: SE+TR-WeM6, 1
Primetzhofer, D.: SE+TR-WeM1, 1
Purandare, Y.: SE+TR-WeM5, 1
— R —
Ramm, J.: SE+TR-WeM13, 2; SE+TR-WeM2, **1**
Rebelo de Figueiredo, M.: SE+TR-WeM12, 2
— S —
Schall, J.D.: SE+TR-WeM10, **2**
Schneider, J.M.: SE+TR-WeM1, 1
Seibert, F.: SE+TR-WeM2, 1
— T —
to Baben, M.: SE+TR-WeM1, 1
— W —
Widrig, B.: SE+TR-WeM2, 1