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SYMPOSIUM K

Protective coatings and thin films – 05

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SYMPOSIUM K

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Morning
Matin

Session I : Multilayer coatings

Session chairs : **M. Benlahsen** (University of Picardie, Amiens, France)
F. Levy (EPFL, Lausanne, Switzerland)

- K-I.1** 9:00 -Invited- MULTIFUNCTIONAL NANOLAMINATED PVD COATINGS IN THE SYSTEM Ti-Al-N-C BY COMBINATION OF METASTABLE FCC PHASES AND NANOCOMPOSITE MICROSTRUCTURES
Michael Stüber, S.Ulrich, H.Leiste, Institut für Materialforschung, Forschungszentrum, Karlsruhe, Germany.
The design and manufacture of wear resistant low friction nanocomposite coatings by simultaneous growth of nanocrystalline hard phases and amorphous carbon is a hot topic of thin film engineering worldwide. The paper will present a new concept of multifunctional nanolaminated PVD coatings composed of different carbon-based nanocomposite layers. In the past, mainly thermodynamically stable binary hard phases such as TiC were used to synthesise such nanocomposite coatings. The presentation will briefly review the state-of-the-art of basic systems like TiC/a-C coatings. As an innovative approach, carbon-based solid lubricant nanocomposite coatings composed of coexisting metastable hard phases like fcc (Ti,Al)(N,C) and amorphous carbon were grown by magnetron sputtering. The microstructure, properties and performance of different coatings will be presented in dependence of the carbon concentration. A 5-step growth model of these coatings will be discussed. Based on these results, advanced nanolaminated composite coatings will be introduced: these coatings have a special nano-architecture and are composed of these different carbon-based nanocomposite layers. In example, a nanolaminated composite coating with a stacking sequence of each 50 layers of TiC/a-C and (Ti,Al)(N,C)/a-C showed promising properties and performance in tribological testing and in tool testing as well. The scale-up of such coatings will be addressed, and, a new route towards industrial manufacture by applying new ceramic composite targets for magnetron sputtering will be reported.
- K-I.2** 9:30 X-RAY RESIDUAL STRESS ANALYSIS ON CrN/Cr/CrN MULTILAYER PVD COATINGS
F. R. Lamastra(a), F. Leonardi(a), R. Montanari(b), F. Casadei(c), T. Valente(d), and G. Gusmano(a), (a)Rome University "Tor Vergata", Department of Chemical Science and Technology, Rome, Italy, (b)Rome University "Tor Vergata", Department of Mechanical Engineering, Rome, Italy, (c)Centro Sviluppo Materiali Spa, Rome, Italy, (d)Rome University "La Sapienza", Department of Chemical and Materials Engineering, Rome, Italy.
Hard physical vapour deposition (PVD) coatings as CrN, TiN, NbN have been successfully exploited for wear and corrosion protection. One limit to their performances under service conditions can be caused by the presence of large residual stresses, which can adversely affect their properties as fatigue, fracture, corrosion, friction, and wear resistance.
X-ray diffraction (XRD) has been used for measuring residual stress on CrN/Cr/CrN multilayer coatings, produced by cathodic arc evaporation on substrates of three different steels (AISI H 13, AISI 1040, K340). The thickness of the external and internal CrN layer was 1.6 micron in all the samples, while three thicknesses of the intermediate Cr layer, respectively 0,5, 1,0 and 1,6 micron were used. Mean stress on different crystallographic planes and stress anisotropy on different directions on the sample surface were measured. The stress on three different directions ($\phi = 0^\circ, 45^\circ$ and 90°) on the coating surface have been investigated by recording the peak positions of CrN reflections for each ϕ at different tilt angles ψ . The experimental results are reported and discussed.

- K-I.3** 9:50 INVESTIGATION OF MICROSTRUCTURAL CHARACTERISTICS IN CrN/TiN SUPERLATTICES
S. Logothetidis, K. Sarakinos, and N. Kalfagiannis, Aristotle University of Thessaloniki, Department of Physics, Thessaloniki, Greece.
Polycrystalline CrN/TiN superlattice (SL) coatings were prepared employing unbalanced reactive magnetron sputtering. The coatings were deposited in a mixed Ar/N₂ atmosphere. The formation of the SL, consisting of alternate single layers of CrN and TiN, was achieved with the rotation of the substrate holder. Throughout the rotation the substrate was sequentially exposed in two diametrically located Cr and Ti targets, leading to the deposition of the CrN and TiN single layers respectively. Deposition was carried out at various values of substrate bias voltage and rotation speed. The microstructure of the SL coatings was investigated in terms of the thickness of the individual CrN and TiN single layers and the bilayer period Λ , namely the sum of the thickness of two sequentially CrN and TiN layers. The values of Λ were calculated employing X-Ray Diffraction (XRD) at both low and high diffraction angles. In the case of low-angle XRD Λ was determined from the angular position of the first and higher order reflections arising from the periodicity of the structure, while in the case of high-angle XRD from the difference in angular position between the (111) reflection and the satellite reflections, symmetrically located round the (111) reflection, which are arising from the composition modulation within the period, but also within the single layers of the SL. Moreover, the thickness of the single CrN and TiN layers was determined from the high angle XRD patterns. Furthermore, the thickness of the single layers was determined from spectroscopic ellipsometry (SE) using the Bruggeman effective medium approximation (BEMA).
- K-I.4** 10:10 OPTICAL MULTILAYERS IN GLASS INDUSTRY: MECHANICAL RESPONSE AND ADHESION ISSUES
E. Barthel, D. Dalmas, M. Klotz, E. Sondergard, and A. Dinescu, Surface du Verre et Interfaces, Unité Mixte CNRS/Saint-Gobain, Aubervilliers, France.
Thin film deposition is a natural route for glass functionalization. As an example, for thermal control in cars, we need to impart high IR reflectivity to the windshield while maintaining high transmission in the visible range. This is achieved by the PVD deposition of a 100 nm thin optical stack comprised of oxide and metal layers. The mechanical resistance of such films and stacks is crucial for further processing and product durability.

To assess the mechanical response of films and stacks, we combine friction, nanoindentation, adhesion and scratch experiments, which altogether catch the main ingredients of the problem. In this presentation, we will start with the example of thin porous silica films with different hardnesses and show that the overall picture which emerges is a competition between the ductile and the brittle (interfacial cracks) stress relaxation mechanisms. In the case of the thin optical multilayers mentioned above, with brittle layers and substrate, crack propagation at weak silver/oxide interfaces dominate and result in film delamination. We have analyzed this process in details with a specific film adhesion energy measurement set-up. The interface of rupture within the film is determined by XPS. We show that adhesion depends not only on the nature but also on the structure of the interfaces.
- K-I.5** 10:30 COMPOSITIONAL DEPTH PROFILING ANALYSIS OF THIN AND ULTRATHIN MULTILAYER COATINGS BY RADIO-FREQUENCY GLOW DISCHARGE OPTICAL EMISSION SPECTROSCOPY
R. Escobar Galindo, E. Forniés, and J.M. Albella Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, Cantoblanco, Madrid, Spain.
In most of the industrial applications of multilayer coatings, a detailed knowledge of the interlayer structure and the interfaces is needed. In comparison with standard surface analysis techniques (SIMS, XPS, AES...), depth profiling by radio-frequency glow discharge optical emission spectroscopy (rf-GDOES) provides rapid information, with a high depth resolution, about the multilayer composition.
In rf-GDOES analysis, the depth resolution mainly depends on the roughening induced during the sputtering, the resulting crater geometry and sputtering of material re-deposited on the crater wall. In this work we have isolated the contribution of these effects in the depth resolution of metal and metal nitride multilayer coatings. The importance of these effects was firstly tested on multilayer stacks consisting of three alternating metal layers, typically of 500 nm each. The profiles of materials with high sputtering rate become less affected than material with low sputtering rate due to lower mixing of the layers. The contribution of these factors increased during the analysis of thinner multilayer coatings (~ 100 nm). After reversing the order of the layer elements, completely different profiles were measured, confirming the role of the differences in the sputtering rate. Similar results have been obtained when metal nitride multilayer coatings were analysed. In a last stage, ultra thin chromium layers of 2.5 and 5 nm, were buried at different depths in a titanium matrix up to a thickness of 3 μ m, to evaluate the depth resolution function of the GDOES technique. The markers were properly resolved both near the surface and deeply embedded in the matrix, demonstrating the excellent capabilities of the GDOES technique to detect thin films in the nanometric range.
- 10:50 **BREAK**

Session II : Solid lubricant and tribological coatings

Session chairs : **J.-P. Celis** (Katholieke Universiteit, Leuven, Belgium)

C. Meunier (University of Franche-Comté, Belfort, France)

- K-II.1** 11:10 -Invited- NANO-STRUCTURED WEAR RESISTANT COATINGS PREPARED BY THERMAL SPRAYING AND LASER CLADDING
Igor Smurov, Ecole Nationale d'Ingénieurs de St-Etienne, DIPI Laboratory, Saint-Etienne, France.
Nanostructured powder developed by mechanical alloying are applied for fabrication of thick (200 - 500 μm) wear resistant coatings. The following deposition techniques are used : HVOF, D-gun, laser cladding with coaxial powder injection. Optical diagnostics (12 wavelengths single spot pyrometer, 2D monochromatic pyrometer, CCD-camera based diagnostic tool) is applied for surface temperature and particles-in-flight monitoring. AFM coatings examination confirmed their nanostructure. The performed wear tests shown the advanced performance : dry friction coefficient may reach the stable value of 0.12.
- K-II.2** 11:40 WEAR AND FAILURE MODES OF PVD COATED CEMENTED CARBIDE CUTTING SAWS
P. Panjan(a), R. Kos(b), M. Cekada(a), (a)Jozef Stefan Institute, Ljubljana, Slovenia, (b)Kolektor d.o.o., Idrija, Slovenia.
Wear and failure modes of PVD coated cemented carbide (HM) slitting saws, which are used for large scale production of small commutators, have been studied by scanning electron microscope (SEM), atomic force microscope (AFM) and profilometer. Such saws are used for cutting the commutator body, which is composed of two parts: the outer ring made of electrolytic copper, and the inner ring made of hard plastic (bakelite filled with glass fibers). Strong wear of the rake face of cutting teeth as well as of the cutting edge were observed. We have improved the performance of HM saws significantly by deposition of various PVD hard coatings. In this work we will present the results of SEM, AFM and profilometer analysis of HM saw teeth, which performed different numbers of cutting cycles.
- K-II.3** 12:00 MECHANICAL AND TRIBOCORROSION BEHAVIOUR OF PLASMA NITRIDED AND PLASMA NITRIDED + OXIDISED Ti6Al4V ALLOY
A. C. Fernandes(a), F. Vaz(a), E. Ariza(b), L. A. Rocha(b), A. R. L. Ribeiro(b), A. C. Vieira(b), J. P. Rivière(c), and L. Pichon(c), (a)Dept. Física, Universidade do Minho, Campus Azurém, Guimarães, Portugal, (b)Universidade do Minho, Dept. Eng. Mecânica, Campus Azurém, Guimarães, Portugal, (c)Laboratoire de Métallurgie Physique, Université de Poitiers, Futuroscope, France.
This paper reports the influence of low pressure plasma nitriding treatments, followed in some cases by plasma assisted oxidising treatment, on the mechanical properties and tribocorrosion resistance of a Ti6Al4V alloy. Nitridation was performed for 640 or 720 minutes at 600 and 700 °C, in a R.F. plasma equipment, using N₂-H₂ gas mixture under 7.5 Pa. Some of the samples were then post-oxidized at 700 °C for 15 to 60 minutes under 9.5 Pa of O₂.
The tribocorrosion behaviour of the samples was investigated in an alternative linear regime of sliding immersed in a 0.9%wt NaCl solution at room temperature. An alumina pin was used as counterface material. The open circuit potential of the samples was monitored during the wear test. In addition, in order to evaluate the passivation characteristics of the material, electrochemical impedance spectroscopy (EIS) tests were performed before and after the wear test. XRD results revealed the occurrence of the Ti₂N phase for the nitrided samples. The TiN phase was also detected in case of nitriding at 700 °C. The oxidized surfaces were mainly composed of rutile TiO₂, although some peaks may be related to the anatase TiO₂. Microhardness tests showed a slight increase of surface hardness with the nitridation temperature. The oxidation led to a significant hardening of the surface, whatever the substrate (untreated or nitrided samples). Cross-section measurements revealed the presence of a microhardness gradient spread over about 20 μm . Tribocorrosion results clearly showed that plasma treatments have a strong influence on the tribocorrosion behaviour of the material. Both the corrosion and wear performance of the samples are improved by the increase of the processing temperature.

K-II.4 12:20

LUBRICIOUS CARBON LAYERS ON HARD COATINGS INTENDED FOR AUTOMOTIVE TOOLING

S. Mutti(a), S. Luridiana(a), L. Guzman(b), and L. Maines (b), (a)Microcoat, Sedriano (MI), Italy, (b)Dip. di Ingegneria dei Materiali, Università di Trento, Mesiano di Povo (TN), Italy. This work concerns the effect of the deposition of mixed (graphitic-nanographitic) top layers on the tribological properties of TiN, in order to achieve a lower dry friction behaviour. The coatings were deposited with a fully automatic industrial Microcoat MA 1000 system, equipped with proprietary cathodic arc sources, pulsed bias and with temperature and gas pressure controls. Polished 100 Cr6 and HSS steels were used as substrates. The TiN layers were obtained by reactive deposition from pure Ti cathodes in nitrogen atmosphere; the C layers were deposited "in situ" on top of the nitride coatings, also with cathodic arc using a pure graphite cathode. An investigation has been carried out to determine the influence of a number of deposition parameters on the tribological properties of the resulting TiN/IC coatings. All coatings had thickness in the range 1- 2 microns, typical for the applications mentioned above. Coatings were characterised with respect to C layer structure, microstructure and scratch hardness of the multilayer, wear and friction coefficient in dry conditions. The results show that the bias voltage duty cycle is the most influential parameter both on hardness and dry friction coefficient. On the other hand, little dependence is shown on deposition temperature. A reduction in friction can be achieved, meeting all usual automotive tooling criteria. The work is regarded as a significant stepping stone in the development of thinner, and mechanically more performant coatings.

K-II.5 12:40

DEVELOPMENT AND TRIBOLOGICAL QUALIFICATION OF A MODIFIED MoS₂ SOLID LUBRICANT FILM

M. Brizuela, J.I. Oñate, J.L. Viviente, I. Braceras, D. Gonzalez, and A. Garcia-Luis, INASMET, San Sebastian, Spain.

MoS₂ is a broadly accepted solid lubricant for space mechanisms. However, a drawback of MoS₂ is its tribo-sensitivity to atmospheric water vapour which renders the film unsuitable for use under high humidity levels at air conditions. This recommends precautions during ground qualification testing and storage of solid lubricated space mechanisms. Recently, coupling a need of extending space mechanisms' life with advances made in PVD technology, efforts have been made in developing more wear resistant MoS₂ and low friction films capable of both: vacuum and atmospheric application. Alloying the MoS₂ films with metals has been reported by several researchers with varying success. This contribution reviews previous work and reports on the work carried out by the authors with MoS₂ solid lubricant films alloyed with Ti and WC. Pin on disk vacuum tribology of these films, at 0.75 and 0.95 GPa contact stresses, has shown friction coefficients similar to those obtained in conventional MoS₂ films, but with a significant improvement in durability. Tribo-performance of these films under atmospheric conditions, at various humidity levels (40 to 75 % RH) has also been very good, with average friction coefficients as low as 0.07 and a durability as high as 450.000 wear cycles. XPS analyses have shown that the WC-MoS_x films consist mainly of a MoS_x lubricating matrix in which a carbide wear resistant WC phase is embedded. This combination ensures a low friction behaviour while providing a higher resistance wear. Tribotests have also been performed with an engineering model of the TriboLAB, an instrument that will be launched to the International Space Station (ISS). Details of the instrument and the comparative results will be provided.

13:00

LUNCH

Session III : Nanostructured coatings and thin films

Session chairs : **A. Korhonen** (Helsinki University of Technology, Finland)
P. Ossi (Politecnico, Milano, Italy)

- K-III.1** 14:30 -Invited- ENCAPSULATION OF METALLIC NANOPARTICLES IN CARBON AND BORON NITRIDE THIN FILMS PREPARED BY ION-BEAM SPUTTERING
David Babonneau, J. Toudert, S. Camelio, T. Cabioch, and T. Girardeau Laboratoire de Métallurgie Physique, University of Poitiers, Futuroscope, France.
Nanocomposite thin films consisting of metallic nanoparticles encapsulated in graphite-like carbon have attracted much attention as possible candidates for a wide range of applications, because graphite not only provides corrosion and wear resistance but also reduces interparticle interactions. Our presentation will focus on the microstructure of Me-C and Me-BN (Me = Cu, Ag, Pt, Fe, FePt) thin films grown by a technique based on dual ion-beam sputtering either by co-deposition or by alternate deposition of Me and C or BN. The influence of the deposition parameters (temperature, assistance...) on the size, shape, organization, and chemical composition of the nanoparticles as well as on the physical properties of the thin films will be discussed on the basis of complementary characterizations by transmission electron microscopy (TEM) and grazing incidence small-angle x-ray scattering (GISAXS) among others.
- K-III.2** 15:00 COMPOSITION, MECHANICAL PROPERTIES AND FRICTION BEHAVIOR OF NICKEL/HYDROGENATED AMORPHOUS CARBON COMPOSITE FILMS
S. Kukielka(a), W. Gulbinski(a), Y. Pauleau(b), S.N. Dub(c), and J.J. Grob(d), (a)Technical University of Koszalin, Faculty of Mechanical Engineering, Department of Physics, Koszalin, Poland, (b)CNRS-LEMD, Grenoble, France, (c)Institute for Superhard Materials, Kiev, Ukraine, (d)CNRS-PHASE, Strasbourg, France.
Nickel/hydrogenated amorphous carbon composite films have been deposited on silicon and stainless steel substrates by combining sputter-deposition of metal and microwave plasma-assisted chemical vapor deposition of carbon from argon-methane mixtures of various concentrations. The composition and crystallographic structure of films were investigated as functions of the CH₄ concentration by Rutherford backscattering spectroscopy and X-ray diffraction techniques, respectively. The carbide phase, Ni₃C, was detected in Ni/C films deposited from a gas phase containing more than 8 % of CH₄. The grain size of Ni and Ni₃C was determined as a function of the carbon content. The maximum magnitude of the compressive residual stresses was 0.6 GPa for films containing 25 at.% of carbon (Ni₃C). The hardness and elastic modulus of films deduced from nanoindentation measurements were studied as functions of the carbon content. The ball-on-disk tribological tests were conducted in room air at room temperature under a load of 1 N with a sliding speed of 3 cm/s. The friction coefficient was determined as functions of the carbon content in the films. The minimum value of 0.25 was obtained from films containing 70 to 80 at.% of carbon.
- K-III.3** 15:20 MICROSTRUCTURES IN CO-SPUTTERED Al-C THIN FILMS DEVELOPING AT ELEVATED TEMPERATURES
D. Biro(a), **A. Kovács**(b), **A. Dévényi**(c), and **P.B. Barna**(b), (a)Petru Maior University, Sapientia University, Tg.Mures, Romania, (b)Research Institute for Technical Physics and Materials Science of HAS, Budapest, Hungary, (c)National Institute of Materials Physics, Bucharest-Magurele, Romania.
The structure of Al-C thin films co-deposited at room temperature was composed by metallic Al and amorphous or nanocrystalline Al₄C₃ phases. At this temperature the Al₄C₃ phase was growing as tissue phase encapsulating the Al crystals [1]. This process resulted in the formation of nanocomposite structure and/or in the development of layered structures of alternating metallic Al and amorphous/nanocrystalline Al₄C₃ phases [2]. In the present experiments the structure evolution of co-sputtered Al-C thin films was investigated at 200C and 300C substrate temperatures in the composition range of 0-30 at % C. The films were prepared in a vacuum system of 10⁻⁷ mbar residual pressure while the argon pressure during deposition was 2.2 x 10⁻³ mbar. Two independent unbalanced magnetron sources with Al and C targets were used. The films were deposited on SiO₂ covered Si wafers and on air cleaved NaCl crystals covered by 5 nm thick C layer. Al and crystalline Al₄C₃ phases developed and grown simultaneously. At low C concentration 3D Al₄C₃ crystals were dispersed in the polycrystalline Al matrix. With increasing C concentration (10-30 at %) the structure is transformed into layered structures of alternating continuous metallic Al and crystalline Al₄C₃ phases. The structure formation is controlled by a variety of atomic mechanisms taking place on the growth surface operating both locally and periodically. Among them the preferential binding of Al species to the metallic Al and that of C species to the Al₄C₃ crystalline phase, the mutual segregation and the surface diffusion of species may be the dominant processes.
[1]P.B. Barna et.al., Surf. Coat. Technol., 125(2000)227
[2]D. Biro et.al., Surf. Coat. Technol., 180-181(2004)425

K-III.4 15:40

NANOSTRUCTURED CHROMIUM-BASED COATINGS DEPOSITED AT LOW TEMPERATURE BY DLI-MOCVD UNDER ATMOSPHERIC PRESSURE FROM Cr(CO)₆

A. Douard(a), F. Maury(a), F. Teyssandier(b), and M. Nadal(b), (a)Centre Interuniversitaire de Recherche et d'Ingénierie des Matériaux (CIRIMAT), Toulouse, France, (b)Institut de Science et de Génie des Matériaux et Procédés, Technosud, Perpignan, France.

Atmospheric MOCVD is an attractive process for large scale deposition of protective metallurgical coatings. Among the advantages, high vacuum technology is not required, which will reduce servicing costs and stop periods. Furthermore, the use of metalorganic compounds as molecular precursors significantly decreases the deposition temperature and extends the application to various metallic alloys and steel substrates for which there is a temperature constraint. As a result, atmospheric MOCVD is particularly promising for continuous deposition and on-line strip coating. For this objective, high flow rates of precursor must be delivered into the reactor with a good reliability and stability. This cannot be achieved easily using conventional vaporization and transport method, i.e. using bubblers or saturators, especially when the precursor is a powder as hexacarbonylchromium, Cr(CO)₆. In this study, this solid precursor was preferably dissolved in solvents. The direct liquid injection of the solutions with fuel injectors delivers constant and accurate flow rates. For the first time, a DLI-MOCVD process for the deposition of Cr-based metallurgical coatings is reported. The films were grown under atmospheric pressure below 450 °C from solutions of Cr(CO)₆ in toluene or THF injected in a flash vaporizer with or without NH₃ prior to the deposition zone. Original nanocrystalline oxycarbide and oxynitride chromium phases were deposited on stainless steel. The influence of the growth conditions has been investigated on the main chemical, physical and structural characteristics of the coatings, as deduced from XRD, SEM, XPS and EPMA analyses. Preliminary mechanical properties from scratch test and nanoindentation measurements as well as corrosion behavior are presented.

K-III.5 16:00

NANO-STRUCTURED COATINGS OF METAL CONTAINING DIAMOND-LIKE CARBON FILMS DEPOSITED BY FEMTOSECOND PULSED LASER ABLATION

N. Benchikh(a,b), F. Garrelie(a), C. Donnet(a), K. Wolski(b), J.N. Rouzaud(c), R.Y. Fillit(b), J. Fontaine(d), M. Belin(d), F. Rogemond(a), and J.L. Subtil(a), (a)Université Jean Monnet de Saint-Etienne, France, (b)Ecole Nationale Supérieure des Mines de Saint-Etienne, France, (c) Ecole Normale Supérieure de Paris, France, (d) Ecole Centrale de Lyon, France.

Metal-carbon based thin films have been realized by ablating alternatively and sequentially graphite and metallic targets under vacuum conditions with an amplified Ti:sapphire laser of 800 nm wavelength and a pulsed duration of 150 fs (Pulsed Laser Ablation, PLD). The metals selected, regarding of their chemical affinities with carbon, are nickel and tantalum. The PLD's device equipped with a multitarget permits us to control the metal concentration introduced in the carbonaceous matrix. a-C:Me films with Me=Ni or Ta have been deposited with Me concentrations in the 2-15 at.% range. The metal content of the a-C:Ni and a-C:Ta films have been investigated by Rutherford backscattering spectroscopy. Their compositions and nano-structures have been characterized by X-ray photoelectron spectroscopy, grazing angle X-ray diffraction, electron energy loss imaging, scanning and high resolution transmission electron microscopies. Nanocomposite coatings have been obtained with clusters in the 100 nm size range. Tribological characterizations of those films show clearly properties of solid lubrication.

16:20

BREAK

Session IV : Composite coatings and thin films

Session chairs : J.I. Oñate (INASMET, San Sebastian, Spain)

V. Teixeira (University of Minho, Guimaraes, Portugal)

K-IV.1 16:40

COPPER/MOLYBDENUM NITRIDE COMPOSITE THIN FILMS – THE STRUCTURE, MECHANICAL PROPERTIES, PHASE COMPOSITION AND HIGH TEMPERATURE TRIBOLOGICAL BEHAVIOR

T. Suszko and W. Gulbinski, Technical University of Koszalin, Department of Mechanical Engineering, Physics Division, Koszalin, Poland.

Thin films of copper doped molybdenum nitride have been deposited on 440C steel substrates by means of reactive, double source, pulsed magnetron sputtering. The structure of coatings containing up to 22 at.% of copper corresponded to cubic γ -Mo₂N. No signature of free, metallic copper was found in x-ray diffraction patterns of studied material, even at the highest copper concentrations. An addition of dopant, immiscible with nitride, has led to creation of Cu/Mo₂N nanocomposite with the gradually decreasing crystallite size of Mo₂N phase, down to about 6nm. Simultaneously, changes of the microhardness, which had reached the maximum value of about 30MPa corresponding to the copper concentration of 1-3 at.%, have been observed.

The tribological properties of films have been studied in ball-on-disc geometry with alumina balls used as a counterpart. Friction tests have been carried out in the air of normal relative humidity (55%) in the temperature range from 20 to 400°C. The thermal and tribological oxidation of the films has been followed by means of X-ray diffraction and Raman microscopy. The role of oxidation products detected in the wear track, which are mainly γ -MoO₃ and copper molybdate CuMoO₄, has been discussed in terms of wear and lubrication mechanism.

K-IV.2 17:00

ENHANCED HARDNESS IN SPUTTERED Zr-Ni-N FILMS

J.Suna(a), J.Musil(a), J.G. Han(b), and V. Ondok(a), (a)Department of Physics, University of West Bohemia, Plzen, Czech Republic, (b)Center for Advanced Technology, SungKyunKwan University, Suwon, Korea.

Recently, it was found that the reactive magnetron sputtering of TiN films with addition of small (10 at.%) amount of Fe makes possible to change the preferred crystallographic orientation of grains in the film when partial pressure of nitrogen in sputtering gas is continuously increased. The films created inside a transition region between these different preferred orientations and on its edges exhibit enhanced hardness [1]. Therefore, correlations between the enhanced hardness, structure and microstructure of films produced in the transition region and in its close vicinity were investigated in detail. For this investigation Zr-Ni-N films with a low content (< 10 at.%) of Ni were selected. The Zr-Ni-N films were reactively sputtered from alloyed ZrNi (90/10 at.%) target in Ar+N₂ mixture. Sputtered films were characterized using XRD, microhardness measurements, FE-SEM, HRTEM, SAED and EDX. The main result of our investigation is the finding that the enhanced hardness arises in two cases: (1) in the materials composed of a mixture of small grains of different crystallographic orientations, i.e. films produced inside the transition region, and (2) in the materials composed of nanocolumns perpendicular to the film/substrate interface, i.e. films produced at edges of the transition region. These findings form basis for the formulation of a complete concept of nanocomposite films with enhanced hardness [2].

[1]J. Musil, H. Polakova, J. Suna, J. Vlcek: Surf. Coat. Technol. 177-178(2004), 289

[2]J. Musil: Chapter 10 in "Nanostructured hard coatings", A. Cavaleiro, J.T.M. De Hosson (Eds.), Kluwer Academic/ Plenum Publishers, New York, 2005

K-IV.3 17:20

STRUCTURAL AND MECHANICAL PROPERTIES OF IBAD DEPOSITED NANOCOMPOSITE Ti_{1-x}Ni_xN_y COATINGS

A. Akbari(a,b), J.P. Rivière(a), C. Templier(a), E. Le Bourhis(a), (a)Laboratoire de Métallurgie Physique, Université de Poitiers, Chasseneuil Futuroscope, France, (b)Department of Materials Engineering, Sahand University of Technology, Tabriz, Iran.

CVD and PVD processes provide new possibilities to produce superhard nanocomposite coatings with ability to control the composition, and the phase distribution in nanometric scale. In these coatings the mechanisms of plastic deformation and rupture are different from traditional polycrystalline materials which generate new mechanical properties. In order to obtain nanocomposite films with nanograins of TiN surrounded by an intergranular Ni/NiTi amorphous/nanocrystalline phase, TiN-Ni films (~0.5µm thick) were deposited on (100) Si wafer and 304L stainless steel, plasma nitrided or not, using an ultrahigh vacuum dual ion beam sputtering technique (NORDIKO-3000). The composite Ti+Ni target was sputtered with 1.2 keV Ar ions and the growing film was bombarded with a mixture of 50 eV Ar and N ions during deposition. In order to obtain optimum structural and mechanical properties, Ni content and temperature were varied from 0 to 60 at% and 25 to 400°C respectively.

Coating composition was obtained from RBS analysis. Phases, grain size, and texture of the coatings were determined by XRD in the θ - 2θ and GIXRD geometries. TiN was the only crystalline phase observed for a Ni composition lower than ~37 at. %. Grain size which was calculated using the Scherrer equation from (200) peaks, decreases from 16 to 2.5 nm when the Ni content varies from 0 to 37 at. %. A texture evolution of TiN crystallites from (111) to (200) was observed with increasing of temperature and Ni concentration. TEM observations also show a nanocomposite structure with very small grain size of TiN (<8 nm) for 25 and 37 at. % of Ni. Nanoindentation tests indicate that superhard coatings with hardness greater than 40 GPa, can be prepared by Ni concentration control.

K-IV.4 17:40

CHARACTERIZATION OF W-Ge-N COATINGS DEPOSITED BY SPUTTERING

A.P. Piedade, M.J. Gomes, and A. Cavaleiro, ICEMS, Departamento de Engenharia Mecânica, Universidade de Coimbra, Portugal.

Thin films of the W-Si-N system are used as protective coatings, especially in applications at high temperatures where thermal oxidation can occur. Nowadays, some research is being done on the effect of the substitution of Si, in similar ternary compounds, by another element of the same periodic table group -germanium. This choice can be justified by the relative similar behaviour of silicon and germanium (atomic radius and ability to form a nitride) and by the lowest price of Ge wafers compared to that of Si.

In this work the effect of the addition of increase Ge concentrations to W-N thin films with different nitrogen contents is investigated. For this purpose W-Ge-N thin films were deposited by reactive magnetron sputtering onto FeCrAlloy substrates from a Ge-doped W target in mixed Ar/N₂ discharge atmospheres. The nitrogen partial pressure and the number of Ge wafers varied, while the total pressure was kept constant at 0,7 Pa. The modified surfaces were characterised in the as-deposited state and after thermal oxidation. The evaluated characteristics included chemical composition (EPMA), structure (DRX), morphology (SEM) and hardness.

K-IV.5 18:00

THERMAL DECOMPOSITION OF Zr_{1-x}Al_xN THIN FILMS DEPOSITED BY MAGNETRON SPUTTERING

R. Sanjinés, R. Lamni, C. S. Sandu, and F. Lévy, Ecole Polytechnique Fédérale de Lausanne (EPFL), Institut de Physique de la Matière Complexe, Lausanne, Switzerland.

The thermal stability of the fcc Zr_{1-x}Al_xN thin films have been investigated by heating the samples in ultra high vacuum (P<10⁻⁷ Pa). For this purpose, two films with chemical composition Zr_{0.73}Al_{0.27}N and Zr_{0.57}Al_{0.43}N have been grown by reactive magnetron sputtering. The phase stability was investigated by annealing the samples from 400 °C up to 850 °C; the heating rate was 10 °C/min followed by a settle time of 1 h at the chosen temperature. The structural evolution of the annealed films has been investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM) and by atomic force microscopy (AFM). Results show that up to the annealing temperature of 650 °C, the pristine structural and mechanical properties of the films were retained. Annealing the films above 650 °C resulted in important structural modifications such as shift of the XRD peaks pointing out the increase of the unit cell, apparent grain size reduction, and hardness enhancement. In Zr_{0.57}Al_{0.43}N films annealed at 850 °C, the chemical analysis by X-ray energy dispersive spectrometry evidenced Al rich regions inhomogeneously distributed in the plane of the film. In from dark and bright field TEM images grains with regions with different contrast having 1-2 nm size were observed. Selected area electron diffraction patterns revealed the presence of poorly crystallized ZrN regions. These results are typical of film decomposition and phase separation process.

