Coatings for Biomedical and Healthcare Applications
Room On Demand - Session D1

Surface Coating and Surface Modification in Biological Environments

D1-1 Physical Vapor Deposition for Growth of Large Area Molecular Sensor Arrays*, N. Glavin, D. Austin, D. Moore, M. Motala,* Air Force Research Laboratory, Materials and Manufacturing Directorate, USA*; **Christopher Muratore (cmuratore1@udayton.edu),*** University of Dayton, USA

Low temperature synthesis of high quality 2D materials directly on flexible substrates remains a fundamental limitation towards realization of robust, strainable electronics possessing the unique physical properties of atomically thin structures. Here, we describe room temperature synthesis of uniform, stoichiometric amorphous MoS_2, WSe_2, and other transition metal dichalcogenides and subsequent large area (>5 cm^2) photonic crystallization to enable direct fabrication of devices based on two-dimensional materials on large area flexible or rigid substrates. Fundamentals of crystallization kinetics for different monolithic and heterostructured TMDs are examined to apply this new synthesis approach for affordable, wearable devices. Example devices include photodetectors with photocurrent output and response times comparable to those fabricated via CVD and exfoliated materials on rigid substrates and the performance is unaffected by strains exceeding 5%. Flexible molecular sensors fabricated in this way detect diverse vapor phase substances with sub-ppm sensitivity. Functionalization of laser-written 2D TMD sensor transducers is also demonstrated for healthcare applications. Other devices and circuits directly written from photonically annealed monolithic TMDs thin films deposited on large area flexible substrates, with no photolithography or patterning, are also presented.

D1-2 Mesenchymal Stem Cells Response to Metal Oxide Thin Films*, **Phaedra Silva-Bermudez (phaedrasilva@yahoo.com),*** Instituto Nacional de Rehabilitación Luis Guillermo Ibarra Ibarra, Mexico*; M. Fernández-Lizárraga,* Escuela Nacional de Ciencias Biológicas, Instituto Politécnico Nacional, Mexico*; S. Rodil,* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico*; J. Garcia-Lopez, R. Sanchez-Sanchez,* Instituto Nacional de Rehabilitación Luis Guillermo Ibarra Ibarra, Mexico

Biomaterials with adequate surface properties to direct the biological response and appropriate bulk properties to meet the biomechanical requirements of bone regeneration applications are essential for orthopedic and dental implants. Mechanical and biodegradation properties are mainly determined by the bulk properties while the biological response is mainly directed by the surface properties. Thus, coatings are interesting options to tailor/functionalize the surface of mechanically adequate bulk materials, to direct the biological response towards enhanced osteoinduction and/or osteointegration. Biocompatible metal oxides such as ZrO_2, Nb_2O_5 and Ta_2O_5 are of great interest as coatings for orthopedic and dental implants. It has been shown that they decrease the biocorrosion of different materials, and they might induce adequate osteointegration and enhanced mesenchymal stem cells (MSC) differentiation towards the osteoblastic phenotype (osteoinduction), in the same way as it has been proved for TiO_2.

Thin films of TiO_2, ZrO_2, Ta_2O_5 and NO_2O_5 were deposited on Si(100) substrates as a model to study the potential of these oxide as biocompatible coatings capable of modulating the biological response. Thin films were deposited from pure metallic targets by reactive magnetron sputtering, under an Ar/O_2 (80:20) atmosphere and using RF-power. The roughness and topography of the coatings were characterized by profilometry and Scanning Electron Microscopy. The surface energy and water wettability were determined by contact angle measurements. To characterize the biological response of the oxide coatings, human MSC were independently plated on bare and oxide-coated Si(100) substrates and cultured at 37 °C, changing the culture media every three days. Cell viability and metabolic activity were assessed at different days of culture using the Calcein-AM/Ethidium homodimer fluorescent kit and the MTT-Formazan assay, respectively . To evaluate early-stage cell adhesion, cells seeded on the samples were harvested after 1 and 4 h of incubation and DNA was isolated and quantified. At 7 days of culture, cells on independent samples were fixed, dehydrated and evaluated by SEM. Potential cell differentiation to the osteoblastic phenotype was assessed at culture day 7 by immunofluorescence assays against characteristic markers of the osteoblastic phenotype such as, osteocalcin and RUNX2. Phosphatase alkaline assays in cells culture supernatants were also performed. Metal oxide coatings studied were biocompatible; however, r esults suggested that number of cells adhered on the substrate and cell differentiation were dependent on the coatings physicochemical properties.