18:20-20:00

POSTER SESSION I

+ in parallel, the special oral session for graduate student award (max. 5 candidates)

This special session for graduate student award would continue on Wednesday, June 2 from 8:30 to 12:10 (max. 10 candidates)

POSTER SESSION I
Tuesday, May 31, 2005
18:20 – 20:00

Multilayer coatings

- K/PI.01** CRYSTALLOGRAPHIC ASPECTS RELATED TO ADVANCED TRIBOLOGICAL MULTILAYERS OF Cr/CrN, Ti/TiN AND TiN/CrN TYPES PRODUCED BY PULSED LASER DEPOSITION (PLD)
L. Major(a), J. Morgiel(a), B. Major(a), J.M. Lackner(b), W. Waldhauser(b), R. Ebner(b), L. Nistor(c), and G. van Tendeloo(d), (a)Institute of Metallurgy and Materials Science PAS, Cracow, Poland, (b)Laserzentrum Leoben, Austria, (c)National Institute for Materials Physics, Magurele, Ilfov, Romania, (d)EMAT University of Antwerp, Belgium.
Hard multilayer coatings have been obtained based on Cr/CrN, Ti/TiN as well as TiN/CrN composition using the Pulsed Laser Deposition (PLD) at room temperature. Transmission electron microscopy (TEM) was performed to study growth mechanism, microstructure as well as defects of substrates. The atomic resolution investigations (HREM) helped both to precise the size of columnar grains and roughly estimate their defect density. The X-Ray texture tomography, giving X-ray information from predetermined depth allowed to compare the texture and stress level of the surface and sub-surface nitride layers. High compressive residual stress, were noticed in 1mm monolayer coatings, however, multilayer composition can cause relaxation with increase number of layers up to 32 layers in 1mm. Multilayers based on Cr/CrN, Ti/TiN as well as TiN/CrN were examined by means of hardness, scratch test and wear test.
- K/PI.02** THE INFLUENCE OF SILVER ON THE FORMATION OF GAMMA-TiAl FROM Ti/Al MULTILAYERS WITH DIFFERENT PERIODS
A. S. Ramos and M. T. Vieira, ICEMS, Departamento de Engenharia Mecânica, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, Portugal.
Titanium aluminides based γ -TiAl are promising materials for high temperature applications. Recently, a significant interest has developed in the production of thin films based on titanium aluminides because they can contribute to a wider use of these materials. Thin films of γ -TiAl, with and without γ -Ti₃Al, can be produced after suitably heat treating Ti/Al multilayers deposited by sputtering from two targets (Ti and Al). In a previous paper, the kinetics from Ti/Al multilayers with nanometric period to ordered γ -TiAl thin films was established. Depending on the multilayer period the formation of γ -TiAl occurred in a single step or it was preceded by the formation of Al₃Ti. Nevertheless, up to a 200 nm period it was always possible to form γ -TiAl as the major phase. In this paper multilayer thin films with higher periods are studied in order to determine the maximum period leading to the γ -TiAl phase. The production of high period multilayers requires the use of the Ti and Al targets one by one. The influence of silver on the thin films transformation Ti/Al multilayer γ -TiAl is also analysed. The introduction of a few percent of silver was performed by superimposing small Ag foils on the aluminium target. The kinetics of the films towards γ -TiAl was studied by differential scanning calorimetry and X-ray diffraction, while the chemical composition was evaluated by electron probe microanalysis. The morphology of the multilayer films was observed by scanning electron microscopy. The silver does not influence the morphology and structure of the films, but the formation of the γ -TiAl ordered phase from Ti/Al multilayers is favoured in the presence of this element.
- K/PI.03** HIGH RESOLUTION ELECTRON MICROSCOPY OF CrN-TiN THIN FILMS GROWN ON Si(100) BY RF MAGNETRON SPUTTERING
N. Frangis, D. Papapetros, I. Tsiaoussis, S. Logothetidis, Solid State Physics Section, Department of Physics, Aristotle University of Thessaloniki, Greece.
CrN-TiN thin films were deposited as successive, alternating layers on c-Si (100) substrates using a closed field unbalanced reactive magnetron sputtering method (CF-UBRMS) at various substrate biases (V_b) and substrate rotation frequencies (f). High resolution electron microscopy (HREM) study showed that the structural properties of the films depend on the growing conditions.
The multilayer character of the films was partially preserved for V_b=V_{floating} and f=4.5rpm. In the case of V_b=V_{floating} and f=6rpm the film consists of two layers with thickness 25 and 135 nm respectively. The first zone contains crystals of both nitrides, with a grain size of 5-9nm, while the second one of crystal columns with a size of 20x90nm. In the second layer the crystals are grown with a preferable orientation relationship: [111]nitrides // [100]Si. For V_b=-50Volts and f=6rpm, also two zones are observed with a preferred growth orientation: [100]nitrides // [100]Si in the first zone and [111]nitrides // [100]Si in the second one. In case of V_b=-50Volts and f=4.5rpm or 10rpm, the films appear with a columnar structure and grain size of approximately 30x120nm, without any preferable orientation.
- K/PI.04** EFFECT OF THE Al₂O₃+Al-Ni MULTILAYERS ON THE MECHANICAL PROPERTIES OF INCONEL 600 ALLOY
H. Garbacz, P. Widlicki, T. Wierzchon, and K.J. Kurzydowski, Warsaw University of Technology, Faculty of Materials Science Engineering, Warsaw, Poland.
The Al₂O₃+Ni-Al multi-layer coatings have been produced on Inconel 600 by glow discharge assisted oxidizing of substrate precoated with aluminum by magnetron sputtering. These layers have a diffused structure and can be produced on parts of complicated shapes. The presence of the Al₂O₃ layer on intermetallic Al-Ni imports high hardness (700HV_{0.5}) and wear and corrosion resistance.
In this paper the influence of the multi-layered coatings on the mechanical properties of Inconel 600 was investigated. The structure of layers was examined on a scanning electron microscope. The surface topography was examined by AFM and using a profilometer. The coated and uncoated samples were subjected to a tensile test at room temperature and 500°C with the two strain rates: 8,3x10⁻³s⁻¹ and 8,3x10⁻⁴s⁻¹. Low-cycle fatigue behaviour was determined. It has been found that the coating slightly decreases the strength of Inconel600. The quantitative analysis of the serrations observed on the stress-strain curves showed that the coating decreased the intensity of the Portevin-Le Chatelier effect. The measurements of dynamic mechanical properties showed that it does not decrease the fatigue strength.

K/PI.05**HIGH STABILITY NANO-MULTILAYER RESISTIVE FILMS**

Arunas Andziulis, Beatrice Andziulienė, Jonas Vaupsas and Marius Zadvydas, Department of Informatics Engineering and Physics, Klaipėda University, Lithuania.

The deposition and research of nano-multilayer resistive films, provided for excellent long-term stability resistors, distinguishing by temperature coefficient of resistance TCR around zero and desirable negative, by using classical Cr-Ni-Si materials are presented in this paper. This multilayer structure consists of 3÷8 nm resistive layers and 1÷2 nm barrier-insulator layers (preventing the vertical coalescence of metal grains) each between another. Resistive thin films were deposited by using magnetron sputtering, while the barrier-insulator layers were formed by plasma assisted oxidation of segregated silicon. Composition and thickness of the resistive layer was chosen in such way as after the magnetron sputtering from Cr-Ni-Si (54-06-40 w/w %) target, we would have enough of silicon necessary to form the Si-amorphous matrix and barrier layer as well. However, there were not overmuch of metals Cr and Ni with intention to avoid of the growing Cr-Ni nano-grains precipitates, which could not form the metal predicted conductivity after annealing. Experimental results show, that two or three resistive multilayer system with $R_s=300\div550 \text{ } \Omega/\text{sq.}$ can give the TCR in range of $\pm 2 \text{ ppm}/^\circ\text{C}$ up to negative value of $-60 \text{ ppm}/^\circ\text{C}$. The long-term stability of those nano-multilayer films is $DR/R(t=1000 \text{ h}, T=85^\circ\text{C}) \approx 100 \text{ ppm}$. Keywords: nano-multilayer, long-term stability, resistive films, TCR.

Solid lubricant and tribological coatings**K/PI.06****WEAR BEHAVIOUR OF NiTi SHAPE MEMORY ALLOY AFTER OXYGEN-PIII TREATMENT**

S. Mändl, A. Fleischer, D. Manova, and B. Rauschenbach, Leibniz-Institut für Oberflächenmodifizierung, Leipzig, Germany.

It was shown in animal tests that oxygen plasma immersion ion implantation into NiTi shape memory alloy considerably improves the biocompatibility of autocompression braces. However, these were applications within a static environment without repetitive relative displacement so that no information on the wear behaviour could be obtained.

In this presentation, results from wear tests of NiTi after oxygen-PIII are reported. The implantation voltage was between 10 and 25 kV, with sample temperatures from 250 up to 550 °C, thus resulting in an oxide layer of up to 200 nm. The wear tests were performed in a rotating ball-on-disc tribometer with additional cyclic impact loading with an alumina ball as counterbody. The linear wear rate of the treated samples was similar to that of untreated samples for contact pressures up to 1.0 GPa, while a significantly increased wear, together with a change from rolling to sliding wear was observed at higher contact pressures. The lifetime of the surface layers, defined as catastrophic failure suddenly occurring after a certain period of normal wear depended strongly on the treatment temperature. With increasing temperature, a reduced lifetime was observed. Correlations with Ni segregation away from the surface and the formation of an Ni₃Ti interlayer which may lead to a decreased interface strength are presented.

K/PI.07**STRUCTURAL AND TRIBOLOGICAL PROPERTIES OF HYDROGENATED AMORPHOUS CARBON (a-C:H) FILMS WITH ACETYLENE (C₂H₂) PARTIAL PRESSURE DEPOSITED BY CLOSED-FIELD UNBALANCED MAGNETRON SPUTTERING**

Yong Seob Park and Byungyou Hong, School of information and communication Engineering, Sungkyunkwan University, Suwon, Korea.

Hydrogenated Amorphous Carbon (a-C:H) were deposited by Closed-Field Unbalanced Magnetron (CFUBM) sputtering with a graphite target and using the acetylene (C₂H₂) Gas and argon mixture gases. The effect of the Hydrogen containing and negative DC bias voltage from 0 to -200 V on structure and tribological properties were investigated. The structure properties of a-C:H films were analyzed by Raman analysis, X-ray photoelectron Spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy. And the tribological performance of a-C:H films were analyzed by nano-indentation, pin-on-disk (POD) tribometer and Atomic force microscopy (AFM). Our study is found that a-C:H films deposited by CFUBM sputtering method have the features of the low friction, smooth surface and high hardness.

K/PI.08**STRUCTURAL, MECHANICAL, TRIBOLOGICAL PROPERTIES OF MoS₂/C MULTILAYERS DEPOSITED BY PULSED LASER DEPOSITION TECHNIQUE**

A. R. Phani(a) and J.E. Kraznowski(b), (a)INFIM and Department of Physics, University of L'Aquila, Coppito, L'Aquila, Italy, (b)Department of Mechanical Engineering, University of New Hampshire, Durham, NH, USA.

Multilayers of MoS₂/C have been deposited on polished AISI 440C steel and silicon substrates by Pulsed Laser Deposition (PLD). MoS₂ and C targets were ablated in a background gas of 10 mTorr Ar at room temperature. Several sets of experiments with increasing MoS₂ content and lowering Carbon content and vice versa have been deposited. Structural, microstructural, and mechanical properties of the multilayers have been measured by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and nano-indentation techniques, respectively. Tribological evaluations were also conducted using a pin-on-disc friction and wear test. The MoS₂/C films were found to have a crystalline structure, although the degree of crystallinity was low. The presence of composition modulations in MoS₂/C multilayered films has been confirmed by both wavelength dispersive spectroscopy (WDS) and X-ray photoelectron spectroscopy (XPS). Nano-indentation tests of the MoS₂/C multilayers showed close to rule-of-mixtures hardness levels (12-16 GPa). MoS₂/C multilayers showed increasing hardness with decreasing MoS₂ content, but reached maximum hardness 16 GPa, possibly due to substrate effects. The pin-on-disc tests gave friction values ranging from 0.08 to 0.2 for different sets of films. These results were correlated with the degree of crystallinity and grain structure of the films.

K/PI.09**COMPUTATIONAL STUDIES OF FLUOROCARBON FILMS**

Inkook Jang, Wendung Hsu, Simon Phillpot, and Susan B. Sinnott, Department of Materials Science and Engineering, University of Florida, Gainesville, Florida, USA.

This talk will address two complementary areas related to fluorocarbon (FC) coatings and thin films. The first is related to FC plasma processing, which is widely used to chemically modify surfaces and deposit thin films. It is well-accepted that polyatomic ions and neutrals within low-energy plasmas have a significant effect on the surface chemistry induced by the plasma. Here, the detailed chemical modifications that result from the deposition of beams of polyatomic FC ions (C₃F₅⁺ and CF₃⁺) on polystyrene surfaces at experimental fluxes are identified using classical molecular dynamics (MD) simulations. Based on the predicted accumulation of ion-surface collisions and accompanying chemistry, we elucidate how the unique chemical properties of incident ions affect surface modification. The second area deals with FC polymer nanocomposites, which have various potential applications as solid lubricant materials. In order to better design these composite structures and improve their tribological properties, it is necessary to understand their tribological behavior and how this behavior depends on molecular structure. Here, the tribological behavior of two polytetrafluoroethylene films in sliding contact with one another is examined in classical MD simulations. The change in frictional behavior as a function of chain alignment with respect to sliding direction, cross-link density, and roughness is determined. This work is supported by the National Science Foundation through grant number CHE-0200838 and the US Air Force through grant number FA9550-04-1-0367.

K/PI.10**TRIBOLOGICAL PROPERTIES OF THE MULTILAYERED DIAMOND-LIKE CARBON (DLC) FILMS PREPARED BY PECVD METHOD**

Yongsook Jeon(a,b), Won Seok Choi(a,b), and Byungyou Hong(a,b), (a)School of Information and Communication Engineering, Sungkyunkwan University, Suwon, Korea, (b)Center for Advanced Plasma Surface Technology, Sungkyunkwan University, Suwon, Korea.

We studied the tribological properties of multilayer structure DLC films on substrate. We used the chromium and DLC as multilayer for the purpose of improvement of the DLC films characteristics. Metal layers of the chromium were prepared by the DC magnetron sputtering method. And DLC films were synthesized by means of RF-PECVD method. In this study, multilayer films were consisted of a stack of DLC films (<20 nm) alternated with metal layers (<10 nm). The thickness of multilayer was observed by field emission scanning electron microscope (FE-SEM) and surface roughness was investigated by atomic force microscopy (AFM). Tribological performances of the DLC films were investigated by AFM in friction force microscope (FFM) mode and pin-on-disk (POD) measurement. The experimental results showed that the total surface energy was characterized by contact angle measures with water. Also Scanning electron microscopy (SEM) was used to examine the surface of the films after the POD tests. From our several measurements, multilayers improved tribological properties of the DLC films.

K/PI.11**TRIBOLOGICAL CHARACTERIZATION OF FUNCTIONALLY GRADED Ti-C-N(H) COATINGS WITH MULTIPLE-LAYER STRUCTURE**

D. Boscarino(a), S. Restello(b), and V. Rigato(b), (a)Thin Films srl, Padova, Italy, (2)INFN-Laboratori Nazionali di Legnaro, Legnaro (PD), Italy.

Thin coatings that combine both load supporting capabilities and self-lubrication properties are of great interest as protective coatings in many application fields. TiC_xNy(H) coatings with a graded composition profile along their thickness have been the subject of intense study because of the possibility of combining the high hardness of a metal transition carbon-nitride (TiN/TiCN) with the low friction and wear resistance of a Ti(H:DLC) surface-layer. Although these coatings have been studied since many years the role of Nitrogen and Hydrogen incorporation in the different layers is still a subject of great scientific interest.

The coatings studied have been deposited by reactive magnetron sputtering, controlling the reactive gas fluxes (N₂ and C₂H₂) by an Optical Emission Monitor. Coatings with different stoichiometry have been obtained by changing the ratio between the reactive gas fluxes: the attention has been focused on the influence of the chemical composition, on the crystalline structure and on the mechanical properties. The overall chemical composition across all the film thickness has been determined by Ion beam Analysis using Rutherford and non-Rutherford Backscattering (RBS, n-RBS), Nuclear Reaction Analysis (NRA) and Elastic Recoil Detection (ERDA). The identification of the crystallographic structure has been performed using X-Ray Diffraction (XRD) in θ - 2θ geometry and Grazing incidence XRD. The residual stress has been measured with the beam bending method using a laser profilometer. Nano-hardness, reduced elastic modulus and a set of information concerning scratch adhesion, dry friction coefficient, failure mechanism and fatigue resistance have been determined by Nano Hardness Test (NHT), Micro Scratch (MST) and Multiple Impact Test.

K/PI.12 TRIBOLOGICAL TESTING OF SELF-MATED NANOCRYSTALLINE DIAMOND COATINGS ON Si₃N₄ CERAMICS

C. S. Abreu(a), M.S. Amaral(b), F.J. Oliveira(b), A. Tallaire(c), F. Bénédic(c), G. Cicala(d), J.R. Gomes(e), and R.F. Silva(b), (a)Physics Dept., Porto Superior Engineering Institute, ISEP, Porto, Portugal, (b)Ceramics and Glass Eng. Dept., CICECO, Univ. of Aveiro, Portugal, (c)LIMHP, UPR 1311 CNRS, Université Paris 13, Villetaneuse, France, (d)IMIP-CNR Sezione di Bari, University of Bari, Italy, (e)Mechanical Eng. Dept., CIICS, University of Minho, Guimarães, Portugal

Nanocrystalline diamond (NCD) coatings are being increasingly developed and tested for tribological applications due to their much lower surface roughness compared to that of microcrystalline diamond. Silicon nitride ceramics can be used as substrates for NCD deposition ensuring simultaneously an adequate film adhesion and load bearing capability for mechanical purposes. Up to now, very little information is available regarding the tribological behaviour of NCD either in dissimilar or in homologous pairs.

In the present work, microwave plasma assisted chemical vapour deposition of NCD was accomplished under Ar/H₂/CH₄ gas mixtures on flat and ball-shaped Si₃N₄ specimens using a conventional continuous mode (CW) and a recently developed pulsed microwave power mode (PW). The tribological characterisation of NCD was done using self-mated pairs without lubrication in order to assess its friction and wear response when subjected to such extreme surface contacts. A frequency of 1Hz and a stroke of 6mm were kept constant, while the applied normal load was varied in the range 10N to 60N for different runs.

The microstructure of the NCD coatings was characterised using SEM and AFM while the diamond grain size was obtained from X-ray diffraction patterns and diamond quality from micro-Raman spectroscopy. Worn surfaces were studied by SEM and AFM topography measurements in order to identify the prevalent wear mechanisms. Friction values reached a steady-state minimum of about 0.04 following a short running-in period where the main feature is a sharp peak of ~0.40. Up to the critical load, corresponding to film delamination, the equilibrium friction values are similar, irrespective of the applied load. The calculated wear coefficient values denoted a mild regime ($K < 10^{-6} \text{mm}^3 \text{N}^{-1} \text{m}^{-1}$) for the self-mated NCD coatings.

K/PI.13 SYNTHESIS OF THE SILICON DOPED a-C:H FILMS FROM HEXAMETHYLDISILOXANE VAPOR BY DC ION BEAM

V. Kopustinskas, S. Meskinis, S. Tamulevicius, M. Andrulevicius. Institute of Physical Electronics of Kaunas University of Technology, Kaunas, Lithuania.

Hydrogenated amorphous carbon films (a-C:H) are in wide use for tribological protection of tools or biomedical implants surfaces. Hard and wear resistant protective coatings are very often deposited onto different steels and other ferrous materials. In this case Fe as graphite formation catalyst complicates all process due to the formation of the soft carbon film and adhesion problems. In addition, high carbon dissolving in Fe and ferrous alloys at high temperatures results in substantially increased diffusion of the carbon and carbides from substrate surface into bulk of the substrate. Therefore, incubation time for the diamond-like carbon layer formation is increased. Different techniques such as silicon interlayer formation are used to control the interface processes responsible for nucleation and initial stages of a-C:H film growth. From the other hand, adhesion can be improved by growing silicon doped hydrogenated amorphous carbon film.

In this research silicon doped hydrogenated amorphous carbon films (a-Si_{1-x}C_x:H) films have been synthesized by direct ion beam deposition using hexamethyldisiloxane vapor as a hydrocarbon source. Protective films with good adhesion were deposited in such a way onto the AISI 316 stainless steel and tool steel. Chemical composition and structure of the films were studied by X-ray photoelectron spectroscopy (XPS), X-ray diffraction and RAMAN spectroscopy. Mechanical stress has been investigated using laser interferometry technique.

Nanostructured coatings and thin films

K/PI.14 DLC-SiO_x NANOCOMPOSITE FILMS DEPOSITED FROM CH₄:SiH₄:O₂ GAS MIXTURES

J.C. Damasceno and S.S. Camargo Jr., COPPE, Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ Brazil. Nanocomposite films DLC-SiO_x were deposited by PECVD from CH₄:SiH₄:O₂ gas mixtures. The effects of gas mixture composition and self-bias voltage on the optical and mechanical properties of these films were investigated. Deposition conditions were: rf frequency 13.56 MHz, gas pressure 0.015 torr, self-bias voltage ranging from -100 to -600 V, SiH₄ content 5 vol.% and O₂ content ranging from zero to 5 vol.%. Characterization of the films was performed by XPS, FTIR, AFM, micro-hardness, internal stress, UV-VIS transmittance, refractive index and contact angle measurements. Results show that high optical gap (~ 3 eV) coatings can be obtained at low oxygen contents in the gas mixture (~ 5 vol.%). At low self-bias voltages oxygen incorporation increases the deposition rate of the films. On the other hand, at bias voltages larger than 200V oxygen incorporation decreases the deposition rate revealing that etching of the films is dominant. Nevertheless, oxygen is incorporated into the films mainly as SiO_x, inhibiting the formation of the DLC phase. Residual internal stress of the films are reduced to about 1 GPa, while hardness is approximately constant in the range from 14 to 16 GPa. Refractive index of the films is also approximately independent of oxygen content in the range from 1.6 to 1.7. All investigated DLC-SiO_x nanocomposite films turned out to be more hydrophilic than pure DLC as determined by contact angle measurements obtained by the sessile drop technique.

- K/PI.15** CHARACTERIZATION OF NANOCRYSTALLINE TiO₂ – HfO₂ THIN FILMS PREPARED BY LOW PRESSURE HOT TARGET REACTIVE MAGNETRON SPUTTERING
J. Domaradzki(a), D. Kaczmarek(a), E. L. Prociow(a), A. Borkowska(a), R. Kudrawiec(b), J. Misiewicz(b), D. Schmeisser(c), and G. Beuckert(c), (a)Faculty of Microsystem Electronics and Photonics, WUT, Wrocław, Poland, (b)Institute of Physics, WUT, Wrocław, Poland, (c)Applied Physics, Sensor Technology, BTU Cottbus, Cottbus, Germany.
Metal oxides, whose metal ions belong to group 4 elements in the periodic table, have been extensively studied for various applications. The objective of the work was to study the structure and optical band gap modification due to the fabrication of thin film of oxide consisted of two oxides with different band gaps. Thin films of oxides were deposited by magnetron sputtering using Ti50Hf50 mosaic target. The low pressure of reactive gas and appropriate power of plasma discharge during deposition assumed pseudoepitaxial conditions of layer growth. Thin films were characterized by means of X-ray diffraction, X-ray Photoelectron Spectroscopy and optical transmission methods. On the basis of obtained results it was stated that fabricated thin films were composed of the HfTiO₄ single phase with average size of grains of 12 nm. Optical absorption spectra, derived in a conventional way from optical transmission measurements, yielded the optical band gap of 3.44 eV. Such films seems to be very attractive for optical coatings which should be transparent up to near UV irradiation of the light spectrum. Transition metal oxides, whose optical band gap might be modified by doping or manufacturing using two (or more) oxides with different band gaps are good candidates for host matrixes in luminescent devices, too.
- K/PI.16** COMPOSITION DEPENDENCE OF THE STRUCTURE AND PROPERTIES OF Ni₃C-CARBON NANOCOMPOSITE FILMS
K. Sedláková(a), Zs. Czirány(b), O. Geszti(b), G. Radnóczy(b), T. Ujvári(c), and I. Bertóti(c), (a)Institute of Electrical Engineering SAS, Bratislava, Slovakia, (b)Research Institute for Technical Physics and Materials Science, Budapest, Hungary, (c)Institute of Materials and Environmental Chemistry, Chemical Research Centre, Budapest, Hungary.
DC sputtered Carbon/Nickel thin films were investigated by electron microscopy, X-ray microanalysis and nanoindentation to clarify the influence of the film composition on the structure formation and mechanical properties. The films were deposited in argon plasma at temperatures from 25 to 400°C onto Si substrates. The Ni content of the films was varied from 5 to 25 at %.
In the whole temperature range columnar nanostructures of rather uniform size distribution of crystalline grains, embedded into an amorphous carbon matrix are formed. The crystalline phase could be identified as Ni₃C phase. The carbon matrix shows an increasing ordering into curved, parallel graphene like layers as the growth temperature increases. The nanohardness of the films is medium high, changing in the 10-15 GPa interval. As the carbon content of the films increases, the thickness of the matrix phase becomes larger, what leads to a softening of the films. Structural, compositional and mechanical properties of the films will be described in detail and the relation between structure and mechanical properties will be discussed. Acknowledgement: This work was partly supported by the EU through the project New Fullerene-like Materials: HPRN-CT-2002-00209 and by the Hungarian Research Fund OTKA T 043359 and T 043437.
- K/PI.17** STRUCTURE AND ELECTRIC PROPERTY RELATIONS IN C-Ni AND CN_x-Ni NANOCOMPOSITE FILMS
Gy. J. Kovács(a), A. Koós(a), G. Sáfrán(a), O. Geszti(a), G. Radnóczy(a), and M. Veres(b), (a)Research Institute for Technical Physics and Materials Science, Budapest, Hungary, (b)Research Institute for Solid State Physics and Optics, Budapest, Hungary.
DC sputtered carbon-nickel and carbon-nitride-nickel thin films were investigated by high resolution electron microscopy, scanning tunnelling microscopy/spectroscopy and Raman spectroscopy to clarify the connection between the structure and the electric properties. The films were deposited in argon or nitrogen plasma at temperatures from 25 to 800°C onto NaCl, HOPG, and oxidised SiO₂ substrates.
The microstructures can be described as composites, built from nanocrystals separated by an amorphous or partly ordered C or CN_x matrix. Below 400°C the crystallites can be identified as Ni₃C phase of columnar morphology. At higher deposition temperatures the crystallites are fcc Ni nanocrystals. The change of the structure and morphology with the increasing deposition temperature can be well traced by Raman spectroscopy. The position of the D band, which we found to have a composite structure, is shifting to higher wave-numbers, and the integral intensity ratio of the D and G bands is decreasing. The electric properties of the films change dramatically with the thickness. The relatively wide (1-2 eV) gap semiconductor behaviour is closely related to the spherical graphene-like shells that encapsulate the Ni particles.
- K/PI.18** STRUCTURE AND MORPHOLOGY OF NICKEL/CARBON COMPOSITE FILMS FORMED BY MICROWAVE PLASMA-ASSISTED DEPOSITION TECHNIQUE
V.V. Uglov(a), A.K. Kuleshov(a), M.V. Astashynskaya(a), M.P. Samtsov(b), Y. Pauleau(c), T.A. Kuznetsova(d), and S.N. Dub(e), (a)Belarusian State University, Minsk, Belarus, (b)Research Institute For Applied Physical Problems of Belarusian State University, Minsk, Belarus, (c)National Polytechnic Institute of Grenoble, CNRS-LEMD, Grenoble, France, (d)BRSPU of Powdered Metallurgy, Minsk, Belarus, (e)Institute for Superhard Materials, Kiev, Ukraine.
Nickel/hydrogenated amorphous carbon (Ni/a-C:H) films produced by plasma-assisted deposition were characterized by various techniques. Depending on the composition or atom number ratio, $N(C) = C/(Ni + C)$, three different groups of films can be distinguished. The images of phase contrast obtained by atomic force microscopy for films with $NC < 38\%$ indicate the formation of Ni and Ni₃C grains. Grains of 200 nm in size acquire accurate borders for films with a carbon content $N(C) = 19\%$.
The nickel carbide phase was identified by X-ray diffraction (XRD) techniques. The size of Ni₃C crystallites was varied from 5 to 20 nm with increasing carbon content up to 34%. Substructure is formed for films with $N(C) = 38-50\%$. The size of substructural formations is in the interval of 20-50 nm. On the basis of XRD data, the structure of films containing more than 38% of carbon was progressively amorphous. Large carbon fragments of ~ 400 nm in size are represented by "drop-shaped" carbon island regions of the size up to 400 nm located near composite surface for films with a carbon content in the range 70-90%. Data obtained by Raman spectroscopy demonstrate that the ratio of sp³/sp² carbon bonds was 1/5 in the hydrogenated amorphous carbon matrix of composite films.

K/PI.19 CORROSION BEHAVIOUR OF NANOCOMPOSITE HARD COATINGS OF TYPE MeN-Me
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MeN-Me nanocomposite hard coatings, compared to MeN have improved hardness and wear properties and promise large application potential. However corrosion properties of such coatings are also important for their future use. TiN-Cu, TiN-Sn, MoN-Cu and CrN-Cu coatings were produced by PVD techniques and their structure and corrosion properties were investigated. Field Emission Gun-EBSD, SEM-EDS, copper decoration, electrochemical polarisation and EIS techniques were used in the investigation. The role of coating porosity on corrosion was discussed.

Composite coatings and thin films

K/PI.20 MORPHOLOGY AND CHARACTERIZATION OF LASER CLAD COMPOSITE NiCrBSi-WC COATINGS ON STAINLESS STEEL
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Laser cladding of Ni-based alloy powders on iron and steel surfaces allows to obtain coatings with good bonding and minimal dilution with the substrate, giving superior capabilities in terms of corrosion and wear resistance. Further improvement on the abrasive wear resistance of these kind of coatings can be achieved by including ceramics, such as WC, in the alloy powder.
In this work, several mixtures of self-fluxing NiCrBSi alloy powder and a nickel-clad WC powder (10 wt% Ni and balance WC) were laser clad on stainless steel substrates of austenitic type (AISI 304). Cladding was achieved by means of a CW 2 kW CO₂ laser and off-axis powder feeding. The effect of other parameters of the treatment, such as the laser energy, beam profile, traverse speed and the mass rate of the feed powder was also investigated. Clad layers of 0.5-1.5 mm height were obtained, its microhardness measured and the microscopic morphology and distribution of tungsten carbide particles within the layer characterized by scanning electron microscopy (SEM). It was found that most clad layer properties such as its porosity, microhardness and homogeneity are determined by the percentage of WC particles in the mixture. Pores were observed for volume fractions roughly above 50%. Owing to the very different melting points of the NiCrBSi alloy and the WC, which causes the presence of non melted WC particles in the melt pool, the pool is made less fluid thus favouring the trapping of gas bubbles coming from the shielding and carrying gas flows involved in the process. Below this limit, homogeneous, dense and crack free clad layers were obtained, with measured hardness ranging between 600 and 1000 HV depending on the WC content.

Surface modifications for biomedical applications

K/PI.21 SURFACE ENERGY OF METAL-IMPLANTED FLUORINE-BASED POLYMER
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Most polymeric materials surface exhibit a chemically inert nature that hinders wider applications in printing, dyeing, as well as biological applications. The change of their surface composition, microstructure and molecular chains directly impact their surface properties and applications. In this work, several transition metals were plasma implanted via a cathodic arc source into fluorine-based polymers to improve the wetting properties and surface energy. Our results show that our process led to the breakage of high molecular weight carbon-fluorine chains and loss of fluorine from the surface. In addition, metallic carbides and fluorides were observed to form on the modified surface. Since the bonding states and structures of carbides and fluorides are totally different from those of high molecular weight carbon-fluorine chains, the enhancement of the surface polar and disperse interaction results in the increase of the surface wettability and energy.

K/PI.22 DISSOLUTION KINETICS OF BIOMIMETICALLY PREPARED MINERAL IN PHYSIOLOGICAL MEDIA
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The synthetic hydroxy apatite coatings have a great potential to apply in orthopedic implant applications due to their excellent biocompatibility and biodegradability. The bone-like mineral layer can be coated biomimetically in the surfaces of polymers or inorganic materials using simulated body plasma. This method has advantages over conventional methods and due to the gentle conditions throughout the process and therefore, biomolecules such as drugs, proteins and growth factors can be incorporated into the bone-like mineral. We have prepared 3D poly(lactic-co-glycolic acid) (PLGA) porous scaffolds by solvent casting/particulate leaching method and solvent-casted 2D PLGA films using chloroform. We have coated the bone-like mineral on 3D PLGA scaffolds as well as 2D films incubating them at 37 °C with modified simulated body fluid (mSFB). This mSFB solution contains the following ion concentrations in mM: Na⁺ (141), K⁺ (6.0), Mg²⁺ (1.5), Ca²⁺ (5.0), Cl⁻ (157.0), HCO₃⁻ (4.2), H₂PO₄⁻ (2.0), SO₄²⁻ (1.5). The mineral formed in PLGA substrates were characterized with SEM, FTIR and XRD. We investigate the dissolution behavior of biomimetic minerals coated on PLGA scaffolds or films when they are in two different physiological medias: phosphate buffered saline (PBS) at pH = 7.4, 2-(N-Morpholino)-ethanesulfonic acid (MES) at pH = 5.5. Release ionic components, especially Ca²⁺ and PO₄³⁻ were analyzed using optical emission spectroscopy. The investigation of mineral dissolution behavior is important when hydroxyl apatite use as a carrier for therapeutic agents in orthopaedic implant applications.

Coatings for biomedical applications

- K/PI.23** THE CHARACTERIZATION OF BIOACTIVE TITANIUM OXIDE OVERLAYER ON NITRIDE FILMS
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The nano-structured titanium oxide overlayer was prepared using the annealing of titanium nitride films in air between 500 to 700°C for 2 h. The titanium dioxide (rutile phase) showed up above 500°C, in which its relative integrated intensity rapidly increased with increasing temperatures. Many nano-pores were observed on the surface over 600 to 700°C. The human osteoblast cells were employed as the test of bioactivity. The number of osteoblast cells attached to the oxide overlayer was higher than that of as-deposited nitride films, which indicates that the oxide overlayer enhances the films bioactivity. Furthermore, the correlation between films microstructure and the bioactivity is further discussed.
- K/PI.24** WEAR CORROSION PROPERTIES OF ELECTROLYTIC Al₂O₃-ZrO₂ COATINGS ON Ti-6Al-4V IMPLANT ALLOYS IN HANK'S SOLUTION
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The bioceramic coatings on metallic implants have the potential to improve the performance with respect to implant fixation, wear and/or corrosion resistance. In this study, a novel method of electrolytic Al₂O₃-ZrO₂ composite coatings on F-136 Ti-6Al-4V alloy were successfully conducted in the mixture of ZrO(NO₃)₂ and Al(NO₃)₃ aqueous solution. The uncoated and Al₂O₃-ZrO₂ coated specimens were evaluated by cycle polarization tests in Hank's solution, wear-corrosion tests (including dry and wet) with UHMWPE (ultra-high molecular-weight polyethylene) pins, and surface morphology observations. The Al₂O₃-ZrO₂ coated specimens have shown the better wear, corrosion and wear corrosion resistance than the uncoated specimen. The Al₂O₃-ZrO₂ composite films with gradient components was identified by AES (Auger electron spectroscopy) components depth profiles. The wear loss of UHMWPE was dramatically reduced by the Al₂O₃-ZrO₂ composite coating. Especially, the nature passivation film of the uncoated was destroyed during the wear corrosion test, while the Al₂O₃-ZrO₂ coated maintained at the passive state. Al₂O₃-ZrO₂ composite coating still remaining on the Ti-6Al-4V alloy after the scratch test indicated the excellent adhesion between the coated film and the substrate.
- K/PI.25** HYDROXYAPATITE PULSED LASER DEPOSITED THIN FILMS BEHAVIOR WHEN SUBMITTED TO BIOLOGICAL SIMULATED TESTS
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Structures of hydroxyapatite as thin films, with and without buffer layers, were deposited on CP Ti Gr4 substrates by Pulsed Laser Deposition. They were afterwards heat treated in water vapors. In this study, processes taking place at the hydroxyapatite/Hank's Solution interface are investigated. The experiment consists of immersing the films in Hank's Solution for 21 days, at a constant temperature of 37°C. The composition and the morphology of the films are investigated before and after the experiment. The deposited layer was neither dissolved nor destroyed due to hydroxyapatite's good chemical stability and adherence to substrate. Moreover, at the hydroxyapatite/Hank's Solution interface the formation of a uniform Ca₂P₂O₇ thin layer is detected, which could lead to a better bio-integrability. Also, single micro-crystals of NaCl are observed on the surface of the samples after the experiment, demonstrating the good surface conditions for cell-adhesion. No Ca₂P₂O₇ is synthesized in the case of the reference sample (CP Ti without deposition), while the NaCl (Halite) crystals were very small.

Innovative coatings, deposition processes and surface treatments

- K/PI.26** Ti ION IMPLANTATION AND ELECTRON BEAM TREATMENT OF Al/Al₂O₃ COATINGS DEPOSITED ON GRAPHITE SUBSTRATE
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Using electro-arc Al metallization and micro-arc oxidation (anode-spark process), a coating of Al₂O₃-Al₂O₃ on a graphite surface (i.e. C/Al/Al₂O₃) has been produced. After this, we applied: Ti ion implantation with 5x10¹⁷ dose, 60 to 90 kV and subsequent high-current electron beam irradiation (HCEB) in two regimes for a part of these samples. For our studies we used: a raster electron microanalysis, X-ray phase analysis, Rutherford ion back scattering and elastic resonance on protons (nuclear reactions), which have demonstrated formation of good quality Al₂O₃ and Al coatings before electron beam irradiation. Implantation of Ti ions into the combined coating surface resulted in a small increase in hardness in spite of a spread in initial state values. HCEB irradiation resulted in total melting of Al-sublayer and partial melting of the oxide layer. The work was funded by Project STCU N3078, and by NAS of Ukraine "Nanosystems, Nanomaterials, Nanotechnologies.

- K/PI.27** APPLICATION OF HIGH-VELOCITY PLASMA JET FOR PRODUCTION OF CERAMIC AND METAL-CERAMIC COATINGS
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 In this report we present the review of results on deposition of WC-Co; Al₂O₃; Cr₃C₂-Ni coatings on a substrate of metallic materials. We applied a pulsed plasmatron with velocities of the plasma jet from 2 to 8 km/sec, temperature of the plasma jet reached 103 to 4x10⁴ K, frequency of pulse repetition was 2 to 7 Hz. The thickness of deposited coatings was 60 to 0,8 mm and the deposition rate was 1 m² per hour and more. For analyses we used the following methods: TEM, SEM, RBS, ERDA, XRD, tests for micro-hardness, adhesion power, corrosion and erosion resistance. In the process of our studies we revealed that a transition layer of 7 to 18-20 μm thickness was formed at the inter-phase boundary, depending on the treatment conditions. The structure of coatings, which was formed as a result of high-velocity plasma jet treatment, was comprised of grains with dimensions from several scores of micron to units of nano-meters. The phase composition of these coatings was various: from fcc to bcc-phases in the case of Al₂O₃, and fcc to bcc-phases in the case of WC-Co, WC had a cubic and hexagonal lattices. An analysis of the coatings showed evidence of the formation of Ni-based solid solution, a complex chromium carbides (Cr₇C₃), and an fcc crystal phase with a lattice parameter of 3,614 Å (Cr₃Ni₂). The local hardness on some areas of the surface and in depth of the coatings reaches 66 to 4,5 HRC, while the coating adhesion strength varies 300 MPa.
- K/PI.28** INFLUENCE OF THE RF-SPUTTERING POWER AND THE NEGATIVE BIAS VOLTAGE ON THE STRUCTURE AND THE MECHANICAL PROPERTIES OF W-C THIN FILMS
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 Tungsten carbide thin films have been deposited on {100} Silicon substrates by reactive RF sputtering from a pure tungsten target (5N) in Ar-CH₄ mixture.
 Various RF-power voltage and substrate bias have been carried out. During deposition the substrate temperature and the total pressure have been respectively set at 150 °C and 2 mtorr for all the films. All samples have the same total thickness of 360 nm.
 Rutherford Backscattering Spectroscopy (RBS), X-Ray Diffraction (XRD), Grazing Incidence X-ray Diffraction (GIXRD), X-Ray Reflectivity (XRR) and X-ray Electron Spectroscopy (XPS) were used to analysed the films. Hardness was obtained by nanoindentation.
 All films exhibits a cubic WC_{1-x} phase structure.
 An increase of the RF-sputtering power from 50 to 260 W results in a decrease of the carbon content of the coating from 47 to 30 at. %. The crystallisation increases with the RF-power. The film prepared at 260 W shows a slight orientation of the nanocrystals constitutive of the layer along the [200] direction of WC_{1-x} phase. This film has the higher hardness of 26 GPa.
 RBS and GIXRD results show that the application of a negative bias voltage during deposition affects significantly the composition and the properties of the films. As the substrate bias voltage is increased from 0 to 80 V, the films composition changed from WC_{0.88} to WC_{0.65}. No influence of the bias on the crystallisation and the hardness have been observed.
- K/PI.29** SURFACE ANALYTICAL CHEMICAL IMAGING AND MORPHOLOGY OF Cu-Cr ALLOY
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 Cu-Cr alloys are very interesting materials to study non-equilibrium phase transformations in binary systems containing immiscible metals as well as for practical applications as high-thermal conductivity and contact materials.
 We studied by high resolution secondary ion mass spectrometry and atomic force microscopy the chemical element distributions and surface morphology of Cu-Cr compounds irradiated at low energy, high current electron beam. Irradiation conditions were: energy density 4 to 6 J cm⁻², pulse duration 2.8 to 3.6 μs, number of shots 4-16. Cu-Cr alloy prepared by powder metallurgy contain 30 wt.% Cr. While in samples irradiated at low energy density maps of surface elements reveal the presence of well separated micrometer-sized domains of Cr and Cu, after irradiation at high energy density submicron spots of coexisting Cu and Cr appear. This is clear indication of CuCr compound formation, as also supported by local mass spectrometry. Irradiated samples have reduced roughness, especially in Cr domains, with respect to the pre-treated sample. However, microcracks and microcraters appear as beam energy density and number of shots increase, thus compromising the smoothening effect and the surface integrity.
- K/PI.30** SURFACE ALLOYING OF STAINLESS STEEL 316 WITH COPPER USING PULSED ELECTRON-BEAM MELTING OF FILM-SUBSTRATE SYSTEM
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 Copper films have been deposited on stainless steel 316 substrates by sputtering of a Cu target in argon microwave discharges. The surface morphology, chemical composition, microstructure, nanohardness and tribological properties of samples subjected to pulsed melting with a low-energy (20-30 keV), high-current electron beam (2-3 ms, 2-10 J/cm²) were investigated as functions of the experimental parameters. To prevent the local delamination of films caused by cratering, the substrates were repeatedly pre-irradiated with an electron beam energy density (EBED) in the range 8-10 J/cm². A single irradiation of samples resulted in the formation of a 0.12-0.17 mm-thick diffusion layer near the interface, irrespective of the EBED. In contrast, an increase in pulse number led to an increase in thickness of this layer up to ~ 2 mm. For samples subjected to a single irradiation, the nanohardness and average wear rate of the 0.5-1 mm-thick surface layer, including the molten film and the diffusion layer, non-monotonically varied with the EBED. Using EBED in the range 4.3-6.3 J/cm², the nanohardness and wear rate values were maximum and minimum, respectively. These results are discussed using calculations of the thermal fields.

K/PI.31**SURFACE MODIFICATION OF Ti_{49.5}Ni_{50.5} WITH LOW-ENERGY, HIGH-CURRENT ELECTRON BEAMS**

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A Low-Energy, High-Current Electron Beam irradiation for surface modification of the biomedical Ti_{49.5}Ni_{50.5} alloy contained $\approx 104\pm 2\%$ phase (90 ± 3) vol.% and Ti₂Ni (10 ± 3) vol.% was used. The samples were subjected to the pulsed surface melting at average electron energy 15-20 keV, energy density 6-7 J/cm², pulse duration 2-3ms, pulse repetition rate of 0,1 Hz and number of pulses was ranging 10 - 50. Using grazing incidence X-ray diffraction and metallographical examination it was found that due to fast ($\sim 10^9$ K/s) quenching from the melt the single-phase (B2) structure in the surface layer of thickness 1,5 μ m is formed. The new B2-phase is characterized by the grain size 1,10 μ m, the lattice parameter $a = 3.0072 \pm 0.0005$ Å, the coherent-scattering region size $D_{cs} = 10,20$ nm, by strong anisotropy of linear expansion coefficient in comparison with an initial state (~ 30 nm, $a = 3.0120 \pm 0.0005$ Å, $D_{cs} = 150,300$ nm). The AES studies have shown that a chemical composition of the modified layers depends on irradiation conditions. Irradiation in oil free vacuum ($\sim 5 \times 10^{-7}$ Torr) does not change the Ni, Ti and O concentration depth profiles. At pressure $\sim 10^{-4}$ Torr the thickness of the subsurface layer (> 20 at.% O) increases in 3-4 times and concentration of Ni is reduced almost twice in this layer. Microhardness of the modified surface layer was found to be ~ 10 GPa (initial value is $\sim 2,5,2$ GPa) and monotonously falls down in depth. Surface melting improves corrosion behavior of Ti_{49.5}Ni_{50.5}.

K/PI.32**PHYSICAL PROPERTIES OF TITANIUM OXYNITRIDE THIN FILMS PREPARED BY REACTIVE SPUTTERING WITH GAS PULSING TECHNIQUE**

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DC reactive sputtering was used to successfully make thin films of titanium oxynitride using titanium metallic target, argon as plasma gas and nitrogen and oxygen as reactive gases. The nitrogen partial pressure was kept constant during every deposition whereas oxygen flow rate was pulsed using a square pattern. The study consisted in analysing the influence of the shape of the pulsed rate on physical properties of these films.

In order to adjust the metalloïd concentration to get films with a wide range of oxygen-to-nitrogen ratios, the reactive gas pulsing process (RGPP) was used. In this process, the oxygen flow switches "on" and "off" periodically with a computer controlled system. The signal pattern used in this paper is the square one and its varying parameter is the duty cycle α (Ton / T). Electrical conductivity measured against temperature was gradually modified from metallic ($\sigma_{300K} = 4.35 \times 10^4$ S m⁻¹) to semi-conducting behaviour ($\sigma_{300K} = 17.8$ S m⁻¹) with an increasing duty cycle. Mechanical properties like nanohardness (Hn) and Young's modulus (E) of the films were investigated. Experimental values of Hn and E obtained by nanoindentation at 10 % depth ranged from 15.8 to 5.2 GPa and from 273 to 142 GPa, respectively. The shapes of Hn and E curves against duty cycle were similar: a regular decrease was observed for duty cycle $\alpha \approx 15\%$ corresponding to the occurrence of TiO_xN_y phase. Higher duty cycles led to the smallest values of Hn and E and correlated with TiO₂ compound composition. At last, the colour variation of these titanium oxynitrides was investigated as a function of α in the La^ab^b* colour space. It was related to the chemical composition of the films.

K/PI.33**LASER TREATMENT OF PLASMA SPRAYED ZrSiO₄ COATINGS**

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Zircon, ZrSiO₄, is one of the technologically important oxide ceramic materials known for its high refractoriness, low thermal expansion and thermal conductivity. We have deposited self-supported ZrSiO₄ coatings by means of atmospheric pressure plasma spraying, a high growth deposition method. However, it is well known that ZrSiO₄ decomposes into SiO₂ and ZrO₂ in the high temperature plasma torch during plasma spraying, the rapid quenching preventing reverse combination of both components into ZrSiO₄. Usually, high temperature annealing (about 1500°C) is applied in order to recombine the SiO₂ and ZrO₂ into ZrSiO₄. In this contribution, we show the results of laser processing on the self-supported coatings, which has been performed with a scanning continuous wave CO₂ laser, as well as with a pulsed excimer laser. The crystalline structure of the coatings has been analyzed before and after treatment by means of XRD. It appears in this contribution that excimer laser treatment is not adapted to form the ZrSiO₄ phase. However, by carefully adjusting the CO₂ laser treatment parameters we show that the SiO₂ and ZrO₂ phases indeed recombine into ZrSiO₄.

K/PI.34**PULSED ELECTRON-BEAM MELTING OF Ti-6Al-4V ALLOY AT ELEVATED TEMPERATURES**

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The effect of pulsed electron-beam surface melting on chemical composition, microstructure, and properties of Ti-6Al-4V alloy has been investigated. Samples were irradiated at initial temperatures ranging from 300 to 850 K with a low-energy (up to 30 keV), high-current (~ 100 A/cm²) electron beam of microsecond duration. It has been established the surface layer cleaning of contaminations takes place at low ($T < 500$ K) initial temperatures of irradiated targets. On the contrary at $T \geq 700$ K an intense dissolution of oxygen from the residual atmosphere of vacuum chamber takes place, which leads to its saturation of surface layers of thickness up to 1 micron. In the last case XRD analysis revealed appearance on the surface the quenching phases which results in increasing of surface microhardness up to 8 GPa and in enhancement of wear behaviour. It has been established also the samples irradiated at low temperatures improved significantly their corrosion resistance. The results obtained have been discussed.

- K/PI.35** PHASE COMPOSITION AND STRESS DEVELOPMENT IN TERNARY Ti-Zr-N SOLID SOLUTION COATINGS DEPOSITED WITH COMBINING OF PLASMA FLOWS
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 Ti-Zr-N coatings were formed by the method of condensation from a plasma phase in a vacuum, with ion bombardment of sample surfaces using combined Ti and Zr plasma flows in a residual N₂ atmosphere. The coatings were deposited at different arc currents of Ti and Zr cathodes. The element and phase composition, preferred orientation and residual stresses were studied by X-ray microanalysis (XMA) and X-ray diffraction (XRD). XMA studies show that the multicomponent systems of different composition are obtained, and the control of the plasma flows gives the possibility to synthesize ternary nitrides of any composition. XRD analysis reveals the formation of ternary nitrides with the structure of TiN-ZrN solid solutions and a (111) preferred orientation. The stress state is strongly compressive (~ 6 GPa) but does not vary with Ti arc current, while an increase in the stress-free lattice parameter (a₀) is observed with decreasing Ti arc current, correlated with the element composition analysis. An original stress analysis, based on a triaxial stress model, is used to separate the respective contributions from chemical alloying effect and growth-induced defects to a₀. The relation between composition and stress is discussed using the model of formation of ternary solid solution nitrides with combining of Ti and Zr plasma flows.
- K/PI.36** STRUCTURAL CHARACTERISATION OF AIR OXIDISED Ti-Si-N COATINGS DEPOSITED BY REACTIVE SPUTTERING
 D. Pilloud(a), M.C. Marco de Lucas(b), and J.F. Pierson(c), (a)Dpt CREST, Institut FEMTO-ST, Université de Franche Comté, Montbéliard, France, (b)LRRS, Université de Bourgogne, Dijon, France, (c)Dpt CREST, Institut FEMTO-ST, Université de Franche Comté, Montbéliard, France.
 Ti-Si-N coatings were deposited on polished X38CrMoV5 substrates by sputtering a titanium target in Ar-N₂ reactive mixture. The silicon concentration in the film was adjusted by varying the number of silicon chips located on the erosion area of the target. The films thickness was close to 3 µm. Oxidation tests were performed in air at 700 °C during 2 h using a conventional furnace. The films composition was estimated by electron probe microanalysis. The films structure was studied by X-ray diffraction (XRD) and micro-Raman spectroscopy before and after oxidation.
 Whatever the silicon content in the range 0 - 4 at. %, no silicon containing compound was detected by XRD before air oxidation and only TiN grains were evidenced. The mean grains size estimated from the full width at half maximum of the TiN (111) diffraction peak was close to 10 nm. After oxidation of the TiN film, XRD and micro-Raman analyses revealed the occurrence of the TiO₂ rutile phase in the whole films thickness, indicating the total oxidation of the TiN film. On the other hand, addition of silicon into TiN-based coatings induces a strong improvement of the films oxidation resistance. Indeed, the oxide thickness was reduced to nearly 0.4 µm for films containing 2 at. % silicon. Moreover, the silicon addition induces a change in the structure of the oxidised layer. Indeed, weak diffraction peaks of the TiO₂ anatase phase were detected by XRD. The presence of the anatase phase was clearly supported by micro-Raman spectroscopy, which is a very sensitive method to detect this TiO₂ phase. The intensity of the anatase micro-Raman bands increased with the silicon concentration, whereas that of rutile decreased.
- K/PI.37** THE MECHANISM OF LOW-DIMENSIONAL SURFACE STRUCTURE FORMATION BY COMPRESSION PLASMA FLOW
V.V. Uglov(a), V.M. Anishchik(a), N.N. Cherenda(a), Yu.V. Sveshnikov(a), Y. Pauleau(b), N.T. Kvasov(c), L.A. Danilyuk(c), A.V. Punko(c), V.M. Astashynski(d), E.A. Kostyukevich(d), and A.M. Kuzmitski(d), (a)Belarussian State University, Minsk, Belarus, (b)National Polytechnic Institute of Grenoble, CNRS-LEMD, Grenoble, France, (c)Belarussian State University of Informatics and Radioelectronics, Minsk, Belarus, (d)Institute of Molecular and Atomic Physics of National Academy of Sciences of Belarus, Minsk, Belarus.
 The experiments of the interaction between a plasma flow and a target surface have shown the possibility of modifying material surface layers and depositing of low-dimensional metal-based coating on the substrate surface. Plasma flows are generated by the quasi-stationary Magnetoplasma Compressor (MPC) of compact geometry. The copper and nickel particles were introduced into the acceleration channel of MPC. According to calorimetric measurements, the value of power density absorbed by sample surface, is 5.25 J/cm² per pulse. The effect of compression plasma flow on the substrate surface results in low-dimensional structure formation. The coating appears as a monolayer consisting of spherical particles bonded to each other and averaging in size of about 100-150 nm. SEM- and AFM-images made it possible to reveal the substructure of these metal particles themselves. In accordance with investigations carried out the theoretical model describing the process dynamics of tip leakage from shock-compressed plasma layer is considered. The concentration of condensing metal clusters on the surface and the number of atoms in the clusters are calculated.
- K/PI.38** POROUS SURFACE OF NiTi ALLOY PRODUCED BY PLASMA ION IMPLANTATION
N. Shevchenko, A. Muecklich, E. Richter, and M.F. Maitz, Forschungszentrum Rossendorf e.V., Institute of Ion Beam Physics and Materials Research, Dresden, Germany.
 For several applications a nanoporous surface layer of titanium oxide on titanium or NiTi is desired, e.g. for surface-increase for catalytical or electrochemical applications, or as carrier in a drug release system. This application requires interconnected pores with the size in the same order of magnitude as the drug molecule, few nanometers. A possibility to produce such a nanoporous structure is seen in the high dose ion implantation of a non reactive gas, which aggregates to nano-bubbles. To our knowledge this type of treatment has not yet been done with the superelastic or memory shape NiTi alloy.
 Helium ion implantation of the NiTi and Ti samples was performed by means of plasma immersion ion implantation at following parameters: ion energy of 20 keV, ion fluence of ~1e18 cm⁻², substrate temperature (100 - 400) °C. The implanted layers were examined by elastic recoil detection analysis, Auger electron spectroscopy, grazing incidence X-ray diffraction analysis, atomic force microscopy and transmission electron microscopy. The He⁺-implanted region of NiTi samples contains a Ni depleted surface layer of TiO_x, a Ni enriched zone with fine Ni₄Ti₃ crystallites and a nanoporous amorphous layer. Structure and morphology of these layers after etching in 1% HF acid were studied in order to characterize a deeper porous layer. An influence of implantation temperature on Ni transport from surface to the deeper layers and nanoporous layer formation are discussed.

K/PI.39**SURFACE MODIFICATION OF COTTON FABRICS BY ATMOSPHERIC PRESSURE PLASMA (APP)**

G. Rombola(a), P. Mandracci(a), C.F. Pirri(a), and F. Parisi(b), (a)Material and Microsystem Laboratory, Department of Physics, Politecnico di Torino, Italy, (b)Gripn s.r.l., Torino, Italy.

Modification of the intrinsically low surface energy of natural cotton fibres is important to achieve improvements in surface properties, such as wettability and dye uptake. The aim of this work is to show results on the characterization of cotton fabric samples chemically and physically modified by Atmospheric Pressure Plasma (APP).

Contrary to low pressure plasma equipments first advantage of an APP system is the possibility to treat large area samples on line without any vacuum pump instrumentation. Thanks to the combination to an APP prototype with a Roll-to-roll system we were able to obtain surface modifications on a two meters large cotton patch. Different plasma conditions were performed on cotton fabrics with the possibility to change the residence time of the patch under the plasma region. Working gases, flows and plasma density firstly influence the cotton surface modifications. Two investigation techniques, ATR-FTIR and XPS, were used to reveal superficial chemically modifications on the cotton fabrics. Both experimental techniques shows a weak penetration depth of plasma treatment but a strong chemical and not selective modification on the surface. BET porosity investigation was carried out to observe physical changes. A physical etching occur on the surface and it involves the increase the distribution of pores with a diameter under 10 nm. Capillarity tests allow us to macroscopically detect wettability improvements of cotton fabrics. Diffusion coefficient of the liquid in the cotton fabrics is strictly related to the type of gas used to obtain superficial modifications. The use of APP on cotton fabrics reveals physical and chemical properties of the fibers which correspond to a new properties of the fabrics and new kind of fashion products.

K/PI.40**FUNCTIONAL COATINGS BY LASER PROCESSING AND CLADDING**

A. Yakovlev(a), Sh. Jumaine(b), and I.Smurov(a), (a)ENISE, DIPI, Saint-Etienne, France, (b)HEF, Saint-Etienne, France.

Injection of various powder compositions coaxially with the laser beam allows producing functional coatings locally, in critical areas in accordance with their operational conditions.

Attempt to mix various materials in a blend to achieve a composite coating combining desired selected properties of components often leads to creation of various phases and compounds having new properties and thus should be carefully evaluated in advance. A number of coatings had been created from the following powders and their combinations: Mo, MoCo alloy, stainless steel, CuSn, nanostructured WC/Co. It is shown that additional relatively quick laser processing of working surface yields in significant improvement of tribological properties of functional coating. The processing creates an array of artificial holes serving as reservoirs for debris and/or solid lubricant, gradually releasing during wear into the contact zone. The coatings were tested tribologically for slow speed high pressure dry friction conditions (valve parts, pumps, etc.). Friction coefficients are ranging from 0.01 to 0.4 for different coating compositions and surface processing. For phase determination selected samples were analysed with X-Ray diffraction.

K/PI.41**AMORPHOUS AlMo THIN FILMS PREPARED BY MAGNETRON CODEPOSITION**

N. Radic(a), T. Car(a), Z. Siketic(a), A. Tonejc(b), I. Djerdj(b), J.Ivkov(c), and M. Metikos-Hukovic(d), (a)Rudjer Boskovic" Institute, Zagreb, Croatia, (b)Faculty of Sciences, Phys. Dept., Zagreb, Croatia, (c)Institute of Physics, Zagreb, Croatia, (d)Faculty Chem. Eng. and Tech., Zagreb, Croatia.

Aluminum corrosion properties are considerably improved when it is alloyed with transition metals. Molybdenum has proven to be one of the most effective additives in that respect. Here we present preparation and characterization of the Al-Mo (10-90 at.%) thin films.

Thin films of AlMo alloys have been prepared by codeposition of pure aluminum and pure molybdenum sputtered, respectively, by two independently controlled magnetron sources. A (nominal) alloy composition range was between Al90Mo10 to Al10Mo90. Deposition rate at the substrate (glass, alumina, sapphire, mono-Si) has been 0,17-0,35 nm/s, and the final film thickness was about 0,5 mm. The prepared films have been examined by the RBS, XRD, electrical and micromechanical measurements. A completely amorphous films have been obtained in a composition range Al85Mo15-Al45Mo55 on the substrates at floating potential and at room temperature. The alloys amorphicity was confirmed by a rather high negative temperature coefficient of electric resistivity (up to -13-10-4 K-1) at room temperature, which in some cases increase upon thermal crystallization. The amorphous AlMo alloys are structurally stable up to at least 460°C. The measurements of corrosion resistance of the as-deposited and corresponding thermally crystallized thin films are in progress.

K/PI.42**VASCULAR PROSTHESES WITH CONTROLLED RELEASE OF ANTIBIOTICS: SURFACE MODIFICATION WITH CYCLODEXTRINS OF PET PROSTHESES**

N. Blanchemain(a), S. Haulon(a), F. Boschin(a), H.F. Hildebrand(a), M. Morcellet(b), and B. Martel(b), (a)GRB, Faculté de Médecine, Lille, France, (b)LCOM, Univ. Sciences Technol. Lille, Villeneuve d'Ascq, France.

PET vascular grafts are used to replace or bypass damaged arteries. To minimise the risk of infection, a vascular PET knitted prosthesis was functionalised with cyclodextrins (CDs) in order to obtain acontrolled release of an antibiotic. This first part deals with the grafting of two parent cyclodextrins (a-CD and b-CD) and their hydroxypropyl derivatives (HP-a-CD and HP-b-CD) and the release ciprofloxacin and vancomycin from these modified prostheses was observed.

A best compromise was found out between the lowest temperature and the shortest time of reaction in order to obtain the desired grafting rate. Both HP-CDs grafting occurred at lower temperatures and reaction times than their parent CDs. Moreover, the grafting rates were proportional to the CDs concentration in the initial impregnation bath. Grafting also provoked a decrease of 80 % of the permeability of the modified prostheses so that it was possible to drastically reduce the amount of initially impregnating collagen. In vitro batch experiments showed a release of the antibiotics from the grafted prostheses during 30 days and reached a final concentration of 140 ppm and 50 ppm against 20 ppm and 15 ppm for the control, respectively. Our results demonstrate the feasibility of grafting CDs onto PET vascular prostheses. The grafting allows to reduce the prior impregnation with collagen. The release over 30 days of ciprofloxacin and vancomycin confirmed that grafted CDs were an efficient drug delivery system.

K/PI.43 VASCULAR PROSTHESES WITH CONTROLLED RELEASE OF ANTIBIOTICS: BIOCOMPATIBILITY OF PET PROSTHESES GRAFTED WITH CDs
N. Blanchemain(a), S. Haulon(a), H.F. Hildebrand(a), M. Morcellet(b), and B. Martel(b), (a)GRB, Faculté de Médecine, Lille, France, (b)LCOM, Univ. Sciences Technol. Lille, Villeneuve d'Ascq, France.
PET vascular grafts are used to replace or bypass damaged arteries. To minimise the risk of infection a vascular PET knitted prosthesis was functionalised with cyclodextrins (CDs) in order to obtain a controlled release of an antibiotic. The first part of our investigations demonstrated the feasibility of grafting CDs onto PET and the release of antibiotics for 30 days after implantation. This second part deals with the cellular reactions to these grafted prostheses.
Viability tests by the colony forming method show no toxicity for all CDs (b-CD, g-CD, HPb-CD and HPg-CD) and their associated polymer. Proliferation tests revealed a low proliferation of L132 cells on grafted vascular prostheses and untreated prostheses and good proliferation on Melinex(r) (film form of PET). A proliferation of 17% is observed after 3 days and 100% for Melinex(r). Vitality tests showed a good vitality of cells. From these experiments it becomes obvious that the decreasing proliferation rate is not a cytotoxic effect but is due to the chemical and/or physical surface characteristics. A similar result is obtained for cell adhesion kinetics between grafted vascular prostheses and control. After 2 hours adhesion, a lower adhesion is observed on untreated prostheses. This cell adhesion inhibiting effect of the PET prostheses contributes to a better "survival" of vascular prostheses without secondary obstruction or stenosis. The tests allowed us to conclude that our treatment don't affect biocompatibility of vascular prostheses.

K/PI.44 COMBINED LASER/SOL-GEL SYNTHESIS OF Si/O/C/N COATINGS
Tamer Ezz, Philip Crouse, and Lin Li, Laser Processing Research Centre, School of Mechanical, Aerospace, and Civil Engineering, The University of Manchester, United Kingdom.
Si/O/C/N coatings show promise of having a low coefficient of friction, being reasonably hard and wear resistant, as well as being non-wettable. Sol-gel methods are normally used for their deposition. Results are presented here which show the use of a new laser-based technology for the deposition of these coating. Synthesis was achieved by both in-process spraying and by irradiation under submerged conditions. A comparison of experimental results using high-power CO₂ (10.6 μm) and diode (0.808 + 0.940 μm) lasers under roughly equivalent experimental conditions are discussed. Coatings are evaluated in terms of Vicker's hardness, microstructure, elemental composition, and contact angle with respect to water. The process conditions are evaluated and compared in terms of a heat transfer model.

Diamond-like carbon films

K/PI.45 FORMATION OF CARBON STRUCTURE FILMS BY PLASMA SPRAY TECHNIQUE
L. Marcinauskas, A. Grigonis, V. Valinčius, and P. Valatkevičius, Kaunas University of Technology, Faculty of Fundamental Science, Department of Physics, Kaunas, Lithuania.
Diamond-like carbon (DLC) and polymeric carbon structure films were deposited by plasma spray (PS) technique at atmospheric and reduced pressure (1000 Pa) conditions. The main advantages of PS method are possibility deposit coatings on large area using rapid deposition rates (1-50 nm s⁻¹). Films were deposited on steel and Si wafers substrates from various rates of acetylene, propane-butane, argon, nitrogen and hydrogen gases mixtures. Carbon coatings morphology, thickness, chemical composition, optical properties and bonding state were investigated by scanning electron microscope (SEM), Rutherford backscattering spectrometry (RBS), Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy. SEM and RBS analysis show carbon films thickness in the range of 1-20 μm. FTIR spectra of our films compared to carbon films show some low shifts in the range of 2800-3100 cm⁻¹ wave numbers, which represent sp² CH_x and sp³ CH_x stretching bands. Diamond phase containing carbon films were produced on steel substrate from nitrogen and propane-butane gas mixture, and on Si wafer from hydrogen and acetylene gas mixture.

K/PI.46 THE INFLUENCE OF BIAS VOLTAGE ON STRUCTURE OF a-C:H FILMS
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a-C:H films were deposited by RF PECVD technique in an asymmetric diode reactor in presence of methane gas plasma. In all deposition experiments, the substrate holder was always polarised in the aim to change structure of the deposited a-C:H films with changing the substrate bias voltage between -50 and -270V. The structure of the deposited films obtained under ion bombardment is studied by FTIR spectroscopy. The deconvolution of the broad absorption peak centred at 2900cm⁻¹ allows the estimation of the relative hybridisation sp³/sp² of carbon atoms. The results showed that the structure of a-C:H films is consisted principally of sp³ and sp² hybridisation.