D1-3 Behavior of a-C:H with Different fs-laser Micro-Patterns against Diamond Tip in Hyaluronic Acid*, **Annett Dorner-Reisel (a.dorner-reisel@hs-sm.de),*** Schmalkalden Universtity of Applied Sciences, Germany*; S. Svoboda,* Schmalkalden University of Applied Sciences, Germany*; A. Engel,* University of Applied Sciences Mittweida*; C. Schürer,* Consultant Chemnitz*; S. Weißmantel,* University of Applied Sciences Mittweida, Germany

Surface micro-patterns like riffles, dimples, grooves can stimulate or supress special interaction with liquids and functionalize surfaces. They can act as reservoir for substances or trap undesired wear particles. In addition, laser treatment kill bacteria and clean surfaces, which is an important aspect in providing medical product to the market.

In nature, many surfaces obtain micrpatterns, like leaves of the lotus plant or cactus family.

Micro-patterns are generated on hydrogenated diamond-like carbon films by femtosecond-laser (fs-laser) irradiation (1028 nm, 220fs). Dimples with a spatial distance of 60 µm were generated. The parameters like fluence H (H: 1.71J/cm^2 or 3.70 J/cm^2) pulse repetition or duration were modified. In addition, a ripple structure (H: 3.03 J/cm^2; 220 fs) was generated. The structural changes are recorded by Raman spectroscopy earlier, while nanotribology was performed for investigating the sliding properties of the micro-patterned a-C:H surfaces. In addition to dry movement for testing the emergency operation, hyaluronic acid is used as an intermediate substance for testing the friction behaviour against a diamond tip in the present study. First impressions about potential interaction of carbon allotropes with hyaluronic acid are discussed.

D1-4 Analysis of a Drug Coated Polymer Stent with XPS and Argon Cluster Depth Profiling*, **David Surman (dsurman@kratos.com),*** Kratos Analytical Inc., USA*; J. Counsell,* Kratos Analytical Ltd., UK*; M. Alexander,* University of Nottingham, UK

The application of cardiovascular stents for cardiovascular interventional therapy has emerged as the most effective method to treat coronary heart disease. Used to widen blocked or narrow coronary arteries by the insertion of a small tube into the vessels supplying blood to the heart, stents permanently allow blood to flow more freely. Cardiovascular stents were originally made from steel, however, they created issues for patients with thrombosis and hyperplasia being the usual pathological responses to the implantation of foreign devices. Despite recent advances in the field leading to the introduction of a new range of stents made from bioresorbable polymers, the undesirable problems associated with the original steel stents, such as thrombosis and hyperplasia, still remain. With these issues proving unavoidable despite the change in material, along with additional problems of overgrowth and subsequent restenosis, anti-inflammatory drugs are now loaded onto the surface of stent implants to suppress this immune response.

Here, we investigate the surface of a drug loaded polymer stent using X-ray Photoelectron Spectroscopy (XPS) and sputter depth profiling with Ar_n^+ clusters. The stents analyzed are composed of Polylactic Acid (PLA) where the outside surface has been doped with an anti-inflammatory drug. With the molecular structure of the drug being $C_{51}H_xNO_{13}$, nitrogen can be used as a marker to analyze the distribution of the drug across this stent surface. Quantitative XPS analysis concludes the drug distribution is higher on the abluminal (outer) surface than the luminal (inner) wall of the stent. Combining Argon cluster sputtering with XPS allows the distribution of the drug through the entire stent material to be fully characterized.

Conventional methods to study the effects of aging and drug mobility in these stents involve their immersion in a buffer solution for varying periods of time. Subsequent analysis of the solution with High Performance Liquid Chromatography (HPLC) can determine the extent of drug dissolution from the stent. Although this approach is accurate in determining the amount of drug dissolved, it is still unknown how much drug remains within the stent material and how it is subsequently distributed. These questions are addressed in this study where the bioresorbable stent had been immersed in PBS buffer solution for 1-3 months. Ar_n^+ cluster depth profiling of the stent materials was then used to determine the effects on simulated ageing and the propensity for the drug to migrate into the solution with time.