K/PI.47 OPTICAL PROPERTIES OF DIAMOND-LIKE CARBON PROTECTIVE LAYERS DEPOSITED ON THE Co-Cr-Ni IMPLANT ALLOY
L. Zieba(a), J.Jaglarz(b), J.Cisowski(a), B.Rajchel(c), and W.Rakowski(c), (a)Institute of Physics, Cracow University of Technology, Centre of Polymer Chemistry PAN, Cracow, Poland, (b) Institute of Physics, Cracow University of Technology, Poland, (c)The Henryk Niewodniczanski Institute of Nuclear Physics Polish Academy of Science, Cracow, Poland.
The diamond-like carbon (DLC) coverings are very attractive materials for creation of hard protective coating layers. The final mechanical properties of DLC layers are strongly determined by the state of surface, especially the adhesion to the substrate and flatness of the surface layer. In this work the ion beam assisted deposition (IBAD) has been applied yielding the excellent adhesion and flatness. The state of prepared coating layers has been investigated in macro- and microscale by optical- and scratch testing techniques, respectively. The investigations have been done before and after mechanical treatment leading to microscratching. For large surface description, the total and diffuse reflectance measurements have been done using a single-beam integrating sphere. In a small spot area, the investigations of reflectance have been performed with a repared probe. An optical raster scan have also done for study of homogeneity of the DLC surface and their locate thickness flaws. For qualitative and quantitative description, the bidirectional reflection distribution function (BRDF) method has been used along with the ellipsometric measurements yielding the optical constants and thickness of the films studied.

K/PI.48 NCD BY HFCVD ON A Si₃N₄ – BIOGLASS® COMPOSITE FOR BIOMECHANICAL APPLICATIONS
M. Amaral(a), E. Salgueiredo(a), F.J. Oliveira(a), A.J.S. Fernandes(b), F. Costa(b), and R.F. Silva(a), (a)Glass and Ceramics Engineering Department, CICECO, University of Aveiro, Portugal, (b)Physics Department, University of Aveiro, Portugal.
When considering biomechanical applications in medicine, smooth and wear resistant surfaces are needed from the very beginning of use. Smooth surfaces, low friction coefficients and high hardness are characteristics of nanocrystalline diamond coatings (NCD) making them ideal for bio-tribological applications. Recently, the feasibility of nanocrystalline diamond (NCD) deposition by both hot filament and microwave techniques on silicon nitride (Si₃N₄) ceramic substrates was demonstrated. Si₃N₄ ceramics are bioinert materials but recently a bio-compatible BIOGLASS(r)-Si₃N₄ composite has been developed. Although the low glass transition temperature of the Bioglass(r) imposes a maximum substrate temperature, it was used in the present work as a substrate for the deposition of NCD by the hot filament chemical vapour deposition (HFCVD) technique. The aim of the present work is to coat this new composite with continuous NCD films and characterize them with respect to microstructure, grain size, quality, surface roughness and adhesion. The deposition was done using Ar-H₂-CH₄ flowing gas mixtures (50mlmin⁻¹), a total pressure of 50mbar and filaments temperatures of 2100°C-2200°C for substrate temperatures of 550°C-750°C. The total pressure, gas-flow, power supply and substrate temperatures in the HFCVD reactor were individually monitored and controlled. The films were analysed by SEM, AFM, micro-Raman spectroscopy, LIBAD (low incident beam angle X-ray diffraction) for microstructure characterization and scratch testing and Rockwell C indentation for adhesion assessment. After optimization of deposition conditions, a NCD growth rate of about 0.5micron per hour was achieved, producing adherent coatings with low roughness surfaces (Ra~20-50nm) and grain sizes of about 10-20nm.

Carbon-based coatings and thin films

K/PI.49 CONSISTENT DESCRIPTION OF BORON CARBIDE FILM GROWTH BY COMBINING SURFACE AND VOLUME ANALYSES
T. Szörényi(a), I. Bertóti(b), J.-P. Stoquert(c), F. Antoni(c), and E. Fogarassy(c), (a)Research Group on Laser Physics, Szeged, Hungary, (b)Chemical Research Center of the Hungarian Academy of Sciences, Budapest, Hungary, (c)CNRS-PHASE, Strasbourg, France.
Stoichiometry control is a critical issue in fabrication of thin films of multicomponent materials. Pulsed laser deposition, PLD is a dedicated technique for preserving the target stoichiometry even in cases hard to handle with other more conventional approaches. Fabrication of boron carbides in thin film form is definitely one of such cases. PLD of B₄C is therefore a challenging approach. Recent results, however, are scarce and inconsistent. In this contribution the results of Rutherford Backscattering Spectroscopy, RBS and X-ray Photoelectron Spectroscopy, XPS analyses of boron carbide thin films deposited by KrF excimer laser ablation of a sintered B₄C target in high vacuum are compared. Instead of the nominal, B/C=4 stoichiometry RBS gives consistently higher B/C atomic ratios, while XPS tells the opposite. The reason of this apparent contradiction is that the films are composites. Parallel SEM imaging, EDS and AFM studies reveal that heavily boron enriched droplets originating from the molten target surface are embedded into a boron depleted matrix. The surface sensitive analytical techniques routinely used, typically XPS, see the matrix component as dominant, while RBS averages out both components. Since the droplets make a significant contribution to the total volume, the average chemical composition determined by RBS is significantly different from that measured by XPS.

K/PI.50 HARD BCN THIN FILMS GROWN BY DUAL ION BEAM SPUTTERING
J. Bareño, C. Morant, P. Prieto, J.M. Sanz, and E. Elizalde, Departamento de Física Aplicada (C-XII), Universidad Autónoma de Madrid, Cantoblanco, Madrid, Spain.
BCN boron carbonitride thin films with different compositions have been prepared in a Dual Ion Beam Sputtering system (DIBS) onto Si (001) and HSS substrates at 200 °C. A Kaufman-type ion source was used to sputter a B₄C target with inert Ar⁺ ions while an end-Hall ion source was used to bombard the growing film with a mixture of Ar⁺ and N₂⁺ ions. The N₂⁺ and Ar⁺ fluxes were varied in the gas mixture in order to change the nitrogen content in the BC_xN_y compound.
The composition, bonding characteristic, structure, morphology and hardness of the films were investigated as a function of the ratio between N₂⁺ and Ar⁺ fluxes of the assisting ion beam. The chemical bonding and the composition of the films were studied by Fourier Transform Infrared Spectroscopy (FTIR), X-ray Photoelectron Spectroscopy (XPS), Rutherford Backscattering Spectroscopy (RBS) and Reflection Electron Energy Loss Spectroscopy REELS. The hardness of the BC_xN_y films was measured with a Nano-Indenter while the surface morphology was characterized by Atomic Force Microscope (AFM). We have found that the chemical bonding is a function of the nitrogen content in the films. Moreover, the mechanical properties and morphology of the films seem also to follow a dependence of the composition in the film. Beside this, and perhaps the most remarkable result, is that BCN coatings containing less than 30% at. nitrogen concentration show a very high values of hardness, similar to the sapphire and greater than the corresponding to the B₄C compounds.

K/PI.51 SURFACE CHARACTERIZATION OF TERNARY CARBIDES OF TRANSITION ELEMENTS PREPARED BY FEMTOSECOND LASER ABLATION AND DEPOSITION
N. Tuccitto(a), A.Licciardello(a), and R.Teghil(b), (a)Dip. di Scienze Chimiche, Catania, Italy, (b)University of Potenza, Italy.
The ternary carbides of transition elements are considered very promising materials for their magnetic properties. Following previous work on the ablation of the same systems, performed by a nanosecond pulse laser, we have studied the femtosecond laser ablation and deposition of Nd - Hf - C and Pr - Zr - C systems. The ablation source was a frequency doubled Nd:glass laser, with a pulse duration of 250 femtoseconds. The target consisted of a mixture of Neodymium oxide, graphite and Hafnium or Zirconium carbide, finely grinded and finally mechanically pressed into pellets. The gaseous phase produced by laser - material interaction was examined by ICCD imaging, emission spectroscopy and quadrupole mass spectrometry. The deposited films were investigated by various techniques including Time-of-Flight Mass Spectrometry, X-ray Photoelectron Spectroscopy, X-Ray Diffraction, Scanning Electron Microscopy, Energy Dispersive X Ray Analysis. The results indicate the absence of mixed precursors in the gaseous phase so the formation of the ternary carbide films seems to depend from surface reactions.

K/PI.52**CARBIDE FORMATION IN TANTALUM THIN LAYERS DEPOSITED ON STEEL SUBSTRATES**

Y. Hadjar(a), R. Halimi(a), and F. Tancret(b), (a)Laboratoire Couches Minces et Interfaces, Université Mentouri, Constantine, Algeria, (b)Laboratoire Génie des Matériaux, Ecole Polytechnique de l'Université de Nantes, France. Hard tantalum carbide coatings were elaborated by depositing a tantalum layer (4 μm thickness) on high carbon steel substrates and, subsequently, annealing the system (substrate/coating) in vacuum at temperatures from 600 to 1100°C. The effects of the annealing on the kinetic of tantalum carbides formation and morphology have been investigated using X-ray diffraction (XRD), secondary ion mass spectroscopy (SIMS) and scanning electron microscopy (SEM). The mechanical characterization was performed by measuring microhardness and adhesion. It is found that at annealing up to 800°C the compounds Ta₂C and TaC are formed. During the subsequent heat treatment from 900°C to 1100°C the final TaC phase grows at the expense of the Ta₂C phase. The final coating layer has a golden color and presents a columnar structure. Moreover, the microhardness and adhesion of the films increase significantly with increasing annealing temperature. The formation mechanisms are discussed.

Boron-based coatings and thin films**K/PI.53****CUBIC BORON NITRIDE PHASE FORMATION AT ROOM-TEMPERATURE UPON RADIO-FREQUENCY PLASMA ENHANCED PULSED-LASER DEPOSITION**

C. Y. Zhanga, J. B. Wang, S. W. Lia, X. Zhoua, and G. W. Yang, State key laboratory of optoelectronic materials and technologies, School of Physics Science & Engineering, Zhongshan University, Guangzhou, China.

Room-temperature (25°C) growth of cubic boron nitride (c-BN) films has been achieved on the polished single crystal Si (100) and Si (111) surfaces, respectively, by radio-frequency plasma enhanced pulsed-laser deposition (RF-PEPLD) assisted with substrate negative bias. Components, structure and surface morphology of the deposited films were identified by Fourier transform infrared spectroscopy, X-ray diffraction, and Scanning electron microscopy. Moreover, the detail forming mechanism of BN cubic phase at low temperature has been investigated upon RF-PEPLD. Notably, the experimental evidence indicated that three deposition parameters, i.e., pulsed laser energy density, RF plasma power, and substrate negative bias were the key roles in the room temperature growth of the resulted c-BN films. Interestingly, we found that c-BN phase didn't form in the grown films at room temperature without RF plasma, furthermore, the content of c-BN phase of the deposited films increased with RF plasma power and substrate negative bias increasing under the condition of a certain pulsed laser energy density. On the other hand, pulsed laser energy density should keep some thresholds for the c-BN phase forming at room temperature, with RF plasma power and substrate negative bias.

K/PI.54**CONSTITUTION OF THICK OXYGEN-CONTAINING CUBIC BORON NITRIDE FILMS**

K. Sell, E. Nold, M. Stüber, S. Ulrich, J. Ye, and C. Ziebert, Forschungszentrum Karlsruhe, Institut für Materialforschung I, Karlsruhe, Germany.

Replacing the tooth-substance lost for various reasons such as caries is still the major issue in dentistry. The conditions in the oral cavity (moisture, acidity, mechanical and thermal stress) had been challenging for material scientists. For decades, dentistry had accepted the sacrifice of healthy tissues in order to restore the lost function and esthetics. The shortcomings of the mostly used artificial materials are lack of strength, adhesive properties and poor esthetics. Recently, a world-wide trend in dentistry has been the use of adhesive bonding techniques. This has led to the treatment alternatives called "Minimal Invasive Treatments". This approach has not been used in replacing missing teeth due to shortcomings of the materials. Ceramics fulfill the requirements of esthetics and adhesive properties but lack strength. Zirconium and aluminium oxide ceramics have adequate strength but lack adhesive properties. Moreover, none of the ceramics can be processed in patients mouth. Therefore, there has been search for high-strength materials with esthetic properties and possibility to process in patient's mouth. Resin-impregnated fiber-reinforced composites (FRC) has been shown to possess adequate properties to function successfully in the oral cavity. The light-polymerizable matrix compositions has extended their use for direct applications, i.e. to replace missing teeth in situ. The method is based on using thin FRC capsulation on the intact enamel having a fibre structure which continues to carry the loads of the bite. The clinical data suggests a high potential for the future use of these materials as a direct coating for enamel and dentine. The treatment combines natural composite of dentine and enamel to the synthetic FRC and particulate filler composites

Session V : Surface modifications for biomedical applications

Session chairs : **A. Garcia-Luis** (INASMET, San Sebastian, Spain)

A. Matthews (The University of Sheffield, U.K.)

- K-V.1** 14:00 -Invited- FIBER-REINFORCED COMPOSITE LAMINATES AS COATING FOR ENAMEL AND DENTINE
Arzu Tezvergil, Institute of Dentistry University of Turku, Finland.
Replacing the tooth-substance lost for various reasons such as caries is still the major issue in dentistry. The conditions in the oral cavity (moisture, acidity, mechanical and thermal stress) had been challenging for material scientists. For decades, dentistry had accepted the sacrifice of healthy tissues in order to restore the lost function and esthetics. The shortcomings of the mostly used artificial materials are lack of strength, adhesive properties and poor esthetics. Recently, a world-wide trend in dentistry has been the use of adhesive bonding techniques. This has led to the treatment alternatives called "Minimal Invasive Treatments". This approach has not been used in replacing missing teeth due to shortcomings of the materials. Ceramics fulfill the requirements of esthetics and adhesive properties but lack strength. Zirconium and aluminium oxide ceramics have adequate strength but lack adhesive properties. Moreover, none of the ceramics can be processed in patients' mouth. Therefore, there has been search for high-strength materials with esthetic properties and possibility to process in patient's mouth. Resin-preimpregnated fiber-reinforced composites (FRC) has been shown to possess adequate properties to function successfully in the oral cavity. The light-polymerizable matrix compositions has extended their use for direct applications, i.e. to replace missing teeth in situ. The method is based on using thin FRC capsulation on the intact enamel having a fibre structure which continues to carry the loads of the bite. The clinical data suggests a high potential for the future use of these materials as a direct coating for enamel and dentine. The treatment combines natural composite of dentine and enamel to the synthetic FRC and particulate filler composites
- K-V.2** 14:30 -Invited SURFACE COATINGS FOR BIOLOGICAL ACTIVATION AND FUNCTIONALIZATION OF MEDICAL DEVICES
Hartmut F. Hildebrand, N. Blanchemain, G. Mayer, and M. Lefèbvre, Groupe de Recherche sur les Biomatériaux, Laboratoire de Biophysique, Faculté de Médecine, Lille, France.
To improve the tissue integration of an implant, its surface can be modified by mechanical, physical, chemical or biological functionalization. In this way, the surface becomes biologically active by further grafting of biomolecules.
Mechanical Functionalization is any machining, polishing, irradiation, etc., which provides the surface with a different but specific roughness, the structure or amplitude of which can optimize cell proliferation and cell adhesion. Physical Functionalization includes processes like oxidation, i.e. passivation of metals and alloys, but also any surface coating leading to a protection or activation. Two principal concepts are considered for materials functionalization. (i) The Drug Delivery Systems (DDS) where the bioactive molecules goes to the target. (ii) The grafting of the bioactive compounds on small strongly bound spacer molecules. In this system, the target goes to the bioactive molecules. The surface preparation is very important, and one of the most interesting methods is LASER irradiation to clean the material surfaces from contaminating molecules. It also can sensibly activate the surface. More will be said about DDS by grafting or by coating with cage molecules such as cyclodextrins. - Definitive grafting of bioactive molecules via small spacer molecules (peptides) is very interesting when the material surface is considered as a whole, which must either attract cells for a better tissue integration or must protect the organism against certain unwanted characters of the surface.
- K-V.3** 15:00 Si-BASED AMORPHOUS THIN FILMS FOR PERFORMANCE IMPROVEMENT OF DENTAL PROSTHESES
P. Mandracci(a), C.F. Pirri(a), C. Carossa(b), and P. Ceruti(b), (a)Material and Microsystem Laboratory, Department of Physics, Politecnico di Torino, Italy, (b)Clinica Odontostomatologica, Università di Torino, Italy.
Thin-film coatings can greatly improve the performance of dental prostheses, acting as diffusion barriers, reducing the deterioration of the prosthesis, protecting from the corrosive action of the saliva and some byproducts of food mastication, improving the aesthetic features by changing the properties of light reflection.
Amorphous silicon-based alloys, such as a-SiO_x, a-SiN_x a-SiO_xN_y are among the most suitable materials for this task due to their physical properties such as chemical inertness, high hardness, transparency and good adhesion properties. They can be deposited by PECVD, that gives the advantage of simplicity, versatility, relatively low cost and makes possible the deposition at very low temperatures, allowing the growth on resins, plastics and other materials that cannot stand high temperatures. Films of thickness varying from 2 to 6 micrometers of a-SiO_x, a-SiN_x and a-SiO_xN_y were grown in a Radio Frequency PECVD reactor using SiH₄, N₂O and NH₃ as precursor gases at temperatures as low as 100°C on different materials on resins and ceramics commonly used for dental prostheses fabrication. The grown films were characterized respect to their surface morphology by Scanning Electron Microscopy, Atomic Force Microscopy and profilometry. Their chemical composition was analyzed by Electron Probe Microanalysis and their mechanical properties were analyzed by a microdurometer while their optical properties were analyzed by a spectrophotometer. The films showed good adhesion properties despite of the low deposition temperature, high transparency in the visible range and very good properties of biocompatibility.

K-V.4 15:20

EFFECT OF A GOLD-PALLADIUM COATING ON THE LONG-TERM ADHESION OF HUMAN OSTEOBLASTS ON BIOCOMPATIBLE METALLIC MATERIALS

K. Anselme(a) and M. Bigerelle(b), (a)Institut de Chimie des Surfaces et Interfaces, Mulhouse, France. (b)Laboratoire Roberval, UTC, Centre de Recherches de Royallieu, Compiègne, France.

Our ambition for several years is to study the in vitro interface between human bone cells and metals used for dental and orthopaedic implants for improving biomedical implants' surface preparation. In previous experiments, we studied extensively the influence of the surface roughness on cellular response. The methods used for surface roughness preparation modify the surface chemistry of the samples too. In order to determine the relative influence of surface roughness and surface chemistry on the cellular behaviour, we coated the substrates with a nanometric bio-inert metallic layer. We quantified the long-term adhesion of human osteoblasts cultured from 24 hours to 21 days on pure titanium, titanium alloy and stainless steel substrates presenting 6 different surface morphologies and 2 different roughness amplitudes (obtained by machine-tooling, sandblasting, acid-etching, electro-erosion and polishing). The half part of the samples were sputter-coated with gold-palladium. The long-term adhesion on titanium alloy was not modified by coating. It was slightly improved on pure titanium but strongly improved on stainless steel substrates after coating. This study demonstrates that the coating by an inert metallic nanometric layer like sputtered gold-palladium could be a way to improve the cellular reaction to stainless steel implants.

K-V.5 15:40

PLASMA SURFACE TREATMENT OF POLYETHYLENE TEREPHTHALATE FILMS FOR BACTERIAL REPELLENCE

E. Amanatides(a), D. Mataras(a), M. Katsikogianni(b), and Y.F. Missirlis(b), (a)Plasma Technology Laboratory, Department of Chemical Engineering, University of Patras, Greece, (b)Laboratory of Biomechanics and Biomedical Engineering, Department of Mechanical Engineering and Aeronautics, University of Patras, Greece.

Although Polyethylene Terephthalate (PET) is used in certain medical devices due to its relatively high biocompatibility and excellent mechanical properties, infection remains a major impediment to its long term use. Among the methods used to overcome this problem, plasma surface treatment presents some major advantages; it is a very fast and economical process performed at room-temperature for treating complex shapes. In this work we investigate the effect of plasma parameters on the surface properties of treated PET. The aim is to identify discharge conditions that optimize bacteria (staphylococcus epidermidis) repellence and to determine the mechanism of PET surface modification. For the surface treatment, 25 % O₂ in He RF discharges were used under variable total pressure (80 to 500 mTorr) and substrate bias (0 to -30 Volt). Precise plasma power and impedance measurements were used to ensure constant power conditions (2Watt) and to follow the variation of the density and energy of charged species. In addition, spatially resolved optical emission spectroscopy was used to record the production and variation of excited He and O species. Furthermore, SEM and AFM were employed for the examination of the surface morphology and the adherence of the bacteria on the treated PET. The results can be summarized as follows: (a) Most of the films treated with plasma prevent bacteria aggregation and adherence much more than the un-treated PET. (b) The increase of pressure or/and the decrease of the substrate bias result in an increase of the surface roughness. (c) The variation of surface roughness in combination with plasma diagnostics reveals that surface modification depends weakly on ion bombardment and is mainly determined by O atoms etching.

K-V.6 16:00

MIXING FLUORIDE POLYMERS WITH STAINLESS STEEL THIN FILMS FOR INVASIVE MEDICAL DEVICES

A.P. Piedade and M.T. Vieira, ICEMS-Departamento de Engenharia Mecânica, Universidade de Coimbra, Coimbra, Portugal.

The present research work concerns the modification of the 316L stainless steel (austenitic steel) used in vascular stents in order to obtain a surface with improved antithrombogenic associated to the biocompatibility. The surface of the steel was modified by the deposition of a thin film with a chemical gradient that starts as steel and finishes as a polymeric material (PTFE), that means the intermediate layers are constituted as stainless steel with a decrease of PTFE content up to down. Within the scope of developing such a device it is of great importance to understand the effect of the sputtered polymer (PTFE) onto the properties of the 316L sputtered thin film. Thin films of 316L were deposited, by r.f. magnetron sputtering, in Ar, Ar+CH₄ and co-deposited with a PTFE target in an inert atmosphere. The presence of the CH₄ in deposition chamber was necessary in order to guarantee the austenitic character of the steel after sputtering, necessary for the applications envisaged. All the thin films with 500 nm, were characterized concerning chemical composition, structure, grain size, residual stress, hardness and Young modulus. Particular attention was paid to ductility, adhesion and wettability of composite thin films. The solubility of fluor in steel resulting from cross-linking of polymer chains was evaluated. The effect of the fluorinated species into the 316L thin films was assessed by comparing their properties with those resulting from a reactive carbon enriched atmosphere.

16:20

BREAK

Session VI : Coatings for biomedical applications

Session chairs : **A. Goulet** (Polytech, Nantes, France)

V.T. Vieira (University of Coimbra, Portugal)

- K-VI.1** 16:40 -Invited- TAILOR-MADE FUNCTIONAL LAYERS ON Ti-IMPLANTS FOR VARIOUS APPLICATIONS IN BIOMEDICINE
Jürgen Breme(a), S. Winter(a), D. Velten(a), F. Aubertin(a), E. Eisenbarth(a), and H.F. Hildebrand(b), (a)Lehrstuhl für Metallische Werkstoffe, Universität des Saarlandes, Saarbrücken, Germany, (b)Groupe de Recherche sur les Biomatériaux, Faculté de Médecine, Lille, France.
Because of the ever present surface oxide layer with its beneficial chemical, physical and thermodynamic properties Titanium and its alloys are the metallic biomaterials of preference. In particular, the strongly negative heat of formation of titanium oxides which also exists for the primary corrosion products with their large surfaces, provides the corrosion resistance, biocompatibility, and low dissolution in the body fluid. Nevertheless, medical devices, implants and biomaterials must keep in step with advances in medicine. Therefore for special applications biomaterials can be tailor-made as composites if a single material is not able to fulfil the various requirements. In most cases a functional surface layer which provides a special required property covers a structured material: titanium and its alloys. In each case for the composite developments the local biocompatibility must be taken into account according to the special application. Examples will be given for such components which are in contact with the hard tissue (prosthetic and dental implants), with the soft tissue (dental implants) and with blood (stents). In each case the objective of the investigation is an improvement of the functionality of the implant.
- K-VI.2** 17:10 ELASTIC TiN COATING DEPOSITED ON POLYURETHANE BY PULSED LASER
R. Major(a), J. Bonarski(a), J. Morgiel(a), **B. Major**(a), R. Kustosz(b), J.M. Lackner(c), W. Waldhauser(c), and P. Lacki(d), (a)Institute of Metallurgy and Materials Science PAS, Cracow, Poland, (b)Foundation of Cardiac Surgery Development, Zabrze, Poland, (c)Laser Center Leoben, Graz, Austria, (d)Czestochowa University of Technology, Czestochowa, Poland.
Titanium nitride (TiN) is regarded as a potential biomaterial for blood-contact applications. TiN thin layers were fabricated by pulsed laser deposition by means of the Nd:YAG laser on biologically applied polyurethane. Transmission electron microscopy (TEM) study of 500nm thick layers revealed columnar structure. Such layers were observed to be brittle, which led to the crack formation and secondary nucleation after bridging. Finite element modeling was performed to establish the temperature distribution in the substrate and in the layer. In order to improve elasticity of the coatings, the thickness was reduced to 50nm, which limited the deposition mechanism operation to the early stage. TEM cross-section observation revealed elastic behaviour for this thin layers. Conventional texture examinations as well as texture tomography were carried out for the deposited TiN. Biological test showed that TiN surface layer produced on polyurethane is characterized by good biocompatibility and decreased surface affinity for cell adhesion, which is expecting for blood application.
- K-VI.3** 17:30 COMPARISON OF HYDROGENATED AND UNHYDROGENATED CARBON FILMS OBTAINED BY FCVA ONTO Ti6Al4V: STRUCTURE, HARDNESS AND BIOCOMPATIBILITY STUDY
C. Meunier(a), Y. Stauffer(b), A. Daglar(a), F. Chai(c), S. Mikhailov(b), and H.F. Hildebrand(c), (a)FEMTO-ST/CREST, Montbéliard, France, (b)CAFI-EIAJ, Le Locle, Switzerland, (c)Groupe de Recherche sur les Biomatériaux (GRB), Lille France.
This work compares hydrogenated and unhydrogenated carbon films as surfaces for implants. Thin films are deposited by a FCVA process in a variable methane pressure in order to obtain very close sets of deposition conditions for the hydrogenated and unhydrogenated films. Ti6Al4V alloy is used as substrate. The structure is investigated by XRR, ERDA-RBS and Raman spectroscopy. The mechanical and physico-chemical properties such as adherence load, hardness and wettability are studied for the two sets of coatings and the metallic substrate. The biological approach is a study of the cytocompatibility of these films with MC3T3-E1 osteoblast-like cells and in particular the adhesion kinetics. The carbon coatings do not influence neither the morphology nor the early adhesion behaviour of these target cells on the substrates. This is probably due to similar hydrophilic surface energies of the tested control and carbon-coated test samples.
- K-VI.4** 17:50 PROCESSING AND IN VITRO BEHAVIOUR OF HYDROXYAPATITE COATINGS PREPARED BY ELECTROSTATIC SPRAY ASSISTED VAPOUR DEPOSITION (ESAVD) BASED METHOD
Xianghui Hou, **Kwang-Leong Choy**, and Sian Ellen Leach, School of Mechanical, Materials and Manufacturing Engineering, The University of Nottingham, University Park, Nottingham, United Kingdom.
Hydroxyapatite bioactive coatings are often used to improve bone attachment and reduce the corrosion of metal prosthesis implants. This paper reports the direct preparation of hydroxyapatite coating using a novel Electrostatic Spray Assisted Vapour Deposition (ESAVD) based method. With appropriate processing conditions, crystalline hydroxyapatite phase can be directed formed in a single-step deposition, without further heat-treatment. The influence of processing parameters on the surface morphology, composition and crystalline phase of the as-deposited coating will be discussed. The in vitro behaviour of the as-deposited hydroxyapatite coating in simulated body fluid will also be investigated.

K-VI.5 18:10

ADHESION STRENGTH OF SOL-GEL DERIVED FLUORIDATED HYDROXYAPATITE COATINGS

Sam Zhang(a), Wang Yongsheng(a), Cheng Kui(a), and Zeng Xianting(b), (a)School of Mechanical and Production Engineering, Nanyang Technological University, Singapore, (b)Singapore Institute of Manufacturing Technology, Singapore.

Fluoridated hydroxyapatite (FHA) coatings are increasingly studied for use as biomaterials owing to their good bioactivity and resistance to dissolution in Simulated Body Fluid. Dense and uniform FHA coatings with different fluorine content have been successfully fabricated on Ti6Al4V substrates by sol-gel dip coating method. The X-ray photoelectron spectroscopy (XPS) and X-ray diffraction analysis (XRD) results show high purity and homogeneous FHA coatings. Scanning scratch tester (SST) is used to measure the critical load as an indication of the adhesion between the coating and the substrate. The results show that the adhesion strength increases with the increase of fluorine content and firing temperature. Based on the cross-sectional XPS analysis, a mechanism was proposed for the increased adhesion strength.

19:00

AWARD CEREMONY

The symposium organizers and the candidates to the graduate student award are requested to attend.

CONFERENCE RECEPTION

Session VII : Innovative coatings, deposition processes and surface treatments

Session chairs : E. Bergmann (Ecole d'Ingénieurs de Genève, Switzerland)

X. De La Fuente (University of Zaragoza, Spain)

K-VII.1 8:30 -Invited-

ION IMPLANTATION FOR SURFACE MODIFICATION OF BIOMATERIALS

Jacek Jagielski(a), A. Piatkowska(a), P. Aubert(b), and L. Thomé(c), (a)Institute of Electronic Materials Technology, Warsaw, Poland, (b)University of Evry-Val d'Essonne, Evry, France, (c)CSNSM, Orsay, France.

One of the main challenges of modern material science is to design materials that can be used for the reparation of the human body. The importance of this topic is obvious; the lack of donors and still unresolved problems of immunological response result in ever increasing need for artificial parts that can replace ill or damaged organs. The properties required from materials used for biomedical purposes can only rarely be fulfilled by single phase materials. An interesting option is thus the use of the appropriate surface modification method. This concept allows one to combine different bulk and surface properties and permits the manufacturing of purpose-designed materials.

The aim of the presentation is to shortly review the use of ion implantation for surface modification of two types of materials widely used in transplantology: polymers and ceramics. Structural modifications caused by high energy ions as well as their influence on hardness and friction properties will be presented. Special emphasize will be given to friction reduction in water-based solutions, a medium characteristic for human body. A clear correlation between friction and wettability will be demonstrated. Finally, the use of more advanced options offered by ion beam techniques as synthesis of nanometer-sized smart materials will be presented.

K-VII.2 9:00

LASER TRANSFORMATION HARDENING OF A TOOL STEEL: SIMULATION BASED PARAMETER OPTIMIZATION AND EXPERIMENTAL RESULTS

C. Alvarez, J. M. Amado, A. Ramil, E. Saavedra, **M. J. Tobar**, A. Yañez Dpto. de Enxeñaría Industrial II. Universidade da Coruña, Ferrol, Spain.

Laser surface heat treatments comprise a wide variety of techniques by which hard and wear resistant layers can be obtained on surface without affecting the bulk material. It is known that the performance of these kind of treatments is highly influenced by the different parameters involved in the process, such as the thermophysical properties of the material or the laser beam settings: width, power and relative velocity to the workpiece. A careful parameter selection is therefore needed in order to get the desired results. In this sense, simulation models constitute a powerful tool not only to predict the more convenient experimental settings but also to provide with a more comprehensive view of the laser process.

In this work a 3D numerical model for laser surface treatment is presented. In this model, the time and space laser intensity distribution is considered as well as the temperature-dependent thermophysical properties of material. The predictive capacity of the proposed method is further enhanced by including a detailed geometrical description of the treated piece and an efficient phase model for the metallurgical transformations. The model has been validated through a laser transformation hardening process on a tool steel. Several combinations of parameters, fulfilling the process requirements, has been derived from the model and tested on the laboratory. The microstructure characterization and microhardness measurements of the processed workpieces is favourably compared with the numerical expectations.

K-VII.3 9:20

PROPERTIES OF TiN FILMS PRODUCED IN HOLLOW CATHODE AND MICROWAVE ECR HYBRID PLASMA SYSTEM

L-E. Gustavsson, H. Baránková and L. Bardo, Ångström Laboratory, Uppsala University, The Plasma Group, Uppsala, Sweden.

Properties of TiN films grown in a hybrid system combining linear magnetized hollow cathode with Ti plates and an Electron Cyclotron Resonance (ECR) microwave plasma were studied. The films of 0.5 - 1.4 μm in thickness were deposited on both high-speed steel (HSS) and Si substrates. High quality films with dense microstructure and high hardness were obtained. Microstructure was studied by X-ray diffraction (XRD), scanning electron microscopy (SEM) was used for study of the surface morphology and the film-substrate interface, and mechanical properties were evaluated by nano indentation. It has been found that the interaction of the microwave power with both the substrate and the growing film can affect the growth regime and consequently the film properties. Formation of film defects is more frequent on Si substrates than on steel due to an absorption of the microwave power in the Si substrate during deposition. This effect was confirmed by temperature measurements. The TiN film properties were compared with reference samples deposited by conventional methods. Due to plasma density as high as $5 \times 10^{11} \text{ cm}^{-3}$ the obtained films reach quality comparable or even better than the best commercial TiN films.

K-VII.4 9:40

OPTIMIZATION OF SPRAY PYROLYSIS ZIRCONIA COATINGS ON ALUMINIZED STEEL

R. López Ibáñez, F. Martín, J.R. Ramos-Barrado, D. Leinen, Laboratorio de Materiales y Superficie, Dpto. Física Aplicada I and Dpto. Ingeniería Química, Universidad de Málaga, Campus de Teatinos, Málaga, Spain.

An exhaustive study of spray conditions is presented for ZrO₂ thin films on hot-dip aluminized steel to be used as protective coatings against degradation. A fractional factorial design (2⁴-IIV) has been applied to reduce the number of experiments and finding out main and secondary effects of spray pyrolysis variables on growth rate. Factors, as substrate temperature, solution concentration, air pressure and precursor flow rate have been studied in two levels. Results from this work will be discussed by X-ray photoelectron and UV-Vis-NIR spectroscopy and scanning electron microscopy, finding great changes in substrate covering, optical and morphological properties for the analysed layers. A statistically significant influence of substrate temperature -in a negative way-, and precursor flow rate -in a positive way- has been found in film growth. The co-optimization of both variables has conducted to a considerable reduction of deposition time, as industrial applications and process improvements require, being that the first step for a later up-scaling of these barrier coatings.

K-VII.5 10:00

PROTECTIVE COATINGS BY CHEMICAL VAPOR DEPOSITION

Sanjay Mathur, Hao Shen, Eva Hemmer, Thomas Ruegamer, Jessica Altmayer and Patrick Kuhn, CVD Division, Leibniz Institute of New Materials Saarland University Campus, Saarbruecken, Germany.

Metal oxides, nitrides and carbides are important materials for protection coatings due to their outstanding mechanical, chemical or high temperature resistance. In view of their potential application as thermal barrier coatings, abrasion resistant films and corrosion protection layers a dense microstructure and good adhesion is required which can be achieved by the Chemical Vapour Deposition (CVD) of molecular precursors. We have deposited nanocrystalline films of titanium and zirconium oxide, zirconium carbonitride and spinel. Hence we focused on the influence of precursor chemistry and process parameters on film characteristics.

Three different Mg-Al alkoxides, [MgAl₂(OPri)₈], [MgAl₂(OBut)₈] and [MgAl₂(OBut)₄H₄], were used in the CVD process to obtain MgAl₂O₄ films. The films deposited using [MgAl₂(OBut)₄H₄] exhibit less dense microstructures than films obtained by [MgAl₂(OPri)₈] or [MgAl₂(OBut)₈] leading to lower hardness of the coatings. Further examples of the influence of precursor design on the material properties are metal carbonitride and oxide films deposited by CVD of corresponding metal amides and alkoxides, respectively. The role of process parameters in particular the deposition temperature and precursor composition on morphology and phase composition was investigated for various materials. A brief overview of our findings on the influence of gas phase chemistry on the final material properties will be presented.

10:20

BREAK

Session VIII : Diamond-like carbon films

Session chairs : J.M. Albella (CSIC, Madrid, Spain)

C. Godet (Ecole Polytechnique, Palaiseau, France)

K-VIII.1 10:40 -Invited-

INTERACTION BETWEEN CARBON COATINGS AND TISSUE

Stanislaw Mitura, and K. Mitura, Technical University of Lodz, Poland.

Nanocrystalline diamond coatings (NCD) are manufactured by the Radio Frequency Plasma Activated Chemical Vapour Deposition. The very extensive and complex investigations demonstrate that carbon coatings are biocompatible based on both in vivo and in vitro tests. Histopathological investigations showed a very good biotolerance of implants coated with the NCD layers.

Additionally, Bakowicz have observed the bioactivity of diamond in human body which is connected to the inhibition of toxic processes (lipid peroxidation) in human organism. The examinations of diamond powder particles (DPP) as the "extended surface" shows the distant results of presence the medical implants covered by NCD. Diamond powder was examined on molecular, cellular and clinical level. The effect of nanocrystalline diamond on the hemolysis of human erythrocytes induced by 2,2'-azobis(2-amidinopropane) dihydrochloride (AAPH) was studied. This research proved the thesis that diamond has specific biological activity in the living organism. Additionally, the different types of carbon powders were examined.

K.Bakowicz, S.Mitura: "Biocompatibility of NCD", Journal of Wide Bandgap Materials, Vol. 9, No. 4 - April (2002) 261-272.

K-VIII.2 11:10**GROWTH OF THIN HYDROCARBON FILMS AND HYDROGEN PRODUCTION IN A CUSP PLASMA DEVICE**

N. Spinicchia(a), G. Angella(b), M. De Angeli(a), G. Gervasini(a), and E. Signorelli(b), (a)Istituto di Fisica del Plasma "P. Caldirola" CNR-EURATOM, Milano, Italy, (b)Istituto per l'Energetica e le Interfasi CNR, Milano, Italy.

A plasma device with a cusp magnetic field configuration operating at steady state condition thanks to a water-cooled solenoid system has been built to investigate surface deposition of hydrocarbon films at low-temperature and, simultaneously, the cracking of methane in a plasma environment to hydrogen production. The cusp magnetic configuration approach is very attractive to study such physical processes, since it is characterized by a very simple geometry and the high magneto-hydrodynamics stability of the plasma allows obtaining high plasma concentrations with a high dissociation of molecules. Furthermore, besides techniques for plasma processing can be easily combined at the plasma loss boundaries (point cusp and line cusp).

The gas (methane or a methane/argon mixture) has been fed to the plasma source (a cylindrical capacitively-coupled rf type) located at one point cusp and the discharge gas pressure has been 10-1 Pa under a flow rate of 2 sccm. Plasma and gas parameters have been acquired by a Langmuir probe and a quadrupole mass spectrometer (QMS), both located at the line cusp, and a plasma density up to 10^9 cm^{-3} with an electron temperature of 10 eV has been achieved. The addition of a static magnetic field has increased the particle confinement time and, consequently, the hydrogen production rate.

Here the preliminary results concerning the growth of thin hydrocarbon deposition films and the dissociation of methane in the cusp plasma are presented. In our case, at the line and point cusp, we have a large flux of energetic particles as well as neutral, ions, thermal radicals that participate in the growth process.

A fraction of the converted methane has been deposited on the samples, at the line cusp, as amorphous hydrocarbon (a-H:C) film and amorphous carbon (a-C) film. The last one kind of films were deposited under conditions where ions dominate the deposition process, in particular ta-C films has been deposited from pure carbon ion beam so that hydrogen was completely excluded from the deposition process.

The surface morphology of the film has been observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) has been used to determine the structure of the film. The results have indicated that the film has a prevalently amorphous structure with a significant presence of crystalline clusters.

The next steps will be devoted to understand the relationship between the film characteristics and the plasma parameters. We are going to apply at the samples the heating, the measurement of temperature and an rf bias, with the purpose to vary the energy of the ions impinging on the substrate.

K-VIII.3 11:30**NEAR-SURFACE MECHANICAL PROPERTIES AND SURFACE MORPHOLOGY OF AMORPHOUS CARBON ULTRA-THIN FILMS**

S. Kassavetis(a), G. Matenoglou(a), S. Logothetidis(a), and S. Kennou(b), (a)Aristotle University of Thessaloniki, Greece, (b)University of Patras, Greece.

As the size of devices consistently shrinks reaching the atomic scale, there is particular need for sophisticated methods to study the properties of ultra-thin amorphous Carbon (a-C) and hydrogenated a-C (a-C:H) films with nm-resolution. The study of the mechanical properties of these ultra-thin films is a very ambitious task and can be accomplished by advanced surface-sensitive techniques. Nanoindentation (NI) has the inherent limitation of the substrate influence to the measured hardness (H) and elastic modulus (E), requiring sophisticated modelling to determine H & E. Surface acoustic methods seem more promising for such study; among them Atomic Force Acoustic Microscopy (AFAM) is a novel technique, based on the resonant vibration of an AFM tip, in contact to the film's surface, when an external ultrasonic signal is applied. In this work, we study a wide variety of a-C and a-C:H films. The studied films are either single layers or multilayer stacks, consisting of independent a-C layers, with variable density and hybridization determined by X-Ray Reflectivity and X-Ray Photoelectron Spectroscopy, respectively. We investigate the mechanical properties of these films using both NI, employing continuous stiffness measurements, and AFAM for the accurate determination of the elastic modulus of ultra thin carbon films. We analyse the NI data using empirical models and we compare the results with the AFAM ones. Finally, we correlate the AFAM and NI results with the density and hybridization of the various films.

K-VIII.4 11:50

CONTROL OF STRESS AND DELAMINATION IN SINGLE AND MULTI-LAYER CARBON THIN FILMS PREPARED BY CATHODIC ARC AND RF PLASMA DEPOSITION AND IMPLANTATION

Peter C.T. Ha(a,d), D.R. McKenzie(a), M.M.M. Bilek(a), E.D. Doyle(b), D.G. McCulloch(c), and P.K. Chu(d), (a)School of Physics, University of Sydney, Sydney, NSW, Australia, (b)Swinburne University of Technology, Melbourne, Australia, (c)Department of Applied Physics, RMIT, Melbourne, Australia, (d)Department of Physics and Materials Science, City University of Hong Kong, Hong Kong, China.

The build-up of intrinsic stress in carbon thin films deposited by vapour deposition can be a major cause of delamination. Arguably this issue has been one of the main reasons why the industrial exploitation of carbon vapour deposited films has so far been of limited success. In the present study we deposited single and multilayer thin films of carbon and found that under certain deposition conditions, we were able to produce thin films free from delamination. Furthermore, we were able to stop a delaminating film by adding a control layer.

Two methods were used to deposit the carbon films: (1) filtered cathodic arc with both negative DC and pulsed bias to the substrate and (2) RF plasma with negative pulse bias up to 30kV, 60Hz, 100ms. Both single and multilayer structures of carbon with different sp² and sp³ ratios were deposited and it was found that, under controlled conditions, the overall stress was maintained at acceptable levels. Moreover, it was found that an additional control layer stopped ongoing delamination of the film. The structures of these multilayers were studied using XPS, SEM and TEM.

Acknowledgement: This project was funded by the Australian Postgraduate Award in Industries 2001-2004 and the Endeavour Australia Cheung Kong Award 2005.

K-VIII.5 12:10

THICK WELL ADHERENT CARBON FILMS WITH REDUCED STRESS

K. V. Oskomov, N. S. Sochugov, and S. V. Rabotkin, Institute of High Current Electronics SB RAS, Tomsk, Russia.

For successful application of hard carbon films it is necessary to reduce intrinsic stress substantially in order to increase the coating thickness up to several microns. One of the way that was demonstrated for the a-C films deposited by FVCA is to apply high-voltage (up to 20 kV) pulsed bias to a substrate thus modifying structure (e.g. graphite clusters size) and properties of the films. However, it is still unclear if this approach is effective for other deposition techniques, e.g. for magnetron sputtering.

Goal of the experiments was to use high-voltage substrate bias ($U = 1-10$ kV, pulse width of 30 microseconds, $f = 100-1000$ Hz) assisted DC magnetron sputtering ($U=500-1000$ V, $I=0.5-2$ A) of graphite (flat target of 12 cm in diameter) for deposition of rather thick (up to 2-3 microns) hard a-C films with reduced intrinsic stress. The magnetron sputtering method was chosen because it could be easily up-scaled for coating of large-area substrates. Besides, it is possible to control ion-to-atom ratio via configuring of magnetic field of the magnetron. It was found that high-voltage substrate bias combined with balanced magnetron sputtering (ion-to-atom ratio is 0.2-0.3) is effective for deposition of medium hard (up to 15 GPa) fine-grained (10-20 nm) nanocrystalline carbon (nc-C) films. The films are low-stressed and have good tribological characteristics because of their mostly graphitic nature (sp³/sp² ~ 0.2-0.3), while their hardness is high enough due to strengthening via grain size reduction mechanism.

12:30

LUNCH

Session IX : Carbon-based coatings and thin films

Session chairs : P. Andreazza (University of Orleans, France)

S. Logothetidis (University of Thessaloniki, Greece)

K-IX.1 14:00

CHARACTERIZATION OF a-CN_x:H PARTICLES AND COATINGS PREPARED IN A CH₄/N₂ R.F. PLASMA

Jérémy Pereira(a), Isabelle Géraud-Grenier(a), Véronique Massereau-Guilbaud(a), André Plain(a), and Vincent Fernandez(b), (a)LASEP, Faculté des Sciences, Université d'Orléans, Site de Bourges, France, (b)LPCM, Institut des Matériaux Jean Rouxel, Nantes, France.

Polymer-like hydrogenated amorphous carbon nitride a-CN_x:H particles and coatings were synthesized in a CH₄/N₂ r.f. plasma with different CH₄/N₂ mixing ratios and various total pressures. Effects of nitrogen incorporation on microstructure, bonding states and chemical composition have been investigated.

Scanning electron microscopy reveals that the particles are spherical with diameters in the range 0.05 to 3 μm. For high nitrogen contents, particles with diameters up to 4 μm have been observed. The increase of the nitrogen ratio leads to modifications in the surface morphology of particles. With low nitrogen percentage, the particles present smooth surfaces whereas for high nitrogen percentage, the particles have an orange-type-peel surface texture with cracks.

Information about chemical bonding and elemental composition has been obtained from XPS and FTIR measurements.

Infrared results suggest the appearance of different bonds between carbon and nitrogen when nitrogen is introduced in the reactor. Four absorption bands associated with C-H, C=C, C=N and/or N-H (1300-1800 cm⁻¹), -C=N and -N=C (2000-2300 cm⁻¹), C-H (2800-3100 cm⁻¹) and N-H and/or O-H (3200-3600 cm⁻¹) bonds are observed [1]. The increase of the nitrogen content leads to an increase of the absorption band at 2200 cm⁻¹ that indicates the continuously increase of -C(N bonds. At the same time, the stretching band around 2800 cm⁻¹ decreases.

Combination between carbon and nitrogen is confirmed from XPS analyses. The nitrogen content in the particles as in the coatings increases monotonically with an increasing N₂ content up to 90 %. Whereas the nitrogen content seems to stay practically constant when the total pressure is increased from 0.7 torr to 2.7 torr. The asymmetry and the width of all the C1s and N1s peaks indicate the existence of different types of bonds in the samples.

[1]I. Géraud-Grenier, V. Massereau-Guilbaud and A. Plain, Surf. Coat. Technol., 187 (2004) 336-342.

K-IX.2 14:20

COMPOSITION, STRUCTURE AND NANOMECHANICAL PROPERTIES OF C-Si-N THIN FILMS DEPOSITED BY ION IMPLANTATION ASSISTED PLASMA BEAM CVD

A. Tóth, M. Mohai, T. Ujvári, and I. Bertóti, Institute of Materials and Environmental Chemistry, Chemical Research Center, Hungarian Academy of Sciences, Budapest, Hungary.

Si- and N-containing a-C:H films were deposited from tetramethyl-silane vapour onto silicon wafers by an electron-cyclotron wave resonance RF plasma beam CVD with simultaneous Ar⁺ and N₂⁺ ion bombardment in a plasma-immersion ion implantation apparatus. Chemical composition and bonding states of the constituent elements were characterised by X-ray photoelectron spectroscopy and X-ray induced Auger electron spectroscopy. Mechanical properties were estimated by using depth-sensing nano-indentation measurement.

Compared to the C/Si=4 ratio of the precursor, significant loss of C may occur during deposition. Silicon in this films is bonded predominantly to carbon, judged by the Si2p binding and Si(KLL) Auger kinetic energy and also by the modified Auger parameter of Si (αSi), which is calculated as the sum of the former two values. αSi increased with increasing C/Si. The αSi values also confirmed fairly homogeneous distribution of the constituent elements in the films, i.e. neither extended silicon clusters, nor crystalline silicon carbide was formed. At nitrogen incorporation Si-C bonds are replaced partially by Si-N bonds. Nanohardness increased with increasing C content. This is correlated with the increased three-dimensional compactness as indicated by higher αSi, reflecting enhancement of the extra-atomic electronic interaction among adjacent atoms in these films. Financial support by the National Scientific Research Fund (Project OTKA T-043359) is acknowledged.

AMORPHOUS SILICON CARBIDE COATINGS GROWN BY LOW FREQUENCY PACVD: STRUCTURAL AND MECHANICAL DESCRIPTION

A. Soum-Glaude(a), L. Thomas(a), R. Berjoan(a), and E. Tomasella(b), (a)CNRS – PROMES - Tecnosud, Perpignan, France, (b)CNRS-LMI, Aubière, France.

Hard coatings have received considerable attention for many mechanical applications. For such uses, diamondlike carbon films (DLC's) have been extensively developed during the last ten years. Due to their high hardness, low friction and low wear versus metals, they find application in aeronautics, space and high precision mechanics, but seem to be limited in use as their microstructure is strongly changed at high temperature. In recent years, the effect of doping DLC's with elements such as silicon (up to 30 at.%) has been studied as it should extend carbon films applications to high temperature environments (typically $T > 400$ °C).

In this work, hard silicon carbide based films (a-SiC:H), grown from the plasma decomposition of a unique precursor (tetramethylsilane = TMS) diluted in argon, are presented. Such coatings are obtained in a capacitively coupled low frequency (≈ 50 KHz, DC bias = -50 to -300 Volts) PACVD device at surface temperature lower than 850 K. The evolution of their microstructure, obtained by the use of Infrared spectroscopy (FTIR), X-ray Photoelectron Spectroscopy (XPS), EDS and RBS, is described in regard with the experimental parameters. Those parameters are chosen in order to check the effect of i) the surface reactivity through substrate temperature variations, ii) the nature of plasma reactive neutrals through gas residence time and TMS content, iii) the energy of ions impinging the growing film through surface DC bias.

An increase of the surface temperature during growth leads to an improvement of film crosslinking, as observed by EDS through Si/C ratio increase, and FTIR, through Si-C band absorption increase in regard to Si-H, C-H and Si-(CH₂)_n-Si ones. The effect of gas residence time in the reactor is more complex. Its increase leads, at the contrary, to a global reduction of bonded hydrogen and silicon contents (Si/C can vary from 1.6 to 0.6), and Si-C band absorption decrease to the benefit of Si-(CH₂)_n-Si environments. Such an effect is discussed in terms of plasma chemical species recombinations already observed by optical emission spectroscopy in microwave TMS plasmas. Concerning the ion bombardment, the energy of impinging ions during growth is of major importance as it can limit the films growth rate through selective sputtering/etching phenomena. As a matter of fact, a comparison between i) characterisations of films grown at various DC bias in Ar/TMS plasmas, ii) characterisations of films post-treated in pure argon plasma (no precursor), and iii) sputtering yields calculation (SRIM simulations), lead to the fact that an ion energy domain exists which limits silicon and C-Csp² contents to the benefit of C-Csp³ environments.

Finally, the hardness and Young modulus of films, determined by nanoindentation technique, are respectively ranging from 15 to 31 GPa, and, 130 to 225 GPa depending on the experimental parameters. By exploiting specifically the ion bombardment (control of C-Csp³ bonds with DC bias), hardness can be significantly improved from 20 GPa to 30 GPa in a DC bias domain ranging from -100 to -250 Volts. However, ion bombardment can give rise to high compressive stresses in the deposited thin films. Hardness is then representative of both the microstructure of the films and the intrinsic stress level. In order to confirm that the increase in C-Csp³ is directly responsible for this mechanical property improvement, a specific study of film stress evolution versus ion energy is presented.

MORPHOLOGICAL CHARACTERIZATION AND SCALING BEHAVIOUR OF WC COATINGS DEPOSITED BY HVOF THERMAL SPRAY

R. Buzio(a), A. Chierichetti(b), G. Bianchi(c), and U. Valbusa(d), (a)INFM-UdR Genova and Dipartimento di Fisica, Genova, Italy, (b)Flame Spray S.p.A, Roncello (MI), Italy, (c)Dresser Italia S.r.l., Voghera (PV), Italy, (d)INFM-UdR Genova and Dipartimento di Fisica, Genova, Italy.

We report experimental results on the morphological characterization of WC coatings deposited by High-Velocity-Oxygen-Fuel (HVOF) thermal spraying technique. Optical and atomic force microscopies have been used to characterize films microstructure from the millimetre down to the micrometer scale; surface roughness and correlation effects have been estimated as a function of films thickness. By applying scaling arguments, we have extracted quantitative information on the deposition process and assembling behaviour of deposited powders. Our predictions are compared with comprehensive theoretical models reported in literature.

K-IX.5 15:20

BORON CARBIDE FILMS BY PULSED LASER DEPOSITION: ULTRASHORT PULSES RESULT IN IMPROVED PROPERTIES

T. Csáki(a), T. Szörényi(b), F. Antoni(c), and E. Fogarassy(c), (a)Department of Optics and Quantum Electronics, University of Szeged, Hungary, (b)Research Group on Laser Physics of the Hungarian Academy of Sciences, University of Szeged, Hungary, (c)CNRS-PHASE, Strasbourg, France.

Pulsed laser deposition, PLD is a well established laboratory technique for pilot production of thin films of materials hard to handle with more conventional approaches. In this contribution growth characteristics and properties of boron carbide films, fabricated by ablating a sintered B₄C target in high vacuum with i) a traditional KrF excimer laser (248 nm, 23 ns, 10 Hz, max. 320 mJ/pulse) and ii) a high brightness hybrid dye/excimer laser system, emitting at the same wavelength, while delivering 700 fs pulses of max. 20 mJ energy at 2 Hz, are compared.

The ultrashort pulse processing is highly effective : energy densities between 0.25 and 2 Jcm⁻² result in apparent growth rates ranging from 0.017 to 0.085 nm/pulse. To the contrary, ablation with nanosecond pulses of one order of magnitude higher energy densities yields smaller growth rates: figures increasing from 0.002 to 0.016 nm/pulse have been derived within the 2-14 Jcm⁻² fluence window. Pulse shortening leads to significant improvement in surface morphology, as well. While droplets with number densities ranging from 1x10⁴ to 7x10⁴ mm⁻² deteriorate the surface of the films deposited by the traditional KrF excimer laser, sub-ps pulses produce practically droplet-free films. The absence of droplets has also a beneficial effect on the stoichiometry and homogeneity of the films fabricated by ultrashort pulses.

15:40

BREAK

Session X : Boron-based coatings and thin films

Session chairs : N.J.M. Carvalho (NV Bekaert SA, Zwevegem, Belgium)

M.-P. Delplancke (Université Libre de Bruxelles, Belgium)

K-X.1 16:00

PHASE FORMATION AND MICROSTRUCTURE OF BORON NITRIDE THIN LAYERS DEPOSITED USING Nd:YAG AND KrF LASERS

W. Mroz(a), R. Kosydar(b), B. Major(b), M. Jelinek(c), T. Kocourek(c), L.Nistor(d), and G. Van Tendeloo(e), (a)Institute of Optoelectronics MUT, Warsaw, Poland, (b)Institute of Metallurgy and Materials Science PAS, Cracow, Poland, (c)Institute of Physics, Academy of Science, Prague, Czech Republic, (d)National Institute for Materials Physics, Magurele, Ilfov, Romania, (e)EMAT University of Antwerp, Belgium.

Boron nitride (BN) thin coatings were produced by pulsed laser deposition from hexagonal BN target. Two types of laser i.e. Nd:YAG as well as KrF coupled with RF generator were used. Deposition by Nd:YAG laser on steel buffered with Ti substrates led to formation of nanocrystalline strongly textured h-BN layers. Substrate temperature or type of background gas did not influence on morphology and phase composition. KrF excimer laser was applied for preparation of nanocrystalline BN layers on Ti₆Al₄V or Ti₆Al₄V buffered with TiN substrates. BN coating deposited on TiN/Ti₆Al₄V consisted of nanometric sp³ phase crystallites together with sp² phase and amorphous BN matrix. Surface morphology of BN/Ti₆Al₄V depended on process parameters. Heating of substrate led to raise of thickness, roughness as well as diameter of crystallites. Slower growth rate favoured formation of larger and better shaped crystallites. Increase of gas pressure caused higher roughness and change of morphology.

K-X.2 16:20

INFLUENCE OF DEPOSITION PARAMETERS ON THE TEXTURE OF BORON NITRIDE THIN FILMS SYNTHESISED IN A MICROWAVE PLASMA ENHANCED CVD REACTOR

P. Thévenin(a), M. Eliaoui(a,b), A. Ahaitouf(b), A. Soltani(c), and A. Bath(a), (a)LMOPS-Supelec, Metz, France, (b)FST Fès-Saïs, University of Fès, Morocco, (c)IEMN, Villeneuve d'Ascq, France.

Thin films of boron nitride (BN) have been deposited at low temperature (300°C) by microwave plasma enhanced chemical vapor deposition (PECVD), using borane dimethylamine, as boron precursor. These BN layers are chemically stable at the atmosphere, and do not delaminate, and depending on the deposition conditions, we can synthesise the cubic or the hexagonal form. The h-BN films are shown to be nanocrystallised and textured, the c axis of the crystallites showing a preferential orientation around the normal of the sample. Infrared transmittance spectroscopy is used for the phase identification, and also to determine the c-axis orientation, thanks to additional absorption band attributed to the excitation of longitudinal optical (LO) modes. These bands can be observed only at oblique incidence according to the Berreman effect. The influence of the deposition conditions on the film's morphology have been studied, by varying independently the plasma power, the pressure and the precursor flux.

K-X.3 16:40

OPTICAL INVESTIGATIONS OF THE EFFECT OF TEMPERATURE AND PLASMA CONDITIONS ON THE GROWTH OF sp^3 -BONDED BN THIN FILMS

A. Laskarakis, S. Logothetidis, and S. Kassavetis, Aristotle University of Thessaloniki, Department of Physics, Thessaloniki, Greece.

Boron nitride (BN) films with high cubic (sp^3) content using various conditions were deposited on c-Si substrates by rf magnetron sputtering. Fourier Transform IR Spectroscopic Ellipsometry (FTIRSE) has been employed for the investigation of the effect of the substrate temperature (T_s) and gas partial pressure on the films bonding structure. A two layer optical model was applied for the analysis of the FTIRSE spectra leading to the determination of the individual layer thickness and optical properties, as a function of the deposition parameters in order to get better insights on the phase evolution and microstructure of the BN films. As a result, the critical experimental conditions required to sustain c-BN growth were determined. It was found that at higher T_s , the formation of c-BN is favored and followed by a significant reduction of the corresponding layer thickness as a combined effect of the reduction of the B atoms sticking coefficient, the preferential etching of the h-BN regions and the existence of thermal spikes in the growing BN films. Furthermore, the investigation of the effect of plasma parameters on BN phase evolution and c-BN optical properties showed that the addition of N atoms in the plasma promotes the growth of c-BN. These results have been supported and justified by the study of the mechanical behavior of the BN films by additional depth sensing Nanoindentation measurements.

K-X.4 17:00

HIGH RESOLUTION DEPTH PROFILING OF MECHANICAL PROPERTIES OF THICK CUBIC BORON NITRIDE COATINGS

C. Ziebert, J. Ye, K. Sell, and S. Ulrich, Forschungszentrum Karlsruhe, Institut für Materialforschung I, Karlsruhe, Germany.

The small angle cross section method (SACS), which has been developed on nanolaminated TiN/ZrN coatings [1], allows a depth profiling of mechanical properties on the nanometer scale. Within this method a cross-section of the sample under a very small angle of about 0.04 to 0.15° with a surface roughness in the lower nanometer range is prepared to enlarge the area to be investigated by nanoindentation. While the nanoindenter performs a linescan across this small angle cross section its travelled distance is translated into depth information by using a simple geometric formula.

The high resolution of the SACS will be demonstrated on nano-scale, multi-functional, superhard, thick cubic boron nitride coatings with low residual stresses. These coatings recently have been successfully deposited by r.f. magnetron sputtering using a tailored coating constitution and an innovative growth concept. This novel concept allowed $2\ \mu\text{m}$ thick c-BN to be grown on top of a coating system initiated by a B-rich base layer followed by a nucleation layer with gradient chemical composition. A small amount of oxygen was incorporated in the coatings to reduce the very high stress usually appearing in c-BN coatings. The SACS permitted a high resolution depth profiling to distinguish between the different layers used in this concept and to measure their different mechanical properties like hardness and elastic modulus as well as interface widths and revealed a maximum hardness of 59 GPa and an elastic modulus of 463 GPa of the thick c-BN top layer.

[1]S. Ulrich, C. Ziebert, M. Stüber, E. Nold, H. Holleck, M. Göken, E. Schweitzer, and P. Schloßmacher, Surf. Coat. Technol. 188-189 (2004) 331.

K-X.5 17:20

STRESS REDUCED NANOCOMPOSITE COATINGS CONSISTING OF CUBIC AND HEXAGONAL BORON NITRIDE

M. Lattemann(a), S. Ulrich(b), K. Sell(b), and J. Ye(b), (a)Linköping University, Linköping, Sweden, (b)Forschungszentrum, IMF I, Karlsruhe, Germany.

Cubic boron nitride (c-BN) thin films can be produced by PVD and PE-CVD techniques. The intensive ion bombardment which is obligatory for the phase formation leads to extreme compressive stress. To overcome this problem nanocomposite boron nitride coatings consisting of predominantly cubic as well as hexagonal phase have been successfully deposited by reactive r.f. magnetron sputtering at conditions close to the resputtering limit. The constitution of the films was characterized using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction/reflectivity (XRD/XRR) and high-resolution transmission electron microscopy (HRTEM). At low ion energies up to a substrate bias of $-150\ \text{V}$ pure sp^2 bonded BN was deposited. Higher ion energies led to a strong increase of the c-BN content as well as the compressive stress in the films reaching their maximum at $-300\ \text{V}$ substrate bias before decreasing again. Both the c-BN content and the residual stress showed qualitatively the same behaviour whereas the stress decrease is steeper near to the resputtering limit. HRTEM investigations of the films with the maximum densification deposited at a substrate bias of $-300\ \text{V}$ showed an h-BN interlayer growing on the Si substrate with the basal planes perpendicular to the substrate surface on which then almost pure c-BN was identified. The density of these coatings was $3.5\ \text{g cm}^{-3}$ and the residual stress was determined to $-29\ \text{GPa}$.

Boron nitride deposited at $-600\ \text{V}$ again comprised a hexagonal interlayer and a c-BN/h-BN nanocomposite on the top showing a lower density of $2.9\ \text{g cm}^{-3}$ and a significantly reduced residual stress of $-9\ \text{GPa}$. A further reduction of the residual stress can be achieved by a following heat treatment at 900°C for 2h resulting in a value of $-3\ \text{GPa}$.

K-X.6 17:40 SYNTHESIS AND CHARACTERIZATION OF Zr-B-N THIN FILMS DEPOSITED BY TRIODE SPUTTERING
A. Chala(a), C. Labidi(b), C. Nouveau(b), B. Angleraud(c), and M.A. Djouadi(c), (a)Département de Physique, Université de Biskra, Algérie, (b)Laboratoire Bourguignon des Matériaux et Procédés, ENSAM, Cluny, France, (c)Institut des Matériaux Jean Rouxel, Nantes, France.
Many attempts have been made by our group in order to improve the adhesion of cubic boron nitride (c-BN) films and thick films with a relatively good adhesion were obtained [1]. Nevertheless, this adhesion was not sufficient for wood cutting applications. The addition of a third element like zirconium can be a means for improving in a significant manner the adhesion of the coating without an important decrease of its hardness. So, the aim of the present study was to deposit ZrBN films by triode sputtering method. The composition of the coatings was determined by Energy Dispersive Spectrometry (EDS) microanalysis and SEM cross section observations were performed. To determine the structure of the layers, IR and XRD analysis were also done. The mechanical properties of the layers were determined by stress measurements. The influence of deposition parameters such as substrate bias and nitrogen content on the properties of the layers was studied.

K-X.7 18:00 PROPERTIES OF BORON CARBO- NITRIDE THIN FILMS OBTAINED BY RADIOFREQUENCY BEAM ASSISTED PULSED LASER DEPOSITION
F. Stokker-Cheregi(a), A. Dauscher(b), A. Moldovan(a), G. Dinescu(a), C. Ghica(c), L.C. Nistor(c), and M. Dinescu(a), (a)National Institute for Laser, Plasma and Radiation Physics, Magurele, Bucharest, Romania, (b)Laboratoire de Physique des Matériaux (LPM), Ecole des Mines de Nancy, France, (c)National Institute for Material Research, Bucharest, Romania.
Boron carbo- nitride (BCN) thin films have been deposited on different substrates (Sapphire, Corning Glass, MgO, Silicon) by alternative and sequential pulsed laser deposition, starting from C and hexagonal BN targets. During the deposition, the laser fluence (3-6 J/cm²), nitrogen pressure (10⁻⁶-10⁻¹ mbar) and laser wavelength (265 nm, 355 nm and 532 nm) were varied. The effect of the radiofrequency addition in nitrogen on the amount of N₂ incorporated in the layer was investigated. Substrate type and temperature influence on layers structure, composition, crystallinity and hardness was checked: the temperature range used was RT- 600 C. For characterization films were investigated by X-ray Diffraction (XRD), Atomic Force Microscopy (AFM), Fourier Transform Infrared Spectroscopy (FTIR), Secondary Ion Mass Spectroscopy (SIMS), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Selected Area Electron Diffraction (SAED), microhardness measurements, scratch tests.