D1-5 Flexible Plasma Jet Source for Biomedical Applications*, Carles* ***Corbella (ccorberoc@gwu.edu)****, S. Portal, L. Lin, M. Keidar,* George Washington University, USA

A new plasma source design that merges characteristics of capacitive dielectric barrier discharge (DBD) and cold atmospheric plasma jet (CAPJ) is presented. The DBD system consists of a porous ceramic material comprised between two planar electrodes. The supply of He flow, in combination with a sinusoidal voltage of ≈5 kV in amplitude and 12.5 kHz in frequency, provides a streamer that propagates beyond the DBD system. The plasma jet system can adopt different shapes with the aim of uniform surface treatment of 3D objects. Aspects like CAPJ extension, performance and lifetime of the plasma device are discussed in this paper. The composition and discharge parameters of the CAPJ are characterized by means of optical plasma diagnostics. Finally, we consider applications in plasma-based cancer surgery, as for example treatment of surgical margins. This novel source is also suitable for situations where plasma parameter adaptation to the environment (atmosphere and target surface) is required.

D1-6 INVITED TALK: Embroidery of Conductive E-Threads: Opportunities and Challenges in Healthcare*, Z. Dalisky, S. Alharbi, V. Mishra,* ***Asimina Kiourti (kiourti.1@osu.edu)****, K. Guido,* The Ohio State University, USA **INVITED**

Rapid advances in bio-electromagnetics and flexible materials are opening unexplored opportunities in body area sensing. Next-generation wireless devices are envisioned that operate either upon or inside the human body and aim to break the state-of-the-art boundaries in terms of seamlessness, capabilities, and performance. To this end, embroidery of conductive threads (namely e-threads) is showing unprecedented potential. Technologies used to realize flexible conductors have long been reported (e.g., conductive inks, conductive fabrics, copper tape), but they exhibit numerous limitations in terms of electromagnetic and mechanical performance. By contrast, our e-textile technology brings forward numerous advantages: (a) the exhibited Radio-Frequency performance matches that of copper up to a frequency of ~4 GHz, (b) prototypes are mechanically and thermally robust, and (c) the printing resolution can be as high as 0.1 mm. Added to the above, polymer-based coatings can readily be integrated with such embroidered surfaces to serve numerous roles per applications requirements. For example, polymer-based substrates can be used to realize flexible multi-layer antennas, circuits, and transmission lines. In other cases, polymer-based superstrates can ensure biocompatibility of wireless textile-based implants or simply protect the exposed e-textile surface from corrosion and weathering. Finally, polymer-based coatings can help realize stretchable prototypes that stretch along with the polymer. Overall, embroidered e-textiles bring forward transformational opportunities in healthcare. Example applications explored to date include, but are not limited to, kinematics monitoring, medical imaging, deep brain sensing, recumbent height monitoring for infants, etc. This talk will present the current status on e-textile embroidered electronics, highlight opportunities in healthcare, and discuss challenges to be resolved in the future.

Coatings for Biomedical and Healthcare Applications
Room On Demand - Session D2

Bio-corrosion, Bio-tribology and Bio-Tribocorrosion-Additive Manufacturing Impact

D2-1 INVITED TALK: Behavior Of Additively Manufactured 316L Stainless Steel Fabricated By Selective Laser Melting In Comparison To Wrought 316L And 317 L Stainless Steels*,* ***Mobin Salasi (mobin.salasi@curtin.edu.au)****, K. Wang, E. Hornus,* Curtin University, Australia*; M. Pabbruwe,* Curtin University, Royal Perth Hospital, Australia , Australia*; T. Pojtanabuntoeng,* Curtin University, Australia , Australia*; M. Iannuzzi, Z. Quadir, W. Rickard,* Curtin University, Australia*; M. Salem, P. Lours,* Ecole de Mines Albi, France*; J. Bougoure,* Curtin University, Australia , Australia*; P. Guagliardo,* Curtin University, Australia **INVITED**

Selective laser melting (SLM) is a type of additive manufacturing (AM) with applications in, e.g., the biomedical and aerospace industries. Studies have been carried out on the localised corrosion behavior of SLM fabricated 316L (UNS S31603) stainless steel. Little is known, however, on the effects of tribocorrosive conditions on the response of stainless steels fabricated by SLM. In orthopedics applications, for example, it is known that the alloys often encounter different modes of tribocorrosion. In this research, the effects of abrasive particles on the tribo-electrochemical behavior of AM 316L (UNS S31603) stainless steel produced by SLM was investigated.

Two series of as-printed and solution annealed samples were first characterized using scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Then, the corrosion-only behavior of these samples was investigated by cyclic potentiodynamic polarization in a 0.6 M NaCl electrolyte. The corrosion resistance of SLM fabricated 316L (UNS S31603) was compared to that of wrought UNS S31603 and S31703 stainless steels in the same environment. Three-body tribocorrosion tests were performed with silica sand abrasive particles, delivered to the interface of the sample and a rotating rubber counterface. Additionally, cyclic and potentiostatic polarization methods were used to gain a better understanding of the interaction between corrosion and abrasion. Lastly, the microstructure and the morphology of the tribocorroded regions were characterized using focused ion beam (FIB-SEM).