18:20-20:00 **POSTER SESSION II**

POSTER SESSION II
Thursday, June 2, 2005
18:20 – 20:00

Structural characterization of coatings

- K/PII.01** INFLUENCE OF HYDROGENATED AMORPHOUS CARBON SUBSTRATES ON THE MORPHOLOGY OF DEPOSITED PARAFFIN THIN FILMS
M.E.R. Dotto, M. Ferreira, and S.S. Camargo Jr., COPPE, Universidade Federal do Rio de Janeiro, RJ Brazil.
Amorphous carbon films and related materials have a wide range of applications due to their outstanding properties including high hardness, chemical inertness, low surface energy and low roughness. Waxes are formed by long-chain hydrocarbons with chain lengths ranging from C15 to C75 that tend to crystallize and precipitate from solution at and below their cloud point. In this work we study the initial stages and the morphology of paraffin films deposited on different amorphous carbon-based substrates. Uncoated crystalline silicon (c-Si) substrates were also used as a comparison. Varying the amorphous carbon substrate composition the substrate surface energy could be varied in the range of 30 - 45 mN/m as determined by contact angle measurements obtained by the sessile drop technique. Paraffin films were grown in a heptane-saturated environment by casting of paraffin-containing heptane solutions. Optical micrographs show the influence of the substrate in the morphology of paraffin deposits or agglomerates. Paraffin films deposited on high surface energy substrates such as c-Si show great agglomerate concentration, decreasing for the low surface energy a-C:H or a-C:F substrates. AFM images show that films grow by the layer-plus-island (or SK) mode, which is related to the three different kinds of crystal formation: monomolecular plates, ultra-thin spiral crystals and larger, thicker crystals. The typical growth morphology of paraffin crystals is spiral corresponding orthorhombic space group, Pca21. Step spacings between the spiral patterns ranging from 0.5 microm to 1 microm and the height of spiral steps and monomolecular layer of paraffin is around 5.5 +/- 0.8 nm. Crossing steps were observed due to the very small height of the steps.
- K/PII.02** PASSIVATION OF Al-SURFACES AGAINST OXIDATION BY MONOATOMIC Sn WETTING LAYERS
B. Schwarz(a), C. Eisenmenger-Sittner(a), E. Klein(a), C. Tomastik(b), K. Mayerhofer(c), P.B. Barna(d), A. Kovac(d), (a)Vienna University of Technology, Institute of Solid State Physics, Wien, Austria, (b)Vienna University of Technology, Institute of General Physics, Wien, Austria, (c)Vienna University of Technology, Institute of Chem. Technol and Analytics, Wien, Austria, (d)Research Institute for Technical Physics and Material Science, Budapest, Hungary.
Tin (Sn) forms monoatomic wetting layers on Aluminium (Al) interfaces under Ultra High Vacuum (UHV) conditions. The wetting layer spreads over the Al-vacuum interface or over Al-grain boundaries via the emergence of Sn atoms from Sn-islands. The islands can be generated by sputter-deposition of a 10 nm thick Sn film on a polycrystalline Al-underlayer. If the Al-Sn bilayer is covered by a Al-capping layer, Sn will penetrate the capping layer along the grain boundaries and form a wetting layer on its surface. Al-surfaces covered by the Sn-wetting layer exposed to oxygen (O) are oxidized significantly slower than bare Al surfaces. The shape of the adsorption isotherms suggests that the oxidation process involves the formation of oxygen nuclei.
Depositing the Al-capping layer in the presence of O leads to a striking effect in the optical appearance and the chemical composition of the capping layer: Light microscopy shows that in the vicinity of Sn-islands the capping layer has a shiny metallic appearance while the residual areas have a dark colour. By scanning Secondary Ion Mass Spectroscopy (SIMS) and Transmission Electron Microscopy (TEM) it could be shown that the dark regions contain significantly more oxygen. This effect can be attributed to the suppression of Al-oxidation during the growth of the Al-capping layer by the presence of Sn in the vicinity of the Sn-islands.
This work is supported by the Austrian Science Fund (FWF) under grant Nr. P-15739.
- K/PII.03** MICROSTRUCTURE AND SURFACE MORPHOLOGY OF YSZ THIN FILMS DEPOSITED BY E-BEAM TECHNIQUE
G.Laukaitis(a), J. Dudonis(a), A. Galdikas(a), R. Cerapaitė-Trusinskienė(a), and D. Milcius(b), (a)Physics Department, Kaunas University of Technology, Kaunas, Lithuania, (b)Lithuania Energy Institute, Kaunas, Lithuania.
In the present study yttrium stabilized zirconia (YSZ) thin films were deposited on the alloy-600 and optical quartz substrates using e-beam deposition technique controlling deposition parameters: substrate temperature and electron gun power influencing the thin film deposition mechanism. The dependence of these parameters on thin film structure and surface morphology were investigated by X-ray diffraction, scanning electron microscopy (SEM), and atomic force microscopy (AFM). It was found that electron gun power has influence on the crystallite size, texture, and roughness of YSZ films. YSZ thin film formation and evolution of surface roughness were analyzed for clarification of the experimental results by the proposed kinetic model. The model was based on rate equations and includes film deposition by single atoms as well as deposition by clusters going on simultaneously during e-beam evaporation of powder target. Obtained theoretical results are in a good agreement with experimental ones and explain elementary steps of film growth by using e-beam technique.

K/PII.04 METALLIZATION OF POLY(ETHYLENE TEREPHTHALATE) IN THE WIDE RANGE SUBSTRATE TEMPERATURES

B. Cyziute(a), S. Tamulevicius(b,a), P. Goudeau(c), M. Andrulevicius(b), and A. Guobiene(b), (a)Department of Physics, Kaunas University of Technology, Kaunas, Lithuania, (b)Physical Electronics Institute of Kaunas University of Technology, Kaunas, Lithuania, (c)Laboratory of Physical Metallurgy, University of Poitiers, Futuroscope, France.

Poly(ethylene terephthalate) (PET) is widely used biocompatible polymer materials. It possesses many excellent properties such as mechanical strength, chemical stability, etc. Metallization of PET can result in improved polymer surface properties, including enhanced resistance to gas diffusion wear, conductivity and appearance. Metallic films on polymers also have wide range of applications in the field of MEMS, sensors and especially in the field of optical devices such as diffractive optical elements.

In this work we present structural, compositional analysis of silver layers on PET and relation between the stress level and technology conditions. The silver thin films (1 μ m thickness) were deposited on PET (25 μ m thickness) by electron beam evaporation in vacuum at different substrate temperatures (20°C, 40°C, 80°C, 120°C). The influence of metal coverage on interface composition, structure, morphology, and particle size of Al/PET films has been studied employing XPS, AFM and X-ray diffraction. The size of the crystal grain was obtained from the peak width of X-ray diffraction using the two major models known and employed in bulk materials: the integral breadth and the Warren-Averbach methods. The classical $\sin^2\psi$ method of X-ray diffraction was used to measure the residual stresses in fine grained polycrystalline materials. Differences between the properties of thin films formed at elevated temperatures and PET glass transition temperatures are found and are explained on terms of mass transfer and interface formation.

K/PII.05 STRUCTURAL STUDY OF EB-PVD ZrO₂ THIN FILMS FOR THERMAL BARRIER COATING APPLICATIONS

I. Muñoz-Ochando, M. Vila, and C. Prieto, Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, Cantoblanco, Madrid, Spain.

Thermal Barriers Coatings (TBC) are usually used to insulate turbine gas components because of the fact that its low thermal conductivity coefficient. Coatings are generally composed by a ZrO₂ ceramic film on a metallic bond layer, which are deposited over a superalloy substrate.

In order to optimize the preparation parameters and to study the effects of the ceramic film crystalline characteristics on the thermal conductivity we have prepared ZrO₂ thin films on top of NiCoCrAlY bond layer over Si (100) wafers. In this work, we present a study of the crystalline properties of ZrO₂ thin films prepared by two different methods (radio frequency magnetron sputtering and electron beam physical vapour deposited (EB-PVD)) over a NiCoCrAlY bond layer prepared by EB-PVD. ZrO₂ crystalline structure and grain size were characterized by X-ray diffraction. Results show tetragonal stabilized phases of zirconium oxide independently of the addition Ytria in the target material. Additionally, the grain size behaviour and microstructure characterization will be studied as a function of the sample growing rate.

K/PII.06 X-RAY DIFFRACTION AND RAMAN SPECTROSCOPY ANALYSIS OF ZrO₂ THIN FILMS DOPED WITH Gd₂O₃ AND Y₂O₃

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ZrO₂ is the most used material as coating for mechanical applications at high temperature. However, it needs to maintain at room temperature the high temperature phases in order to have the better performance. In this work we produced thin films of ZrO₂ doped with Gd₂O₃ and co-doped with Y₂O₃ and Gd₂O₃ by reactive magnetron sputtering with the aim to stabilize the zirconia.

This paper discusses the structure and phase analysis of the deposited thin films by X-Ray Diffraction and Raman Spectroscopy in as-sputtered condition considering the deposition parameters and also after annealing at 1000°C. The composition of the ZrO₂Gd₂O₃ thin films ranges from 2.1 to 17.5 mol % of Gd₂O₃. The transition from the tetragonal to the cubic phase was clearly observed in the range of 5 to 6.5 mol % of dopant. These films present a preferred orientation for the <200> direction of the both tetragonal and cubic phases. The average grain size is almost constant for the different dopant percentage and increases after annealing.

Adhesion of coatings

K/PII.07 THE INFLUENCE OF ARGON AND NITROGEN RF PLASMA PRE-TREATMENT ON THE ADHESION STRENGTH OF PVD COPPER COATINGS

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A new approach to tailor the interface in the copper-carbon system is based on a systematic analysis of the influence of a plasma pre-treated carbon substrate in order to enhance the adhesion strength of a subsequent deposited copper coating. A Cu coating on a flat carbon substrate acts as a simplified model system to identify suitable plasma parameters. The knowledge of suitable pre-treatment conditions of carbon surfaces is later on of interest for the production of copper carbon composites.

Plasma pre-treatment is a common used method in vacuum deposition techniques to clean or to modify the surface of a substrate prior to the deposition in order to improve the adhesion of the film or to modify the microstructure of the coating. In this work argon and nitrogen plasma is used to modify the adhesion strength of a copper film on a carbon substrate. For the characterisation of the surface topography of the plasma modified carbon substrate Atomic Force Microscopy (AFM) is used. By means of a pull-off test it is shown that there is a significant influence of the pre-treatment on the adhesion strength of the copper coating.

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K/PII.08**SCRATCH TEST AND MULTILAYER POLYMERIC COATINGS**

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Gloss painted steel sheet are made of several different layers. The designing and the characterization of such high technology products are difficult to take into custody. They are manufactured by the combination of bulk layers and thin pigmented or/and added films that are painted, extruded or glued on steel sheet. The multiplicity of materials, components and manufacturing processes is similar to the multiplicity of their specifications, often difficult to define and evaluate.

Among them, the scratch ability demands a particular attention because of the numerous inherent properties implied (adherence, hardness, elasticity, visco-elasticity, cohesion, etc.). Some descriptions (scratch morphology) combined with 3D and 2D topographical assessments methodologies have been developed and put into practice on a wide range of industrial products made of several organic layers. Some singular mechanical responses have been noticed (cyclical slips and unsticking, degradation modes, etc.), sometimes valued, allowing us to improve our knowledge and expertise of the interactions materials - properties / process.

K/PII.09**CONTRIBUTION TO THE STUDY OF REACTION BETWEEN HARD COATINGS OF TITANIUM AND STEEL SUBSTRATES**

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In this work we have studied the influence of the heat treatment and Ar⁺ ionic bombardment on the chemical composition at the interface as well as the adhesion and the hardness, caused by the reaction between steel substrates and titanium thin solid films deposited by the magnetron sputtering. For the chemical composition study, x-ray diffraction and Auger electron spectroscopy were used. For the morphological study and hardness measurements, a scanning electronic microscopy and Vickers microhardness tester were used. Under the heat treatment effect the reaction between substrate and titanium films leads to the formation and growth of titanium carbide (TiC), also we notice their effect on the hardness which increases from 450.23 to 3529.3 Kg/mm² and decreases again between 950 and 1000°C. The ionic bombardment of substrate before deposition have an important influence on the adhesion of thin films to the substrates.

K/PII.10**ELECTROCHEMICAL PREPARATION OF HAp/ZrO₂ COATINGS ON TITANIUM FOR BIOMEDICAL APPLICATIONS**

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Providing titanium metal with bioactive coating, fixing implants to the bone, and reducing the metal ion release are the most significant factors in order to obtain satisfactory clinical outcome in applications such as dental implant and total hip replacement. The composition of hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂, HAp) is similar to bone, enamel and dentine, it can induce bone in-growth and future formation of chemical bonding to achieve the fixed function. However, the weak adhesion between HAp and metal substrates is the major problem in the applications. In this study, a novel method of electrolytic HAp/ZrO₂ double layers coatings on biomedical Ti was conducted to improve the adhesion, corrosion resistance, and osteoconduction. The surface morphology, crystal structures, and cell proliferation of the coated specimen were also characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), electrochemical polarization test and osteoblast-like culture, respectively.

K/PII.11**EVALUATION OF ADHESION OF TANTALUM OXYNITRIDE THIN FILMS DEPOSITED BY REACTIVE MAGNETRON SPUTTERING ONTO STEEL SUBSTRATE**

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Ta-O-N coatings were deposited on stainless steel by DC reactive magnetron sputtering from a Ta target in O₂-N₂-Ar atmosphere. The O₂/N₂ ratio in the plasma was varied between 0.08 and 1.33. The depositions were performed without substrate heating.

The O/N ratio in the films varied between 0.07 and 25.56. All films are poorly crystallized, and disorder becomes even more pronounced with increasing O/N ratio. Mechanical properties (hardness, Young modulus), adhesion to the substrate and wear resistance of the Ta-O-N coatings were studied. Regarding these properties three groups of films can be distinguished: 1) nitride - like, with low (0.07-0.23) O/N ratio; 2) films with intermediate (0.44-3.99) O/N ratio; and 3) oxide - like, with high (13.67 - 25.56) O/N ratio. The hardness decreases with increasing O/N in the films from 27GPa for O/N=0.07 to 6GPa for O/N=25.56, fluctuating around 12GPa for the films with intermediate O/N. The adhesion of the coatings to the substrate was evaluated from the critical loads (L_c) from scratch tests. First cohesive failure (forward or backward crack) occurs at L_{c1}=1-3N for the films with low and intermediate O/N. At higher loads, films with low O/N fail by discontinuous perforation or interfacial cohesive spallation. Films with intermediate O/N undergo a gross interfacial shell-shaped spallation at L_{c2}=2-3N, and a continuous ductile perforation at L_{c3}=22-26N. The films with high O/N ratio show poor adhesion to the steel substrate: L_{c1}=2.5N is attributed to a large area interfacial spallation. The tribological behaviour of the coated samples against 100Cr6 steel in pin-on-disc tests will be discussed with respect to wear resistance and friction coefficients.

K/PII.12**ELABORATION OF ZINC OXIDE COATING ON PEN : EVALUATION OF ADHESION**

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Zinc oxide coatings were deposited on polyethylene naphthalate (PEN) films by r.f. magnetron sputtering. The PEN surface was subjected to various plasma treatments before the deposition of the thin ceramic layer. The influence of these treatments on the polymer surface was examined by wettability measurements.

The influence of the sputtering parameters (oxygen partial pressure, r.f. power, total pressure) on the composition, the structural and optical properties of zinc oxide films was studied. The O/Zn atomic ratio was found to increase with oxygen and total pressures and to decrease when a high r.f. power is applied to the target. X-ray diffraction patterns show that the zinc oxide films are crystallised in the würtzite form. The films deposited at low oxygen partial pressures have a preferred orientation along the (002) direction while those elaborated at high oxygen partial pressures have a random orientation and are almost amorphous. The crystallinity was high when an intermediate total pressure is used. Scanning electron microscopy (SEM) studies showed a good agreement with the Thornton's structure zone model. A progression from a columnar structure to a dense one was observed when the kinetic energy of the sputtered particles increases. The adhesion strength of zinc oxide coatings on virgin and CO₂ plasma treated PEN films was found to vary in a wide range with the deposition conditions and an optimisation of the sputtering parameters was performed.

K/PII.13**TiN/ZrN NANO-HETEROSTRUCTURE DEPOSITION AND CHARACTERIZATION**

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Heterostructures containing from several to tens alternative TiN/ZrN layers with thickness in the nanometer range/layer have been deposited by cathodic arc, magnetron sputtering and pulsed laser deposition on plain carbon steel, stainless steel, high-speed steel, cemented carbide and double phase polished quartz substrates. All nano-heterostructures were characterized by X-ray Diffraction (XRD), Atomic Force Microscopy (AFM), Secondary Ion Mass Spectroscopy (SIMS), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Selected Area Electron Diffraction (SAED) and depth profiling Auger Electron Spectroscopy (AES), microhardness measurements and scratch tests. A comparison between the hardness and adhesion properties of films obtained by the three different methods was done for a wide range of experimental growth conditions.

Mechanical properties of coatings**K/PII.14****REACTIVE RADIO-FREQUENCY SPUTTERING DEPOSITION OF TITANIUM NITRIDE ON SILICON AND STEEL**

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Titanium nitride (TiN) is used as coating on cutting tools because of their excellent mechanical properties of this material such as high hardness and high wear resistance. Its chemical inertness gives rise to its application as corrosion protective coating. It's an excellent barrier material with good electrical conductivity in various metallization structures of advanced microelectronic devices. Finally, the golden glance of TiN established its use as decorative coating in the fashion jewellery and in architecture [1].

Usually, TiN films are produced by chemical vapour deposition (CVD) [2]. However, these methods require high temperature (>600°C) substrates to achieve the deposition, which sometimes causes thermal damage to the deposited films. So, different physical vapour deposition (PVD) [2-4] processes for titanium nitride at low temperatures have been used through the years. In general, these processes are based on sputtering of solid TiN target in argon atmosphere, or on reactive sputtering of titanium target in nitrogen atmosphere.

The deposition process studied, in this work, use RF sputtering of a pure titanium target in a reactive nitrogen/argon gas mixture, at various conditions. The substrates are silicon and steel. The main variables investigated are the composition of the Ar/N₂ gas mixture, the total pressure, the deposition time and the discharge power. The aim of this work is to evaluate the performances of a local-made RF plasma reactor. The attention was given to the study of the structure, the composition of titanium nitride deposits, which have a considerable influence on their hardness. The deposited coatings were characterized by X-ray diffraction, Rutherford backscattering (RBS), energy dispersive spectroscopy (EDS) and micro-indentation.

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K/PII.15**INFLUENCE OF ION ENERGY ON PROPERTIES OF Mg ALLOY THIN FILMS FORMED BY ION BEAM SPUTTER DEPOSITION**

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Magnesium and its alloys could meet the claims of light weight constructions in transportation. But, one important reason limiting the use of magnesium in wider fields of application is its poor corrosion behaviour. New approaches in alloy development promising improvements include both amorphous materials and very fine-grained alloys. One possible route to obtain amorphous or fine grained material is thin film deposition, from which ion beam sputter deposition offers very high cooling rates.

An RF ion source operated with Ar is used to produce magnesium alloy coatings of AM 50, AZ 91, and AE 42 alloys on silicon substrates at a beam energy between 800 and 1200 eV. With increased ion energy, an increase in the deposition rate, albeit with additional influences of the alloy composition was found. At the same time, a decreased content of Al and the other major constituents was found, indicating a preferential sputtering during the deposition process. Surface roughness using AFM and microhardness measurements also indicate an influence of the ion energy. These results are correlated with XRD and corrosion data.

K/PII.16**MECHANICAL PROPERTIES OF Cr₂O₃ COATINGS SYNTHESIZED BY LASER ABLATION**

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Dichromium trioxide (Cr₂O₃) is the most stable phase of chromium oxide and, in thin film form, this material has been shown to have very attractive mechanical properties such as high hardness and low friction coefficient. Cr₂O₃ coatings, applied to tape and digital magnetic recording heads, have considerably improved wear resistance and reduced head corrosion and damage due to electrostatic discharge. This work is devoted to the analysis of the mechanical properties of Cr₂O₃ coatings synthesized by KrF excimer laser ablation of a pure Cr₂O₃ target in oxygen ambient. The coatings were grown on Silicon (100) substrates at temperatures ranging from 20 to 950 °C and laser energy between 200 and 450 mJ. The hardness and elastic modulus of the films were determined by nanoindentation while the crystalline structure and composition were studied by Grazing Incidence X-ray Diffraction (GIXRD) and Rutherford Backscattering (RBS). All the films were found to have a Cr/O elemental ratio of 2/3 but the GIXRD analysis indicates that a significant improvement in the crystalline quality of the films is observed at temperatures above 600 °C. Deposition temperature has also a dominant effect in determining the mechanical properties of the films. Indeed, films deposited at temperatures ranging between 25 and 700 °C have hardness and elastic modulus values of about 20 and 220 GPa, respectively. At higher temperatures, and despite the enhanced crystallinity in the layers, the hardness falls off rapidly to a value of 9 GPa while the elastic modulus reaches 180 GPa. The observed deterioration of the mechanical properties at high deposition temperatures could result from an interdiffusion between the Si substrate and the Cr atoms, as deduced from the RBS analysis.

K/PII.17**SURFACE PREPARATION OF ALUMINIUM ALLOYS IN ORDER TO IMPROVE THE MECHANICAL PROPERTIES OF STRUCTURAL ADHESIVES**

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Adhesive bonding is an alternative way to traditional methods and has been subject of interest in the aerospace industry. Surface treatment is critical in joint preparation as it affects joint's strength and durability. Chemical and electrochemical treatments were standardised in the past years and are industrially used. The most common chemical treatment was the FPL Etch based on chromic acid and/or chromate solutions. Environmental restrictions limited the use of chromic solutions. An alternative, recently proposed, is the electrochemical anodization in phosphoric acid solutions. In this work the aluminum surfaces were anodized in phosphoric acid solutions and the influence of the main electrochemical parameters on joint's performance is presented.

AA 2024-T3 and 99.99% pure aluminum were used. Before the electrochemical treatments, the samples were degreased by dichloromethane, abraded to provide the mechanical interlocking and chemically etched using a chromate-free, sulphuric acid- ferric sulphate based treatment. Then the adherends were anodized in phosphoric acid solutions. Various voltages have been applied between 10-140 V at constant anodizing time. At the voltage showing the best result, time was changed from 20 to 60 min. The adhesives used were FM350 and FM300K kindly supplied by Cytec (Wilton, UK). The adhesion was made through thermal curing in oven or in autoclave up to 175 °C. The joints were tested via lap-shear and t-peel tests and results related to surfaces morphology by means of SEM analysis. Mechanical tests indicate an improvement of the joint performances increasing the applied voltage up to 120 V, while no significant effect of anodizing time has been evidenced.

K/PII.18**THE EFFECT OF STRUCTURE ON MECHANICAL PROPERTIES OF TiB₂-W₂B₅ NANOCRYSTALLINE COATINGS**

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The effect of the structure on the nanohardness and elastic modulus of nanocrystalline TiB₂-W₂B₅ coatings has been studied. It was found that the presence of nonequilibrium borders of grains decreases the elastic modulus, while the relatively high hardness is maintained. Characteristic values of the hardness and elastic modulus of the hexagonal (Ti, W)B₂ phase having an average crystallite size of 50 nm and the titanium-tungsten ratio of 3:7 are respectively 38 GPa and 390 GPa. An increase of the specific contribution of grain boundaries with decreasing crystallite size to 10-20 nm and the formation of the orthorhombic and cubic (Ti, W)B phases decrease the elastic modulus to 160-200 GPa and the hardness to 16-22 GPa. Our findings as to the variations of the hardness and elastic modulus of the TiB₂-W₂B₅ composition coatings can be used in designing highly wear-resistant ceramic friction pairs.

K/PII.19**THE MECHANICAL PROPERTIES OF PECVD a-SiC:H FILMS PREPARED FROM METHYLTRICHLOROSILANE**

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Amorphous hydrogenated silicon carbide (a-SiC:H) thin films were deposited by means of PECVD apparatus from methyltrichlorosilane (MTCS) onto Si (100) substrates varying deposition temperatures (TS, from 200 to 600 °C) and substrate bias (UD, from 0 to -150 V). An increase in TS leads to enhancing both the nanohardness (H) and elastic modulus (E). The values of H and E reach as high as 19 and 200 GPa, respectively, at TS= 600 °C. The infrared spectra of the films point to increasing the Si-C bond density and weakening the Si-H and C-H bonds in the high temperature films, although the noticeable trace of the C-H fragments was detected. An increase in UD results in reducing the nanohardness and elastic modulus of a-SiC:H films. The preliminary results of Auger measurements shows that the silicon content in the films increase with the substrate bias. So, the noticed film hardening is related to the high carbon content in the films deposited at low UD. The films were found to exhibit high abrasive wear resistance. In particular, it follows from the plane-on-ball tests carried out in the presence of diamond paste that the wear coefficient of the silicon wafers covered with a-SiC:H coatings is lower several times than that of the clean substrates. So, taking into account the comparatively high wear resistance and mechanical properties of the MTCS based PECVD films, one can recommend them for tribological application.

K/PII.20 NANOINDENTATION HARDNESS AND STRUCTURE OF ION BEAM SPUTTERED TiN/W MULTILAYER HARD COATINGS

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Mechanical behavior and stability of thin film structures consisting of alternating layers with thickness in the nanometer range has been the subject of great research activity over the past decade due to the technological impact of such nanoscale systems, but also to understand the plastic mechanisms operating at small-scales. Significant enhancement of hardness and tensile strength as compared to the rule of mixture values for their bulk phase counterparts have been reported in a large variety of systems. These include the case of isostructural, miscible metal/metal or nitride/nitride multilayers, but also non-isostructural and immiscible metal/nitride systems, such as Mo/NbN, W/NbN or W/ZrN. For the last two systems, epitaxial growth has been obtained due to the relatively small lattice mismatch (2%).

The present study reports on the structure and mechanical properties of TiN/W multilayers, whose lattice mismatch is large (5.4%). The coatings (0.2 microns thick) were deposited at room temperature using a dual-target ion beam sputtering in Ar-N₂ mixtures, on Si wafers and MgO(001) substrates. The bilayer period was varied between 3 and 50 nm. X-ray diffraction and X-ray Reflectivity were used to characterize the microstructure, state of stress and interfacial roughness. Mechanical properties of the multilayer coatings were studied by nanoindentation using a Berkovich tip, with a maximum load of 2 mN. Additional tests with loads at 50 mN were performed to study the coating/substrate adhesion

K/PII.21 PROPERTIES OF NbSi_yN_x THIN FILMS DEPOSITED BY DC REACTIVE MAGNETRON SPUTTERING

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Thin films of NbSi_yN_x have been deposited using two confocal targets: Nb and Si, in Ar+N₂ atmosphere. Total pressure, substrate temperature and current on the Nb target were kept constant. In order to obtain NbSi_yN_x thin films with various Si concentrations (CSi) the current on the Si target was varied. XPS and FTIR studies show the presence of Si-N bond in the NbSi_yN_x thin films. Thin films with CSi ≤ 16 at.% crystallize in a fcc structure, whereas pure NbN film are a mixture of fcc and hexagonal phases. For CSi ≤ 16 at.%, the films exhibit a pronounced columnar structure. At CSi = 20 at.% the columns are separated by wide amorphous regions rich in Si. For CSi ≥ 24 at.% the films are quasi-amorphous. The observed columns are an aggregate of NbN crystallites, whereas the amorphous region is the SiN_x phase. For CSi up to 5 at.%, the hardness increases with increasing the Si content. A hardness plateau was observed for 5 at.% < CSi < 13 at.%. Further CSi increase leads to hardness decrease. Residual stress, determined by deflection method, is compressive for every film. The variation of the stress with CSi can explain the variation of the hardness. After heat treatment in N₂ at 600°C, no significant changes were found in both hardness and stress of the films with 2at.% < CSi. NbSi_yN_x thin films for 5at.% < CSi < 13 at.% appear to be suitable protective coatings. They are hard and resist well to oxidation.

K/PII.22 MORPHOLOGICAL, STRUCTURAL AND MECHANICAL PROPERTIES OF NbN THIN FILMS DEPOSITED BY REACTIVE MAGNETRON SPUTTERING

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Hexagonal β-Nb₂N, cubic δ-NbN and hexagonal δ-NbN films were deposited by reactive magnetron sputtering from a Nb metal target in Ar+N₂ atmosphere at various nitrogen partial pressures (PN₂) and substrate temperatures (Ts). Structural and mechanical properties of these films were investigated by X-ray diffraction, Electron Probe Microanalysis, Transmission Electron Microscopy (TEM), Rutherford Backscattering Spectroscopy, residual stress and nano-indentation measurements. TEM studies reveal that the films have a columnar morphology. The hardness of the films depends on the film phase: the hardness reaches 35 GPa and 40 GPa for hexagonal β and δ phases respectively, and 25 GPa for the cubic δ phase. The δ phase films show a compressive residual stress of about 3.5 GPa, whereas no residual stress can be measured in δ and β phase films. No significant changes of the residual stress values are observed after annealing at 600 °C in nitrogen atmosphere. The relative density (compared with the bulk value) of films depends on the film phase: 0.8 for δ, 0.86 for δ and 0.96 for β. It is remarkable that the hardness of the hexagonal δ phase films is significantly higher than the hardness of the fcc phase films, in contrast with generally accepted morphological trends.

K/PII.23 RESIDUAL STRESS CONTROL IN MoCr THIN FILMS BY IONISED MAGNETRON SPUTTERING

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This study reports on the MoCr intrinsic stress control by ionised magnetron sputtering using a secondary plasma created through a radio-frequency (13.56MHz) antenna [1,2]. The elastic and refractory MoCr alloy has been chosen for its good mechanical and electrical properties for applications as micro-springs interconnects in microtechnologies [3].

The efficiency of the additional antenna has been investigated by optical emission spectroscopy, for Cu and MoCr targets. It appears that in both cases the ionisation rate increases significantly compared to a classical magnetron sputtering. Moreover, by controlling the substrate bias, the RF power on the antenna or the discharge gas pressure (argon), the ion energy and flux can be strongly modified. Therefore, we have the ability to act on film composition, growth rate, microstructure and residual stress of the deposited film. Indeed, the films exhibit residual stresses varying from compressive values (-3.4 GPa) to tensile ones (1.7 GPa). These results enable us to elaborate stress-engineered micro-objects such as micro-springs.

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K/PII.24 MICRO AND NANOSTRUCTURES FOR BIOLOGICAL ANALYSIS, BASED ON AMORPHOUS THIN-FILMS GROWN BY PLASMA TECHNIQUES

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This research is focused on the realization of micro and nano-structures, based on amorphous materials grown by plasma assisted techniques, to be used in the fabrication of advanced devices and sensors for genomics, post-genomics and proteomics analysis. Alloys based on carbon, silicon and titanium were deposited by means of Physical Vapor Deposition (PVD), Chemical Vapor Deposition (CVD) and Plasma Enhanced Chemical Vapor Deposition (PECVD) and were implemented in miniaturized cantilever microbalances.

The deposited films were characterized with respect to their surface morphology by Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and profilometry. The chemical composition was analyzed by means of Electron Probe Microanalysis and the mechanical properties were analysed together with the interaction with biological structures. Cantilever structures were realized by MEMS techniques. Vibrational properties such as stiffness and oscillation eigenmodes as well as static mode bending were characterized for free cantilever or for cantilever interacting with biological materials. Also simulations of structures behavior have been carried out by means of finite difference analysis for design purpose. Aim of the research activity is to develop microgravimetric technologies employing cantilevers in order to build MEMS/NEMS-based arrays of microbalances ("cantarray") by means of different plasma processes that allow reaching the sensitivity sufficient to detect and identify of nucleic acid molecules. This sensor technology, to be developed as nano-balances with integrated readout, holds great promises as a fast and cheap 'point of care' device (avoiding polymerase chain reaction- PCR) as well as a powerful research tool.

K/PII.25 MICROINDENTATION DEPTH PROFILING OF SELECTED PVD HARD COATINGS

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A comparative analysis of microindentation results is presented on selected commercially available as well as experimental PVD hard coatings. Using a Fischerscope H100C device the load between 1 mN and 1000 mN was applied. The discussed quantities included the Vickers and Martens hardness, indentation modulus and the elastic/plastic energies. Depth profiling was done in three ways: indirectly by applying progressively increasing loads, low-load measurements on a low-angle cross-section and low-load measurements on perpendicular cross-section (for thick films only). Various nitride- and carbide-based coatings were analysed, both single-layer, gradient and multilayer. The influence of substrate pre-treatment such as nitriding was also considered. It is shown that low-angle cross section is a simple yet efficient way of depth profiling.

Plasma nitriding of surfaces

K/PII.26 ACTIVATED GAS NITRIDING OF 17 – 4PH STAINLESS STEEL

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Results of the investigation of nitrided precipitation hardened steel 17-4 PH surface have been presented. The layers have been created in the process of gas nitriding in a partly dissociated ammonia. Hydrogen chloride admixture to ammonia was used as a steel surface activator. The influence of the steel heat treatment before nitriding on the diffusive process has been considered. 17 - 4PH stainless steel was nitrided at various stages of steel heat treatment, i.e. in supersaturated or precipitation hardened state. The nitrated layers were studied by scanning and transmission electron microscopy, X-ray microanalysis (EDX and WDX), and X-ray diffraction. Hardness of the generated layers reached 1300 HV. The optimum temperature range of the thermo-chemical treatment was determined. The influence of precipitation processes taking place during the heat treatment before nitriding on diffusive process kinetics, surface geometry and created layer properties was proved. The tests results showed, that nitrated layers thickness is bigger on a base of the 17 - 4PH stainless steel in pre-cipitation hardened, than in supersaturated state. Also increase of steel ageing temperature before nitriding effects on an increase of the nitriding process intensity. There were observed differences of surface morphology, thickness, phase composition and nitrogen concentration of the diffusion layers created at the same nitriding conditions, but various conditions of 17 - 4PH steel heat treatment before nitriding.

K/PII.27 INFLUENCE OF ANNEALING CONDITIONS ON ION NITRIDING OF MARTENSITIC STAINLESS STEEL

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Lattice expansion in austenitic stainless steels after nitrogen insertion in the temperature range between 350 and 380 °C is a well established phenomena whereas conflicting data on the existence of an expanded martensitic phase is published. However, inferring the structure from X-ray diffraction data alone can be misleading as the distinction between a martensitic structure obtained after rapid quenching and a ferrite/cementite mixture after additional annealing is not straightforward.

In this presentation, the results of ion nitriding at elevated temperatures are reported for the steel 1.4104 in a martensite structure as well as a ferrite/cementite structure. XRD data are presented as well as metallographic cross-sections and micro-hardness results. SIMS imaging is employed to identify wear debris and elemental mixing after reciprocating ball-on-disc wear measurements against a WC ball. Nevertheless a completely different structure is present, the treated martensitic steel shows very similar wear data as a nitrogen-implanted austenitic steel (1.4301).

K/PII.28 EFFECT OF DUPLEX TREATMENTS BY PLASMA NITRIDING AND TRIODE SPUTTERING ON CORROSION BEHAVIOR OF 32CDV13 LOW ALLOY STEEL

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This paper presents the corrosion behaviour of duplex treated low alloy steel. Different kinds of samples were tested: non treated, plasma nitrided, ZrBN-triode sputtered and ZrBN-duplex treated samples. The corrosion behaviour was evaluated by electrochemical techniques (corrosion potential and polarisation resistance evolutions versus immersion time, potentiodynamic curves). The corrosion tests were carried out in neutral and acid aqueous saline solution (NaCl 30 g.l-1) naturally aerated. The potentiodynamic scan was conducted from -100 to +400 mV (SCE) with scan rate of 10 mV.min-1. The composition and structure layers was determined by EDS and XRD respectively. The morphology was observed by SEM.

Experimental results showed that the corrosion current density I_{corr} increased with decreasing white layer thickness in plasma nitrided specimens, the duplex treated samples exhibit the highest corrosion resistance among the three others. Keywords: protective coating, triode sputtering, plasma nitriding, duplex treatment, corrosion.

K/PII.29 MICROSTRUCTURE AND PROPERTIES OF THE PROTECTIVE LAYERS ON CHROMIUM STEEL

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Nitriding of chromium steel is surface treatment which is applied to improve its hardness and wear resistance. Treatment conducted in elevated temperatures (above 773 K) usually affects negatively its corrosion resistance therefore so big effort is made to develop low temperature nitriding. In this conditions so called "expanded austenite" is formed which has very good corrosion resistance. It was also found that it is possible to obtain this phase in ferritic steel but the mechanism and condition of this process is not well know.

In the present paper the results of the work on the nitride layer formation on the chromium steel with various structure (austenitic and/or ferritic) are presented. The experiment was made in temperature 623-773 K in gas atmosphere. Microstructure of the layers was investigated using SEM and LMA techniques. The phase build-up was checked by XRD and GXR methods. Chemical composition was evaluated by microprobe analysis. Moreover the thickness and microhardness of the layers were measured.

K/PII.30 THE INFLUENCE OF THE THICKNESS OF THE CrN COATING ON PROPERTIES OF THE COMPOSITE "NITRIDED LAYER/CrN COATING" OBTAINED BY CONTINUOUS DUPLEX TREATMENT METHOD

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The paper presents the results of durability investigations of laboratory hot forging dies made of steel DIN 1.2367 and covered by the composites "nitrided layer/CrN coating" with different thickness of the CrN coating. The nitrided layer with the mono-phase structure ϵ -Fe(N) was obtained by the plasma nitriding process and the CrN coating was deposited on the substrate with the nitrided layer by the arc-vacuum method. For the composite "nitrided layer/CrN coating" prepared by the continuous duplex treatment method the authors carried out the wide materials investigations (phase composition with the use of the X-ray diffraction method, chemical composition with the use of the GDOS method and adhesion with use of the scratch-test method). After forging tests the authors carried out the analysis of the influence of the thickness of the CrN coating on the wear intensity of forging dies with the use of the metallographic and Scanning Electron Microscope observations. Based on the obtained results and taking advantage of Elastica computer software authors determined the influence of the thickness of the PVD coating on the "nitrided layer/PVD coating" composite durability.

Wear-resistant coatings

K/PII.31 MODELLING ROUTE FOR WEAR-PROTECTING ABRADABLE COATINGS

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Improving sealing between rotating and stationary parts in aerospace gas turbines significantly increases engine performance by improving thermal efficiencies. To reach this end, abrasible seals are being incorporated into turbines coatings to reduce clearances. With an abrasible seal, the blade tips incur into the shroud, thereby reducing the gap between the rotor and the coating to a minimum. These coatings are generally multiphase materials applied by thermal spray techniques and consisting in a combination of metallic matrix and additional dislocators phases with a controlled amount of porosity. The sealing effectiveness requires a combination of properties that are usually optimised empirically with thermal spray coatings generally made up from a range of simple two-phase powder mixtures.

The aim of the present study was then to initiate a theoretical approach for the study of these materials aiming at developing a prediction strategy for structures improvement. Image analysis and finite element calculations were used to examine the effect of phase morphology on the mechanical behaviour of two reference abrasible systems, namely AISi-hBN for compressor stages and NiCrAl-Bentonite for turbine stages. Scanning Electronic Microscopy (SEM) was used to obtain a series of micrographs for coating characterization. Those micrographs were then treated to create equivalent images based on geometrical description of the inherent morphology. The resultant reduced images are used to carry out finite element calculations, in order to determine the mechanical properties of each coating. This innovative approach was found to provide consistent results and is believed to be a reliable starting point for further coatings elaboration.

K/PII.32 INFLUENCE OF THE MORPHOLOGICAL TEXTURE ON THE LOW WEAR DAMAGE OF PAINT COATED SHEETS

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The influence of the morphological texture (flat and structured) of a polyester based paint coating on the low wear damage is assessed by means of roughness and gloss measurements. The aim of the investigation is to determine without preconceived opinion the most relevant surface roughness parameters with regard to the morphological texture and the wear behaviour of polymer coatings. The relative relevance of a hundred of roughness parameters is thus quantitatively determined by statistical indexes of performance defined and calculated by combining the two-way analysis of variance and the computer based bootstrap method.

The fractal dimension is shown to be the most relevant parameter for characterising the different morphological textures of studied coatings and the number of inflexion points of the profiles for characterising the wear effect. Even if the gloss reduction related to the low wear damage is more marked for the flat products than for the structured ones, the magnitude of this damage is shown to be almost similar whatever the morphological texture of the paint coatings. The higher the magnitude of the wear damage, the higher the number of inflexion points of the profiles.

K/PII.33 HARD Ti-Si-N SPUTTERED COATINGS FOR WOOD PROCESSING

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Ti-Si-N coatings were deposited on silicon, X38CrMoV5 substrates and WC-Co carbide inserts by sputtering a titanium target in Ar-N₂ reactive mixture. The silicon concentration in the film was adjusted by changing the number of Si chips located on the erosion area of the target. The films composition was estimated by electron probe microanalysis and their structure was studied by X-ray diffraction (XRD). Hardness and Young's modulus were determined by depth sensing indentation. Finally, Ti-Si-N treated carbide inserts were tested in routing of Oriented Strand Board (OSB) to determine their abrasion wear resistance in wood machining in comparison to untreated inserts. The wear of the carbide inserts and the coatings reduction were quantified by optical observations.

Whatever the silicon content, no silicon containing compound was detected by XRD and only TiN grains were evidenced. The mean grains size estimated from the full width at half maximum of the TiN (111) diffraction peak was close to 10 nm. The films texture was dependent on the silicon concentration. As commonly reported for Ti-Si-N films, the hardness and the Young's modulus showed a maximum versus the silicon content. The higher values noticed were 49 GPa and 480 GPa for hardness and Young's modulus, respectively. The wood machining tests with Ti-Si-N treated carbide inserts revealed that after 4500 m of routing of OSB, the treated carbide inserts present a lower cutting edge's wear than the untreated ones.

K/PII.34 THE STRUCTURE AND HARDNESS OF MAGNETRON SPUTTERED Ti-Al-N THIN FILMS WITH LOW N CONTENTS (< 42 at. %).

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There are still unsolved problems in the mould injection industry that may be overcome by applying the thin film technology. This is the case of the poor oxidation and mechanical resistance of the low series aluminium moulds which can be considerably improved by coating with an adequate thin film, such as Ti-Al-N. The present investigation reports on the deposition of Ti-Al-N films by closed field unbalanced magnetron sputtering. Two different target configurations were used: two pure Al and Ti targets at 90° (pure targets configuration) and two facing Ti targets incrustated with Al rods (composite targets configuration).

Chemical analysis of the films deposited using the pure target configuration showed that the Al/(Al+Ti) ratio and the N content ranged from 19 to 35% and 0 to 42%, respectively. The h.c.p. Ti phase was detected in all the low N content films (under 30 at. %) which hardness ranged from 12 to 21 GPa. For the higher N contents, the crystalline structure collapsed and amorphous films were deposited which gave rise to a steep increase in hardness. A maximum of 40 GPa was attained for the film with the highest Al content. For the films deposited using the composite target configuration, Al/(Al+Ti) atomic ratios and N contents in the ranges of 21 to 29% and 0 to 33% were measured, respectively. As for pure targets, low N contents lead to deposition of the h.c.p. Ti phase, although, in this case, vestiges of the Ti₃Al compound were also detected. Amorphous coatings were also deposited at the higher N contents. However, the amorphous films were much softer with hardness values lower than 27 GPa.

K/PII.35 THE CHARACTERISTICS STUDY OF Fe-Mn-Al-C ALLOY COATINGS DEPOSITED BY HVOF SPRAY

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The sliding wear resistance, microhardness and electrochemical behavior of Fe-Mn-Al-C alloy coatings deposited by High Velocity Oxy Fuel (HVOF) spray have been studied. The Fe-Mn-Al-C alloys were reported to exhibit good mechanical properties, and with better corrosion resistance than carbon steels. The alloy powders for HVOF spray were prepared by water atomization and mechanical ball milling methods. Half of the as deposited samples were nitridation heat treatment after HVOF spray. The wear test were performed using a ring-on-disk type wear tester with a load of 50N, and a sliding speed of 0.4m/s against a hardened high-speed steel (M2) ring. A dynamic polarization test was used to compare the corrosion resistance of coatings in as deposited condition and that after nitridation heat treatment.

After nitridation heat treatment, the microhardness of the coatings from water atomization powder is increased from 485 to 500 Hv and those from ball milling powder is increased from 590 to 620 Hv. The wear resistance of coatings after nitridation heat treatment is better than hardened M2 ring. The polarization curves indicated that the coatings after nitridation heat treatment exhibited better corrosion resistance than those of as deposited in 3.5% NaCl solution. The crystal structures of coatings were analyzed by X-ray diffraction (XRD) method, it is found that k carbide (Fe, Mn)₃AlC_x and nitride could form after nitridation heat treatment. It is suggested that the Fe-Mn-Al-C coatings could have a widespread application in molding industry.

K/PII.36 WEAR PHENOMENA INVESTIGATION OF CERAMIC COATINGS PROCESSED USING ATMOSPHERIC PLASMA SPRAYING
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Wear resistance ceramic coatings were processed using atmospheric plasma spray technique for which operating conditions were varied. The conditions were divided into three main categories: energetic, injection and environmental parameters. The Friction and wear behavior of the ceramic coatings were investigated using a single contact arrangement. Laser profilometry of wear tracks generated during the sliding process was considered. This permitted to correlate the process parameter to the friction and wear rate of the studied coatings.

Corrosion-resistant coatings

K/PII.37 CHARACTERIZATION OF ALUMINIZED LAYER FORMATION ON Ti ALLOYS COATED BY Al FILM DURING ANNEALING
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Intermetallic compounds of the Ti-Al system and alloys based on such compounds have been considered extensively for high-temperature structural applications because they offer a combination of low density, good oxidation resistance, and useful mechanical properties at temperatures higher than those possible with more conventional titanium alloys. The available experimental data show that aluminide phases can be used as a protective coating for industrial titanium alloys. In present work we have studied the kinetics of structural formation of aluminized layers on the surface of industrial titanium alloys. The Ti-5Al-3Mo-1V and Ti-5Al-2Mn (in wt.%) alloys and commercial titanium has been used as a substrate. The ultrafine-grained, coarse-grained and martensite like structures of initial substrates have been formed by heat treatment. The Al layer on the surface of substrates with thickness of about 3, 5 and 7 μm has been formed by the thermal deposition. During annealing on the surface Al₃Ti, Al₂Ti, TiAl, Ti₃Al and a solid solution of Al in Ti are formed successively. The kinetic of the structural formation of aluminide phases is function of annealing temperature, exposure time and thickness of the initial Al layer. The thicker initial Al layer the thicker layers of aluminide phases are formed, as a result the more time or higher temperature is necessary for their diffusion cementation and decomposition. The kinetics of structural formation and the microstructure of aluminide overlayers depend on the grain structure of the initial substrates. During annealing quenched samples coated by aluminum film the decomposition of metastable phases of substrate takes place. This process influences strongly interdiffusion growth and the morphology of forming aluminized layers.

K/PII.38 THE HIGH TEMPERATURE CORROSION OF PACK ALUMINIZED Co-BASE SUPERALLOY IN Na₂SO₄ AND NaCl MOLTEN SALT AT 1173 K
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Pack aluminizing is a simple and effective process to produce an aluminum rich phase on the alloy surface, which can form protective alumina layer during high temperature operation.
A cobalt base superalloy, AMS 5608, was pack aluminized with Al-Cr powder at 1223K for 9 hrs. A hot corrosion test of both untreated and aluminized alloys was carried out by immersing in the mixture of 10 wt% NaCl and 90 wt% Na₂SO₄ molten salt at 1173K for 1, 3, 24 and 49 hrs. The phases, microstructures and chemical compositions of alloys were characterized by the X-ray diffractometry (XRD) and Electron Probe Microanalyzer (EPMA), respectively. An aluminide layer ranging 60 μm in thickness was found on the pack-aluminized alloy surface. The main phase of the aluminide layer was CoAl. Some chromium-tungsten carbide precipitates were also found. An interdiffusion zone around 8 μm thick was observed between the aluminide layer and alloy matrix. The chromium content near the surface of the aluminide layer is higher due to the aluminizing process with Al-Cr powder. It is observed that only limited weight loss was found for each aluminized specimen after hot corrosion test. The calculated parabolic rate constant of the aluminized AMS 5608 alloy after 49 hrs of hot corrosion at 1173K is $1.99 \times 10^{-12} \text{ g}^2\text{cm}^{-4}\text{sec}^{-1}$. The hot corrosion resistance of the untreated superalloy matrix was very poor. Almost every untreated superalloy specimen was penetrated by the molten salt and failed in each test. It is concluded that the hot corrosion resistance of the aluminized cobalt base superalloy AMS 5608 in the mixture of 10 wt% NaCl and 90 wt% Na₂SO₄ molten salt at 1173K was excellent due to protective alumina layer formed on the surface.

K/PII.39 EFFECTS OF ALLOY ELEMENTS ON THE HOT CORROSION BEHAVIOR OF ALUMINIZED ALLOY STEELS
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Three Fe-base alloy steels including plain carbon AISI 1020 steel (Fe-0.2%C), SUS430 stainless steel (Fe-18%Cr) and Fe-Mn-Al alloy steel (Fe-29%Mn-9%Al-0.9%C) were pack aluminized with Al-Fe powder at 1073K for 4 hrs. Some aluminized specimens were pre-oxidized at 1273K for 1 hr to produce dense alumina layer on surface. Hot corrosion tests were conducted in the mixture of 90 wt% Na₂SO₄ and 10 wt% NaCl molten salt at 1173K for 6, 12 and 48 hrs, respectively. The X-ray diffractometer (XRD) and Electron Probe Micro Analyzer (EPMA) were employed to examine the phases, microstructures and chemical compositions of each aluminide.
It is found that the FeAl phase is formed on the aluminide layers of three steels. The thickness values of aluminide layer of AISI 1020 and SUS430 are all around 55 μm . However, an interdiffusion zone containing lamina (Fe,Mn)₃AlC_x phase, ranging 30 μm in thickness is observed between the surface aluminide layer and matrix of Fe-Mn-Al alloy steel. The hot corrosion resistance of the aluminized plain carbon AISI 1020 steel was poor due to the spallation of aluminide layer and rapid inward and outward diffusion of Al during tests. Only limited weight loss was found for the aluminized SUS430 and Fe-Mn-Al specimens after test. The parabolic rate constant of these two alloys was around $10^{-11} \text{ g}^2\text{cm}^{-4}\text{sec}^{-1}$. The hot corrosion resistance of the aluminized SUS430 and Fe-Mn-Al steels was improved due to the protective alumina layers formed on the surfaces. It was observed that the outward diffusion of Cr from SUS430 matrix to the surface aluminide layer retarded the corrosion attack during tests. On the contrary, the outward diffusion of Mn from FeAl phase degraded the corrosion

- K/PII.40** MICROSTRUCTURE STUDIES OF AN ALUMINIDE COATING ON 9Cr-1Mo STEEL DURING HIGH TEMPERATURE OXIDATION
Yo. Yu. Chang and Charng-Cheng Tsaur, institute of Occupational Safety and Health, Sijhih City, Taipei, Taiwan. 9Cr-1Mo steel coated by hot-dipping into a molten mixture with 7wt%Si/93wt%Al was oxidized at 750, 850, and 950°C in static air. The oxidation kinetics followed a parabolic rate law at all temperatures. Intermetallic iron-aluminum compounds FeAl₃, Fe₂Al₅, and FeAl₂ initially formed on the steel substrate at elevated temperature. At 850°C the Fe_xAl_y layer thickness increased rapidly during the first 20min and Fe₂Al₅ mixed with FeAl₂ became the main phases in the aluminide layer. Some cracks propagated through the Fe_xAl_y brittle FeAl₂ and Fe₂Al₅ layers. After 24hr oxidation at 850°C, all FeAl₂ + Fe₂Al₅ transformed to FeAl, while FeAl₂ + Fe₂Al₅ still existed at 750°C after 56hr exposure. The Kirkendall effect is a plausible mechanism for the voids observed at the interface between the aluminide layer and the steel substrate.
- K/PII.41** A COMPARATIVE STUDY OF THE STRUCTURE AND THE CORROSION BEHAVIOR OF ZINC COATINGS DEPOSITED WITH VARIOUS METHODS
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 A very effective method for the corrosion protection of ferrous substrates is hot-dip galvanizing. Although its effectiveness, it is characterized by hazardous byproducts. However there are more environmentally friendly methods to form zinc coatings, such as pack cementation and fluidized bed technology.
 In pack cementation the substrate is covered by a powder mixture composed by Zn, Al₂O₃, ZnO, NH₄Cl and ZnCl₂. Substrate and powder mixture are stored in a sealed crucible and heated up to 450°C for time up to 6 hr. Optical and electron microscopy, X-Ray diffraction and Auger analysis were used for structure determination of the as-formed coatings. Two layers were observed referring to the gamma and the delta phase of the Fe-Zn phase diagram, while in some cases inclusions were observed with about 50 wt.% Zn and 50 wt.% Fe. To obtain coatings with fluidized bed the specimens were hanged at the center of the fluidized bed reactor. Temperature, time, and powder mixtures were similar to those in pack cementation. The fluidization gas was Ar. The structure of the as produced coating was also determined with the same techniques. Regarding the corrosion behavior, the samples have been placed in a salt spray chamber together with a hot-dip galvanized specimen for comparison reasons. The chamber conditions were settled at 40°C and 100% relative humidity and the corrosive medium was a 5 wt.% NaCl aqueous solution. The exposure time ranged from 3 up to 14 days. The as-corroded samples were examined with the same methods. Observations showed that in every case Zn and Fe hydrated chlorides and oxides were the main corrosion products, while the damages depend on exposure time. Alterations between samples, which were differently produced, were observed.
- K/PII.42** CORROSION-PROTECTIVE BEHAVIOR OF THIN CERIA LAYERS ELECTRODEPOSITED ON STAINLESS STEEL
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 The use of stainless steel as construction material for instruments and equipment working in strongly aggressive media requires additional surface modification. Among the numerous chemical and physical methods for deposition of protective layers, the electrodeposition represents an attractive alternative due to its simplicity and reliability.
 We used the electrochemical deposition to obtain thin (1-3µm) layers of CeO₂ on stainless steel. The corrosion behavior of this coating was studied by electrochemical techniques in strongly aggressive media (HNO₃, H₂SO₄, NaCl). The subsequent changes in composition and structure of the surface layers of stainless steel were investigated by XPS and SEM. An extremely strong influence of the electrodeposited CeO₂ layers on the corrosion resistance of the stainless steel was found. This effect became more pronounced after thermal treatment of the ceria coating which is promising in regard to possible practical implementation.
- K/PII.43** THE HIGH-TEMPERATURE OXIDATION BEHAVIOR OF HOT-DIPPING Al-Si COATING ON CARBON STEEL
 Chaur-Jeng Wang and Shih-Ming Chen, National Taiwan University of Science and Technology, Department of Mechanical Engineering, Taipei, Taiwan.
 SB450 carbon steel was coated by hot-dipping into a molten bath containing Al-10wt%Si. The phase transformation and structure formation were studied after continuous or cyclic oxidation at both 750 and 850°C in static air. After hot-dip treatment, the coating layers consisted of three phases, where Al, FeAl₃, Fe₂Al₅ were detected from external topcoat to the aluminide/steel substrate. The result of high temperature oxidation test showed, the oxidation kinetics basically followed a parabolic rate law at 750 and 850°C. The FeAl₃ and Fe₂Al₅ were transformed into FeAl because the phase transformation of aluminized layer occurred with increasing oxidation time. In the present study, Kirkendall voids were found to form in any of the interfaces in the coating or at the coating/substrate interface due to the rapid inter-diffusion of ferrite and aluminum during oxidation processes and, therefore, the adherence of the coatings should be compromised. It is also indicated that the adding of Si into aluminide layer can further effectively the formation of the continuous alumina in the scale during high temperature oxidation.

- K/PII.44** CORROSION BEHAVIOUR OF ZIRCONIA BARRIER COATINGS ON GALVANIZED STEEL
 R. Romero Pareja, R. López Ibáñez, F. Martín Jiménez, J.R. Ramos-Barrado, and D. Leinen, Laboratorio de Materiales y Superficie (Unidad Asociada al CSIC), Dpto. Física Aplicada I & Dpto. Ingeniería Química, Universidad de Málaga, Campus de Teatinos, Málaga, Spain.
 Amorphous ZrO₂ thin films were deposited for corrosion protection on galvanized steel by spray pyrolysis, using zirconium acetyl acetonate in aqueous and alcoholic solutions. Different spray conditions and posterior thermal treatments have been studied. The corrosion protective effect of the coatings is discussed in relation with results from scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and UV-VIS-NIR spectroscopy data of samples subjected to the corrosion test. The corrosion behaviour of coated and uncoated zirconia galvanized steel in aqueous NaCl and H₂SO₄ electrolyte solutions were studied by potentiodynamic polarization curves and cyclic voltametry. Measurements in NaCl solution indicated a decreased pitting of the galvanized steel when coated with zirconia. However, the protection against corrosion depends on the preparation conditions. In H₂SO₄ solution, zirconia coatings (thickness < 50 nm) act as an effective corrosion barrier as revealed by a reduction of the current density. Furthermore, these films are highly transparent and thus have low visual impact on the substrate material.
- K/PII.45** ELECTROLYTIC Al₂O₃/Y₂O₃ DOUBLE-LAYER COATINGS ON IN-617 SUPERALLOY
 C. T. Hsu, C. C. Chang, T. N. Chang, and S. K. Yen, Department of Materials Engineering, National Chung Hsing University, Taichung, Taiwan.
 Ceramic coatings seem ideal for using materials at high temperatures and in severely corrosive environments. Since superalloy was used at high temperatures and in severely corrosive environments, ceramic coating was usually applied to enhance operation property. In this study, IN-617 superalloy was coated with Al₂O₃/Y₂O₃ double-layer films by electrolytic deposition in Al(NO₃)₃ and Y(NO₃)₃ aqueous solutions. Characterization of coated specimens was conducted by XRD, SEM, aqueous corrosion tests in 3.5% NaCl and 0.5M Na₂SO₄ solution, hot corrosion test in 2mg/cm² Na₂SO₄ contained environment at 1050°C; and scratch tests. The coated alloy revealed much better performances in oxidation and corrosion resistance than the uncoated. Also, the adhesion between coated film and substrate is greater than the yield stress of substrate.
- K/PII.46** MICROSTRUCTURAL CHARACTERIZATION AND STUDY OF CORROSION BEHAVIOR OF PLASMA-SPRAYED TiN COATINGS
 N. Pistofidis(a), G. Vourlias(a), E. Pavlidou(a), P. Patsalas(b), G. Stergioudis(a), E. K. Polychroniadis(a), and D. Tsipas(c), (a)Aristotle University of Thessaloniki, Department of Physics, Thessaloniki, Greece, (b)University of Ioannina, Department Materials science & Engineering, Ioannina, Greece, (c)Aristotle University of Thessaloniki, Department of Mechanical Engineering, Thessaloniki, Greece.
 The tin (Sn) coatings on ferrous substrates can provide low shear conditions and consequently improve the tribological properties of surfaces in contact. Their performance is highly affected by their structure. Furthermore, Sn offers anticorrosive protection to the substrate.
 In this work the structure and the anticorrosive behavior of Sn coatings deposited on steel St-37 with plasma spray is characterized with Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Conventional Transmission Electron Microscopy (CTEM), High Resolution Electron Microscopy (HREM), Auger analysis and microhardness measurements. The porosity of the as-produced coating is very low and it is rather unlikely to affect its tribological properties. Furthermore the coating is mainly composed of pure Sn, while interdiffusion of Fe and Sn takes place at the interface between the coating and the substrate and Fe-Sn phases are formed. This phenomenon ensures good adhesion of the coating to the underlying steel. Also, amorphous Sn or SnO_x were detected in the coating. Their presence could be of great importance for the coating properties. Finally, the corrosion behaviour of the coatings was investigated by exposing the specimens in a salt spray chamber for 10 days at 40°C and 100% relative humidity. The corrosive medium was a 5 wt.% NaCl aqueous solution. The corrosion products were characterized with XRD, SEM and Auger analysis. This examination showed that Sn hydrated chlorides and oxides were the main corrosion products, while the damages that the samples suffered depended on exposure time.
- K/PII.47** THE CORROSION RESISTANCE OF CHROMIUM CARBIDE COATINGS DEPOSITED ON STEEL BY FILTERED CATHODIC VACUUM ARC DEPOSITION
 Han C. Shih, Chun-Chun Lin, and Ku-Ling Chang, Department of Material Science and Engineering, National Tsing Hua University Hsinchu, Taiwan, ROC.
 Deposition of chromium carbides film using a 90°-bend filtered cathodic vacuum arc (FCVA) system is highly promising for industrial applications, because chromium carbide films uncontaminated by macroparticles exhibit excellent characteristics. Chromium carbide films were synthesized from a Cr target (99.95%) and C₂H₂/Ar pressure (5/5, 10/10, 10/30, 20/20 and 60/10) with a substrate voltage of -50 V at 500 Torr. The corrosion resistance of the chromium carbide coated steels were studied and compared in terms of open-circuit potentials and polarization resistance (R_p) resulting from electrochemical impedance spectroscopy (EIS) in an aerated 3.5 wt% NaCl aqueous solution. Our findings revealed that the crystalline structure of the coatings depended on the C₂H₂/Ar pressure. As the C₂H₂/Ar pressure decreases from 60/10 to 5/5 (4.6×10⁻³ to 1.4×10⁻³ Torr), the phase was transformed from amorphous to crystallized Cr₃C₂. The chromium carbide coatings are nobler than the uncoated steel and the R_p of the coatings is higher than that of uncoated steel which also accounted for the crystalline nature of the dense and compact microstructure.

K/PII.48 PLASMA DEPOSITED SiO_x COATINGS FOR THE CORROSION PROTECTION OF ALUMINUM AND MAGNESIUM ALLOYS

Ch. Voulgaris(a), E. Amanatides(a), D. Mataras(a), S. Grassini(b), E. Angelini(b), and F. Rosalbino(b), (a)Plasma Technology Laboratory, Department of Chemical Engineering, University of Patras, Greece, (b)Department of Materials Science and Chemical Engineering, Polytechnic of Turin, Turin, Italy.

The protection of corrosion sensitive metallic surfaces is an important issue for the automotive, aerospace and construction industries. Plasma Enhanced CVD is an attractive, environmentally safe alternative to the currently used methods to produce very dense film structures with uniform, pinhole-free thicknesses, offering satisfactory corrosion resistance. In this work, is presented a study of the effect of RF power on the electric and optical properties of TEOS/O₂ plasmas, as well as on the composition, structure, uniformity and corrosion characteristics of thin SiO_x coatings deposited on aluminum (5018-O) and magnesium (AZ91) substrates. An effort is made, using plasma power and impedance measurements and spatially resolved optical emission to distinguish the elementary processes leading to the observed quality differences between the layers deposited on each of the two materials. In addition, SEM and AFM are used to examine the surface morphology and the thin film failure mechanism, while the thin film composition is determined through FTIR spectroscopy. Finally, Electrochemical Impedance Spectroscopy is used for checking the corrosion protection performance of SiO_x thin films. The results show that the coatings are very sensitive on the RF power level. Namely, films deposited at low power are highly organic while those deposited at high power are inorganic but suffer from adhesion problems resulting in low corrosion protection in both cases. Finally, the films deposited at an intermediate optimized power level have shown the best surface coverage and corrosion protection properties that are better than those obtained with the standard anti-corrosive coatings, while the coated aluminum substrates present much higher corrosion resistance.

K/PII.49 CORROSION RESISTANCE OF NITRIDED LAYERS ON AUSTENITIC STEEL

J. Baranowska(a) and B. Arnold(b), (a)Institute of Materials Science and Engineering, Szczecin University of Technology, Szczecin, Poland, (b)Institute of Materials Science and Welding, Hamburg University of Applied Science, Hamburg, Germany.

Austenitic steel are widely applied because of its excellent corrosion resistance mainly in food and chemical industry. It is also one of the most popular biomaterial for implants and surgeon instruments. To improved mechanical properties of its surface the heat-chemical treatment could be applied. It was find that nitriding could increase the surface hardness and wear resistance without affecting the corrosion resistance therefore could extend the range of application of this steel.

The paper presents results of investigation on the influence of nitriding atmosphere composition on the layers morphology, phase composition and surface defects. Treatment was made in gas atmosphere in the temperature range 688-748 K. The microstructure and phase composition of the layers were investigated using scanning and light microscopy an X-ray diffraction. The elements composition was evaluated using electron probe microanalysis. The corrosion resistance were determined on the basis of the corrosion tests in NaCl solution. It was stated that it is possible to control the layer morphology by changing the nitriding atmosphere composition and in this way to influence the corrosion resistance of nitrided layers. Moreover it is shown that it is possible at the same time to obtain the corrosion resistant layers with a high growth rate.

K/PII.50 HAFNIUM DIBORIDE COATINGS BY CHEMICAL VAPOR DEPOSITION

S. Jayaraman(a), Y. Yang(a), J.E. Gerbi(a), A. Chatterjee(a), P. Bellon(a), J.R. Abelson(a), D.Y. Kim(b), G.S. Girolami(b), and J.-P. Chevalier(c), (a)Dept. of Materials Science and Engineering, University of Illinois at Urbana Champaign, IL, USA, (b)Dept. of Chemistry, University of Illinois at Urbana Champaign, IL, USA, (c)Centre d'Etudes Chimie-Metallurgie, Vitry, France.

Transition metal diborides are refractory materials with high electrical and thermal conductivity and high hardness. They are chemically inert in harsh environments such as molten zinc and have low diffusion rates for impurities such as copper. Hafnium diboride (HfB₂), the material under study, has a melting point of 3250(C and a bulk hardness of 29 GPa; these attractive properties make it a good candidate for wear resistant or protective coatings. We report the chemical vapor deposition (CVD) of HfB₂ thin films using the single-source borohydride precursor Hf[BH₄]₄. This precursor is entirely free of organic ligands and halogens; it only contains excess B and H, which can be rejected by the growth surface as volatile B₂H₆ and H₂ molecules. Deposition occurs at temperatures as low as 200(C, which should allow film growth on plastic substrates. At such low temperatures, where the surface reaction probability is very low, we obtain excellent conformal coverage, e.g., a nearly uniform film thickness within a trench of 22:1 depth:width aspect ratio. The films grown at low temperatures are X-ray amorphous and exhibit a respectable nanoindentation hardness of 20 GPa and an elastic modulus of 300 GPa which is well matched to metals such as molybdenum. A short duration annealing at temperatures above 700(C yields a nanocrystalline material, and the hardness increases to 30 GPa. These numbers represent values for a single-phase coating and are not yet optimized. We are currently developing a growth process intended to directly yield nanocomposite material at low temperatures. The approach is to introduce a second phase such as BN that will force the constant re-nucleation (and thus small size) of HfB₂ grains. We do this by adding a flux of atomic nitrogen from a remote plasma source during film growth. This remote plasma CVD process readily produces ternary Hf-B-N thin films; continued work is needed to obtain the desired multiphase nanocrystalline microstructure. We will report the composition, microstructure, hardness, wear rate, and growth kinetics for the films of interest, and indicate routes for engineering optimization of this process.

K/PII.51**LOW PRESSURE PLASMA PROCESSES FOR CORROSION PROTECTION OF METALS**

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An interesting new field of application of low pressure plasma processes is the surface modification of metals in order to increase their corrosion resistance. PECVD barrier layers show high potential for corrosion protection and may be proposed for replacing conventional approaches, sometimes responsible for severe environmental concerns. Among the main technological advantages of PECVD it is important to mention the possibility of depositing multiple and graded layers with different chemical composition and properties, and of carrying our suitable plasma pre-treatments in order to improve coating-substrate performances.

Interesting results were obtained in the evaluation of the protective effectiveness of SiO_x and SiN_x thin films deposited on steel and light alloys in an RF parallel-plate reactor from different organosilicon monomers (HMDSO, TEOS, HNDSN, etc.) in mixture with argon and/or oxygen. The corrosion behaviour of coated samples was evaluated by means of Electrochemical Impedance Spectroscopy, testing the samples in aerated electrolyte solutions. The protective properties of the coating are strongly affected by the variation of the experimental process parameters. As a matter of facts, a marked increase in the protective effectiveness is obtained with the increase of the oxygen content of plasma and of the discharge input power. Plasma pre-treatments, carried out in H₂, O₂ and CF₄ and NH₃ containing plasmas, as a function of the particular metal under study, play an important role in determining the inhibiting properties of deposited layer. XPS analyses show that pre-treatment removes the surface contamination, thereby reducing the defectiveness degree of the coating and enhancing its adhesion to the substrate.

K/PII.52**HOT CORROSION OF LASER-GLAZED PLASMA-SPRAYED THERMAL BARRIER COATINGS**

C. Batista(a), A. Portinha(a), R. M. Ribeiro(a), V. Teixeira(a), and C.R. Oliveira(b), (a)University of Minho, Physics Department, Campus de Gualtar, Braga, Portugal, (b)IDIT, Instituto de Desenvolvimento e Inovação Tecnológica, Santa Maria da Feira, Portugal and University Lusíada, Vila Nova de Famalicão, Portugal.

Thermal barrier coating (TBC) systems are frequently used in gas turbine engines to provide thermal insulation to the hot-section metallic components and also to protect them from oxidation, hot corrosion and wear damage. Surface sealing treatments, namely laser-glazing, have been showing a high potential for extending in-service lifetimes of these systems by improving, among others, chemical and oxidation resistance. In this investigation, both as-sprayed and laser-glazed TBCs are exposed to hot corrosion in molten salts. The TBC system comprises an atmospheric plasma-sprayed (APS) yttria partially stabilized zirconia (YPSZ) top coat and a vacuum plasma-sprayed (VPS) MCrAlY bond coat deposited on inconel alloy. The glazed coatings were obtained by scanning the surface of the plasma-sprayed coatings with a high power continuous wave CO₂ laser. The hot corrosion investigation was accomplished by subjecting the specimens to an isothermal air furnace testing under 25mg/cm² of a salt mixture of 60%wtV₂O₅-40%wtNa₂SO₄ in a temperature of 1000°C for 100 hours. The corrosion mechanisms were investigated from post-test image analysis using scanning electron microscopy (SEM) and from energy dispersive X-ray analysis (EDX) to find the elements deriving from the corrosive compounds along through-thickness. X-ray diffraction (XRD) was also used to monitor structural changes on the coatings surface. Substrate and bond coat corrosion is discussed as well as top coat destabilization mechanisms.

K/PII.53**OXIDATION TUNING IN AlCrN COATINGS**

J.L. Endrino(a), A. Reiter(a), R. Escobar(b), and J.M. Albella(b), (a)Balzers AG, SBU Tools, Balzers, Liechtenstein, (b)Instituto de Materiales de Madrid, C.S.I.C., Cantoblanco, Madrid, Spain.

Chromium based hard coatings such as CrN and Cr_{1-x}Al_xN have been successfully applied as protective layers in stamping and forging tools because of their capacity to redirect the heat from the workpiece. Recently, the use of aluminum chromium nitride hard coatings has also been extended to cutting and machining applications such as dry machining and high speed cutting (HSC). This was possible, in great part, because of the superior hot hardness and oxidation resistance of Cr_{1-x}Al_xN in comparison to Ti_{1-x}Al_xN films. In this study, we have explored the concept of AlCrN layers with tunable oxidation behavior by embedding a 100 nm thick titanium nitride (TiN) layer at different depths in a high oxidation resistant 3-micron thick Cr₃₀Al₇₀N coating. A total of eight coatings were deposited onto cemented carbide (WC-Co) substrates by the cathodic arc vacuum (CAV) deposition technique using a Balzers' rapid coating system (RCS) deposition machine. The deposited coatings were then annealed at 950°C for 3-hours in air. Afterwards, the chemical stoichiometry profile for the different oxidized surface layers and interfaces of the coating systems were analyzed by glow-discharge optical spectroscopy (GDOES). The results indicate a tunable oxidation behavior of AlCrN layers due to the presence of a near surface buried layer with a relatively higher thermal conductivity (TC).

K/PII.54**TRIBOCORROSION BEHAVIOUR OF ZrN_xO_y THIN FILMS FOR DECORATIVE APPLICATIONS**

S.C. Ferreira(a), E. Ariza(a), L. A. Rocha(a), F. Vaz(b), L. Cunha(c), P. Carvalho(b), L. Rebouta(b), E. Alves(d), Ph. Goudeau(e), and J. P. Rivière(e), (a)Universidade do Minho, Dept. Eng. Mecânica, Azurém, Guimarães, Portugal, (b)Universidade do Minho, Dept. Física, Azurém, Guimarães, Portugal, (c)Universidade do Minho, Dept. Física, Campus de Gualtar, Braga, Portugal, (d)ITN, Departamento de Física, Sacavém, Portugal, (e)Laboratoire de Métallurgie Physique, Université de Poitiers, Futuroscope, France.

The main aim of this work is the investigation of the tribocorrosion behaviour of single layered zirconium oxynitride, ZrN_xO_y, thin films in alternative linear regime of sliding and immersed in an artificial sweat solution at room temperature. The films were produced by rf reactive magnetron sputtering, using a pure Zr target at a constant temperature of 300° C. Two different sets of samples were produced. In the first set of films the substrate bias voltage was the main variable, whereas in the second set, the flow rate of reactive gases (oxygen/nitrogen ratio) was varied. The control of the amount of oxygen allowed the film properties to be tailored from those of covalent zirconium nitride to those of the correspondent ionic oxide. During the wear test both the open circuit potential and the corrosion current were monitored. Also, Electrochemical Impedance Spectroscopy (EIS) tests were performed before and after sliding in order to evaluate, in detail, the modification of the protective character of the coating introduced by the joint action of wear and corrosion. The modifications of the coating microstructure and/or chemical composition induced by the variation of the deposition parameters was also evaluated and correlated with the corrosion mechanisms occurring in each system.

Session XI : Structural characterization of coatings

Session chairs : J.Th.M De Hosson (University of Groningen, the Netherlands)

O. Zywitski (FEP, Dresden, Germany)

- K-XI.1** 8:30 -Invited- STRUCTURAL AND MECHANICAL PROPERTIES OF NANOSTRUCTURED METALS: SYNERGIES BETWEEN SIMULATION AND EXPERIMENTS
Helena Van Swygenhoven, P.M. Derlet, A. Froseth, and S. Van Petegem, Paul Scherrer Institute, ASQ/NUM, Materials Science and Simulation PSI-Villigen, Switzerland.
Atomistic simulations have provided unprecedented insight into the structural and mechanical properties of nanocrystalline materials, highlighting the role of the non-equilibrium grain boundary structure in both inter- and intra-deformation processes. One of the most important results is the capability of the nanosized grain boundary to act as source and sink for dislocations, in other words a deformation mechanism that does not leave behind dislocation debris. The dislocation activity suggested by molecular dynamics for four different nc-fcc metals, Al, Cu, Ni and Au are discussed in terms of the inherent restrictions and caveats of the simulation technique, in terms of material properties such as the generalized stacking fault energy curves (Nat. Mat. 3(2004)401) and in terms of grain boundary structures. In order to validate the results of the simulations, a new type of in-situ X-ray diffraction experiment was developed at the Swiss Light Source in which the peak shift and peak broadening during deformation can be followed time-resolved. Measurements show that for the smallest grain sizes, peak broadening is reversible upon unloading, demonstrating the absence of a remaining dislocation debris (Science 304 (2004)273). Applications of this new technique for the investigation of size effects in mechanical properties of free standing thin films are presented together with dedicated simulations and efforts to bridge simulations to experiments by means of diffraction pattern calculations.
- K-XI.2** 9:00 MICROSTRUCTURE AND MECHANICAL INVESTIGATIONS OF TUNGSTEN CARBIDE FILMS DEPOSITED BY REACTIVE RF SPUTTERING
K. Abdelouahdi(a), C.Legrand-Buscema(a), C.Sant(a), J.Perrière(b), G.Renou(a), and P.Aubert(a), (a)Laboratoire d'Etude des Milieux Nanométriques, Evry, France, (b)Groupe de Physique des Solides, Université Paris VI, Campus Bouicaut, Paris, France.
Tungsten carbide thin films were deposited on {100} Silicon substrates by reactive RF sputtering from a tungsten target in Ar-CH₄ mixture.
In order to observe the influence of grow parameters on structural and mechanical properties, Various CH₄ concentration in the gas flow, substrate bias and RF-power were carried out. During deposition the substrate temperature and the total pressure were respectively set at 150 °C and 2 mtorr. The thickness was 360 nm. Rutherford Backscattering Spectroscopy (RBS), X-Ray Diffraction (XRD), Grazing Incidence X-ray Diffraction (GIXRD), X-Ray Reflectivity (XRR) and Atomic Force Microscopy were used to analysed the films. Hardness was obtained by nanoindentation. In the range between 1 - 2 % CH₄ gas admixture, the films structure exhibits a mixture of cubic WC_{1-x} phase and hexagonal W₂C phase, between 2 - 4 % CH₄ an amorphization of the layers was observed. At high methane concentration (5 %), the films become essentially amorphous. As the substrate bias level is increased from 0 to 80 V, the films composition changed from WC_{0.88} to WC_{0.65}. The crystallographic structure also changes from dominant WC_{1-x} phase to dominant W₂C phase. The change in structure and composition are accompanied by a decrease in the deposition rate. Increasing the RF-sputtering power from 50 to 260 W resulting in decreases in the carbon content of the coating from 47 to 30 at. %. The film prepared at 260 W shows (200) preferential orientation of WC_{1-x} phase. This film has the higher hardness (26 GPa). Nanoindentation measurements showed that hardness generally decrease with carbon content. The influence of the substrate will be also discuss.
- K-XI.3** 9:20 COMPOSITION AND STRUCTURE OF THIN FILMS. SPECTRAL SIMULATION AND EXPERIMENTAL RESULTS
E. Mielczarski and J.A. Mielczarski LEM, CNRS/INPL, Vandoeuvre lès Nancy, France.
Infrared external reflection technique with very unique properties has been developed to characterize thin films at solid substrates. This technique supported by spectral simulation of surface composition and structures allows obtaining almost all the information about thin films including: (i) composition, (ii) film thickness, (iii) surface distribution (uniform layer or patches with determined thickness), (iv) molecular orientation, organization in surface layer, (v) kinetic of surface processes such as surface deposition, surface diffusion, stability of surface products and structures. The variety, precision and reliability of information about surface phenomena are unique. The experiments are fast and non-destructive. High sensitivity (less than monolayer) and possibility to perform characterization of monolayer films in region of very strong absorption of substrate makes this technique a very valuable characterization tool. The complexity of recorded reflection spectra, their sensitivity to any variation of the optical properties of all investigated phases in the system are in fact the major strength of the technique. The example of characterization of thin films and self-assembled monolayers will be discussed in this presentation.

K-XI.4 9:40

SIMULATED SPUTTERING AND NANOSCUPTING IN THIN FILMS

P. Süle and M. Menyhárd, Research Institute for Technical Physics and Materials Science, Surface Physics, Budapest, Hungary.

Molecular dynamics simulations have been used to simulate ion sputtering induced structural and morphological changes in Co/Cu bilayer. Particular attention is paid to the ion induced interfacial mixing as well as to adatom island growth. Systematic studies have been carried out to account for the sputtering induced growth as a function of various conditions such as temperature, ion impact angle and ion fluence. We study the early formation of periodic surface patterns, such as ripples on the Co(001) surface.

P. Süle, M. Menyhárd, Strong mass effect on ion beam mixing in metal bilayers, accepted in Phys. Rev. B (2005), P. Süle, M. Menyhárd, K. Nordlund, Nucl. Instrum. Meth. B226, 517 (2004), B222, 525 (2004)

K-XI.5 10:00

MICROSTRUCTURE EVOLUTION AND GRAIN GROWTH OF TiN-TiB₂ NANOCOMPOSITE FILMS : EXPERIMENT AND SIMULATION

Y.G. Shen, Y.H. Lu, and Z.-J. Liu, Department of Manufacturing Engineering & Engineering Management, City University of Hong Kong, Kowloon, Hong Kong.

Titanium-boron-nitride films deposited onto Si (100) at room temperature with different boron contents by reactive unbalanced close-field magnetron sputtering have been analyzed by a combination of high-resolution transmission electron microscopy, x-ray photoelectron spectroscopy, and x-ray diffraction. Microstructure studies revealed that incorporation of boron (up to about 19 at.%) into a growing TiN film formed a two-phase nanocomposite structure, showing nanocrystalline (nc-) Ti(N,B) grains with a [111] preferred orientation embedded in amorphous (a-) TiB₂ matrices. As the B content further increased to about 27 at.%, nc-Ti(N,B) grains became smaller and separate, accompanying with the formation of a-BN. Simultaneously their preferred orientations gradually transformed from [111] to a mixture of [111] and [200]. When the B content reached about 42 at.%, the distribution density of nc-Ti(N,B) rather than grain size decreased, nc-Ti(N,B) grains with a mixed preferred orientation of [111] and [200] were embedded in a-(TiB₂, BN). Using Monte Carlo simulations, the effects of the amorphous TiB₂-BN phase on the microstructure evolution and grain growth in nanocrystalline-Ti(N,B) were also studied. The results indicated that the formation of such an amorphous phase at the grain boundary could hinder the growth of Ti(N,B) grains and the mean grain size showed an exponential decay with boron concentration, in good agreement with our experimental observations.

10:20

BREAK

Session XII : Adhesion of coatings

Session chairs : F. Maury (INP Toulouse, France)

N. Radic (Ruder Boskovic Institute, Zagreb, Croatia)

K-XII.1 10:40

MULTI-SENSOR TECHNOLOGY FOR SCRATCH, ADHESION, AND DURABILITY CHARACTERIZATION OF THIN FILM COATING

J. Xiao, N. Gitis, and M. Vinogradov, Center for Tribology, Inc., Campbell, CA, USA.

Numerous durability tests have been performed on the precision micro-tribometer UMT, which allows for evaluation of both adhesion/delamination and wear/scratch aspects of the coating durability. The tests included various upper tools like hard tungsten carbide ball, ceramic balls, pins, blades and diamond stylus, in such testing modes as uni-directional or reciprocating linear and rotational motions. Multiple test parameters were monitored in-situ, simultaneously at a high sampling rate, including new developed contact and surface electrical resistance, servo-controlled vertical load, lateral friction force, and high-frequency contact acoustic emission.

The experimental results include comparison of diamond-like carbon coatings of different thickness levels for magnetic disk, comparison of diamond-like carbon coatings of different deposition process on indium tin oxide film for LCD display, and comparison of indium tin oxide coatings of different deposition process on polyethylene terephthalate for LCD display. The multi-sensing technology allowed for comprehensive characterization of the scratch, adhesion and durability of thin coatings. Keywords: durability, scratch, adhesion, coatings, multiple sensors, disk, LCD.

K-XII.2 11:00

OPTIMIZATION OF ADHESION AND RESIDUAL STRESSES IN THERMALLY SPRAYED COATINGS

S. Guessasma(a) and D.H. Bassir(b), (a)LERMPS-UTBM, Site Sévenans, Belfort, France, (b)Institut FEMTO-ST, Département LMARC, Université de Franche Comté, Besançon, France.

This study deals with the effect of the process parameters on the adhesion and residual stresses of thermal sprayed alumina-titania coatings. Process parameters affecting the adhesion property were varied taking into account cooling system, energetic parameters and injection parameters of the atmospheric plasma spraying technique. Experimental results were correlated to the residual stresses as they might have significant influence on the adhesion property, especially in the case of ceramic materials. The correlations were established using a robust statistical analysis method based on hybrid optimization algorithm that uses neural networks and genetic algorithm with parallel selection. Finally, the efficiency of the developed approach was validated using a design of experiments.

K-XII.3 11:20

INVESTIGATION OF HIGH POWER IMPULSE MAGNETRON SPUTTERING PRE-TREATED INTERFACES FOR ADHESION ENHANCEMENT OF HARD COATINGS ON STEEL

M. Lattemann(a), P.A.O. Persson(a), J. Bohlmark(a), U. Helmersson(a), and A.P. Ehiasarian(b), (a)Linköping University, Linköping, Sweden, (b)Sheffield Hallam University, Sheffield, UK.

In order to improve the adhesion of hard coatings (CrN, TiN) a surface pre-treatment by the novel HIPIMS technique followed by reactive unbalanced d.c. magnetron sputtering deposition was performed using a metal target (Cr, Ti). The HIPIMS plasma comprising a high metal ion-to-neutral ratio consisting of single and double charged metal species identified by mass spectrometry increased the metal ion flux to the substrate. When applying a substrate bias higher than -400 V the adhesion was enhanced due to sputter cleaning of the surface and metal ion intermixing in the interface region. This intermixing resulting in a gradual change of the composition is considered to enhance the adhesion of the hard coatings on steel substrates. During the pre-treatment, HIPIMS was operated with a peak voltage applied to the metal target of up to 2.4 kV corresponding to a peak power density of about 3 kWcm⁻² and a duty cycle of <1%. The pretreatment was carried out in an inert gas atmosphere at a set of pressures between pAr=1-10 mTorr, the duration was varied between 5 and 75 min, whereas the substrate bias was varied between -400 V and -1200 V. The adhesion was found to be depending on the substrate bias as well as on the target power and, for low substrate bias, on the duration of the pre-treatment. For TiN and CrN the critical load of failure determined in scratch test could be increased by a factor of about 3 to 4 in comparison to conventional Ar etching. The influence of the target peak voltage, the substrate bias as well as pre-treatment time on the constitution and morphology of the interface after the pre-treatment is discussed applying scanning transmission electron microscopy (STEM) and atomic force microscopy (AFM) as analysis methods.

K-XII.4 11:40

XPS STUDY OF THE DLC/Ti AND DLC/a-Si INTERFACES

S. Meskinis, V. Kopustinskas, K. Slapikas, M. Andrulevicius, and S. Tamulevicius, Institute of Physical Electronics of Kaunas University of Technology, Kaunas, Lithuania.

In this study ultrathin diamond-like carbon (DLC) films have been grown onto the titanium and amorphous silicon (a-Si) overlayers by direct ion beam deposition using acetylene gas as a hydrocarbon source. Ti and a-Si film has been used as the most common adhesion increasing interlayer for DLC coating deposition onto the steel. X-ray photoelectron spectroscopy (XPS) was used for study of the DLC-Ti and DLC-Si interfaces.

There were revealed, that a-Si is good interlayer for improvement of the adhesion in the case of the diamond-like carbon films deposition onto the steel substrate at room temperature. Formation of the Si-C interlayer (few monolayers thickness) at interface and growth of the diamond like carbon film was observed. From the other hand adhesion between the Ti interlayer and diamond like carbon film depended onto the structure of the Ti thin film and mechanical stress in it. Bad adhesion between the deposited DLC film and Ti interlayer was observed despite formation of the TiC. From the other hand, formation of the TiO₂ wasn't obstacle for good adhesion.

K-XII.5 12:00

THE INFLUENCE OF Cr-BASED COATINGS ON THE ADHESION FORCE BETWEEN EPOXY MOLDING COMPOUNDS AND IC ENCAPSULATION MOLD

Sung-Mao Chiu, Institute of Materials Science and Engineering, National Sun Yat-Sen University, Kaoshiung, Taiwan.

IC encapsulation molds have been coated with electroplated hard chromium traditionally, while need to promote the surface properties like anti-sticking, wear resistance and corrosive resistance when using environmental friendly epoxy molding compounds (EMC). In this paper, the surface properties of physical vapour deposition (PVD) Cr-based coating is evaluated not only in the laboratory stage but also in the industrial production lines.

The sessile-drop technique, Atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), low-angle X-ray diffraction and transmission electron microscopy (TEM) were used to characterise properties of PVD Cr-based coating. The adhesion force between mold surface and EMC was measured by newly design automatic EMC adhesion force test instrument. By using Taguchi's method, we could determine what parameters are important for reducing the magnitude of adhesion force between EMC and mold surface. The unbalanced magnetron sputtering PVD technique allowed to deposit bcc Cr, hcp Cr₂N, and fcc CrN phases individual. Suitable control CrN_x phase and surface morphology of coatings had the highest contact angle with water, which reached as high as 110°. The contact angle with water only had 72° for electroplated hard chromium. The polar component of surface energy played the predominant factor for hydrophobic property of coatings. The most significant factors affected adhesion force between EMC and mold surface as the surface treatment, surface roughness, and resin preheating time. The experimental results indicated the surface energy of coating has closely relation with hydrophobic property and adhesion force. In the industrial evaluation, PVD Cr-based coatings could increase 50% of molding shots in the IC package production lines.

12:20

LUNCH

Session XIII : Mechanical properties of coatings and thin films

Session chairs : D. Leinen (University of Malaga, Spain)

G. Radnoczi (RITPMS, Budapest, Hungary)

K-XIII.1 14:00

INFLUENCE OF APPLIED BIAS ON THE STRUCTURAL AND MECHANICAL PROPERTIES OF TUNGSTEN OXYNITRIDE FILMS DEPOSITED BY D.C. SPUTTERING

N.M.G. Parreira, N.J.M. Carvalho, and A. Cavaleiro, ICEMS – Dep. of Mechanical Engineering, University of Coimbra, Portugal.

In the moment, the research on reactive sputtering process concerns the application of a single target and dissimilar reactive gases to deposit coatings with a large span of properties. Specifically, when nitrogen and oxygen are used as reactive gases, it is possible to prepare coatings with a large range of optical and mechanical properties.

This study consists of preparing tungsten oxynitride coatings by d.c. reactive sputtering mode using a tungsten target and a reactive atmosphere constituted by argon as sputtering gas and oxygen and nitrogen as reactive gases. The main goals of this work concerns the characterisation of WO_xN_y thin films as a function of their metalloid element (O/N) concentration and the study of the influence of bias on the structure, morphology, and mechanical properties. The coatings were prepared in order to cover a wide range of chemical compositions from 0 to 75 % at. of oxygen and from 0 to 55%at. of nitrogen analysed by electron probe microanalysis. The content of metalloid elements is related to the applied bias for a constant partial pressure, where it is observed a decrease with the increase of bias. The structure of the coatings was investigated by X-ray diffraction. For low O/N content (< 20%) a solid solution of a-W was observed. With the increasing of the O/N ratio the structure started to become amorphous, and for higher contents in the system W-O a nanocrystalline structure was observed, whereas in the W-N system the phase β-W₂N was detected. The mechanical properties (hardness and Young's modulus) were evaluated by depth sensing indentation and the values range between 6 and 20 GPa in the system W-O and between 20 and 40 GPa in the system W-N. Further, the cohesion/adhesion of the films was investigated using a scratch-test apparatus.

K-XIII.2 14:20

COMPARISON OF STRUCTURE AND MECHANICAL PROPERTIES OF SiO₂-LIKE FILMS DEPOSITED IN O₂/HMDSO PULSED AND CONTINUOUS PLASMAS

A. Bousquet(a), V. Bursikova(b), A. Gouillet(a), A. Djouadi(a), L. Zajickova(b), and A. Granier(a), (a)LPCM-IMN, Université de Nantes, France, (b)Department of Physical Electronics, Masaryk University, Brno, Czech Republic.

In many applications (ophthalmic lenses, car headlights...), silicon oxide films are used as protective coatings in order to improve the mechanical properties of polymers. The Plasma Enhanced Chemical Vapour Deposition (PECVD), which allows deposition of dense films at temperature near the ambient, is particularly relevant for this. In this work, SiO₂-like films have been deposited in a helicon reactor operated in inductive mode at low pressure with O₂/HMDSO mixture. We compared films obtained with an input power 100%rectangular-wave modulated at 50Hz (pulse mode) or applied continuously (continuous mode).

Ellipsometry and infrared spectra confirm both samples are SiO₂-like films, transparent in visible, with refractive index ($n = 1.46$ at 1.95eV) close to the thermal oxide one. Good mechanical properties are observed for both films from the depth sensing indentations by Fischerscope tester. The plastic hardness is found to be 12.5 and 11 GPa for films deposited in continuous and in pulse mode respectively, whereas the elastic modulus is the same (78GPa). In continuous mode, the hardness value obtained is higher than the fused silica one (10GPa) which is explained by a high compressive stress of 185MPa, as determined from reflectometry measurements. Plasma pulsing allows to reduce this compressive stress to 95MPa. Moreover, both films present a good resistance to delamination. On the AFM micrographs, one can observe a buckling around the indentation print due to the compressive stress in films. The interfacial fracture toughness can be estimated from the radius of the delaminated area and linked to the stress measurements.

K-XIII.3 14:40**THE ROLE OF PSEUDOMORPHIC STABILIZATION IN CRYSTAL STRUCTURE AND MECHANICAL PROPERTIES OF NANOCOMPOSITE THIN FILMS**

G. Allidi, R. Sanjines, and A. Karimi, IPMC, Faculty of Basic Science, Swiss Federal Institute of Technology (EPFL), Lausanne, Switzerland.

As the dimensions of materials are reduced to the nanometer scale, the stabilization of pseudomorphic crystal structures that differ from their bulk equilibrium phases can occur. The pseudomorphic growth is well documented in nanolayered thin films and recognized to provide a substantially larger bulk modulus and greater hardness than the average of the constituent materials. In this paper we show that similar mechanisms can operate in nanocomposites when the mean grain size is reduced below 10 nm. For this purpose, a series of Ti_{1-x}Al_xN films with x values up to 0.7 were deposited onto WC-Co substrates using cathodic arc plasma, and were investigated to describe mechanical properties in terms of microstructures.

Chemical composition by RBS together with HRTEM, XRD, and SAD analysis showed that for the Al content below $x = 0.4$ a solid solution single-phase film is formed, while for x values beyond 0.5 mixed structures made of fcc-TiN and wurtzite AlN, or nanocomposites of fcc-TiN, fcc-AlN, and wurtzite AlN appeared depending on deposition conditions. Hardness of solid solution films was found to increase almost linearly with the Al content, while two opposite behaviours were distinguished for higher values of Al. Hardness rapidly decreased according to the rule of mixture as soon as solid solution phase began to separate into TiN and AlN growing in their natural structures with misfit dislocation at the interface to relieve the strain. In contrast, further hardness enhancement was measured when nanocomposite with coherent interfaces were formed due to pseudomorphic stabilization of fcc-AlN on fcc-TiN crystallites. In this paper different hardening mechanisms operating in solid solution and nanocomposite films will be developed and discussed.

K-XIII.4 15:00**STRUCTURE AND THERMAL STABILITY OF SUPERHARD NANOCRYSTALLINE TiAlN LAYERS DEPOSITED BY REACTIVE PULSED MAGNETRON SPUTTERING**

O. Zywitzki, H. Klostermann, F. Fietzke, and T. Modes, Fraunhofer Institut Elektronenstrahl- und Plasmatechnik, Dresden, Germany.

Stoichiometric Ti_{1-x}Al_xN layers with $0.5 < x < 0.7$ have been deposited by adjusting working point and pulse times for reactive pulsed magnetron sputtering of aluminium and titanium target. By variation of substrate bias voltage between floating potential and 80 V the hardness of the layers is drastically raised up to 38 GPa. The aim of the present work is the identification of structural reasons for the achievement of this very high hardness values. XRD investigations with grazing angle of incidence have revealed that the layers consist of two phases with predominantly cubic rock salt and minor amounts of hexagonal wurtzite structure, respectively. The structure of the layer with the maximum hardness has been additionally investigated by cross-section TEM. It can be shown that the microstructure consists of repeated interrupted columns with a lateral size of about 25 nm. Within these columns, globulitic nanocrystallites with a grain size between 6 and 12 nm are present. By electron diffraction studies it could be verified that (111) lattice planes of cubic phase and (100) lattice planes of hexagonal phase are predominantly oriented parallel to the layer surface. Further the TEM investigations have shown that the layer is characterized by alternating aluminium rich and titanium rich layers with a period of about 3 nm. It is concluded that the maximum hardness values are mainly caused by the presence of the superlattice and nanocrystalline two phase microstructure which hinders the formation and motion of dislocations. In addition, the effect of heat treatment of 1 h at 600 and 800 °C on oxidation and hardness of the layers has been investigated.

K-XIII.5 15:20**TENSILE AND COMPRESSIVE STRESS IN HARD METAL FILMS**

G.C.A.M.Janssen, Delft University of Technology, Materials Science and Engineering, Delft, The Netherlands.

Thin films on substrates are usually in a stressed state. An important, but trivial, contribution to that stress stems from the difference in thermal expansion coefficient of substrate and film. Much more interesting are the intrinsic stresses, resulting from the growth and/or microstructure of the film. Intrinsic compressive stress was explained by Francois d'Heurle in 1970. Intrinsic tensile stress for recrystallizing metal films was treated successfully by Doljack and Hoffman in 1972.

We explain the occurrence of tensile stress in non-recrystallizing metal films. The explanation is based on modern grain growth models and accurate stress measurements. The key ingredient to the explanation is the proof of the existence of a stress gradient in non-recrystallizing metal films. From a comparison of stress versus thickness to average grain size versus thickness we infer that tensile stress is generated at the grain boundaries.

In polycrystalline hard metal films the grain structure evolves during growth, leading to wider grains higher up in the film. The tensile component of the stress in the film is generated at the grain boundaries and therefore depends on film thickness. The effect of ion bombardment is independent of grain size, therefore compressive stress does not depend on film thickness. As a result in polycrystalline films deposited under a bias voltage a stress gradient exists from tensile at the interface to compressive at the top of the film. We use the distinct features of curvature stress measurements and XRD stress measurements to demonstrate the additivity of stresses caused by atomic peening and grain boundary shrinkage.

STRESS IN SPUTTERED HARD FILMS : ORIGIN AND EVOLUTION AFTER ION IRRADIATION

G. Abadías, A. Debelle, A. Michel, and C. Jaouen, Laboratoire de Métallurgie Physique, Université de Poitiers, SP2MI, Chasseneuil-Futuroscope, France.

In sputter deposited hard polycrystalline films intrinsic stresses are regularly observed associated with growth conditions. For techniques involving high energetic particles, stress is usually compressive, originating from atomic peening mechanism: the self-bombardment during growth results in excessive concentration of interstitial defects, including inert gas trapping and/or self-interstitials.

In the present study, a post-growth ion irradiation technique is employed to investigate the origin of the stress-field in ion beam sputtered overlayers. Strain measurements were performed by X- ray Diffraction (XRD) using the $\sin^2(\psi)$ method. The evolution of the $\sin^2(\psi)$ plots with ion irradiation shows that the usual assumption of a biaxial stress state is not adequate to determine the true stress-free lattice parameter of the film. A new stress model based on a triaxial state of stress, which includes a hydrostatic component linked volume distortions induced by point defects [1], is derived to interpret the XRD results. Illustration of the model is given for two types of fiber-textured layers: a hard metal (Mo) and a hard nitride (TiN) one. The more complex case of an epitaxial overlayer will also be discussed. We show that the evolution of the distinct stress components during ion irradiation differs significantly: a stress relaxation of the intrinsic growth stress (hydrostatic component) occurs with the ion dose, while the epitaxial stresses remain unaltered.

[1] A. Debelle, G. Abadías, A. Michel, C. Jaouen, Appl. Phys. Lett. 84, 5034 (2004)