It was found that presence of Mo had a much more effective role in the tribocorrosion behavior than the manufacturing method. To understand the role of Mo nano-scale secondary ion mass spectroscopy (nanoSIMS) were used to understand the effects of Mo on the passivity. The implication of passivity and tribocorrosion behavior is discussed.

Key words: additive manufacturing, tribocorrosion, polarization

D2-3 Sputtered Thin Film Systems As Anode Materials for Biodegradable Battery*,* ***Waseem Haider (haide1w@cmich.edu)****,* Central Michigan University, USA

The biodegradable battery is a promising choice to provide power to implantable medical devices. However, the anode material in such batteries, usually Mg or its alloys, suffer from parasitic hydrogen evolution and faster discharge kinetics that limits the lifet ime of these devices. In the pursuit of finding a better anode material, herein, the idea of combinatorial development is employed to fabricate a material having a good combination of corrosion resistance properties and discharge characteristics by exploring a wider $Mg_{100-x}Zn_x$ (0 < x < 50 at.%) system. Structural characterization of the Mg-Zn systems via X-Ray Diffraction manifests range of microstructures dictated by percent species and sputtering conditions. The corrosion investigation of the systems is done using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) in a conventional three-electrode configuration. Additionally, the discharge performance of the Mg-Zn anode systems is investigated, coupled with sputtered iron as the cathode in Phosphate Buffered Saline (PBS) solution as the electrolyte. The EIS and galvanostatic discharge tests reveal that discharge performances of the anode materials can be effectively tailored via a prudent design of alloy composition and microstructure.

D2-4 In Vitro Degradation of ZrO_2 Coated Magnesium Alloys*,* ***Benjamin Millan (bmillan@ciencias.unam.mx)****,* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México*; O. Depablos-Rivera,* Universidad Nacional Autónoma de México, México*; P. Silva-Bermudez,* Instituto Nacional de Rehabilitación Luis Guillermo Ibarra, Mexico*; S. Rodil,* Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico

The main limitation of the Mg-based alloys as a biodegradable implant material for bone repair application is

their rapid corrosion rate, especially in solutions containing chloride, including human body fluid and blood plasma. The initial fast degradation lead to the production of H2 bubbles and pH changes that affect the surrounding tissue. The long-term degradation of Mg-based implant materials induces a loss of their mechanical strength and integrity before the recovery of newly formed bone.

Different strategies have been applied to improve the corrosion resistance of Mg-based alloys, and some s urface modifications, such as the use of thick polymeric or ceramic-based coatings, have proven to be effective.

In this work, we evaluated the effect of dense but thin ZrO_2 coatings on optimized MgZnCa alloys. ZrO_2 coatings were chosen due to their excellent biocompatibility, good corrosion resistance and potential to induce osteoblasts differentiation.

The ZrO_2 coatings were deposited on 2 x 2 cm^2 MgZnCa pieces by reactive magnetron sputtering under Ar/O_2 atmosphere, at a deposition pressure of 4 Pa and RF power of 200 W. Thicknesses between 100-300 nm were evaluated. The in vitro corrosion of the uncoated and coated samples was evaluated by measurement of the open circuit potential at long immersion times, potentiodynamic polarization and electrochemical impedance spectroscopy in a 0.89 wt% NaCl solution. A reduction in the corrosion current density of 50% was achieved, without observing significant changes in the corrosion potential. The electrochemical response was compared to the degradation rate measured by immersion tests.

D2-5 In Solution, A New Representation to Link the Corrosion Degradation Consistent with Wear: Smooth and Hard Coatings are Well Discriminated.*, Jean Geringer (geringer@emse.fr), A. Boyer,* Mines Saint-Etienne, France*; H. Ding, V. Fridrici, P. Kapsa,* Ecole Centrale de Lyon, Ecully, France*; T. Tayler, L. Semetse, P. Olubambi,* University of Johannesburg, South Africa

Prosthetic hip joints are nowadays common issues due to people aging. Restoring gait is a heath issue from the patient benefits and the economical one. Due to taper junction manufacturing process some corrosion and fretting corrosion (friction under small displacements, lower than 100 micrometers) issues are appearing concerning the implants lifetime. In this study we are suggesting a not well used representation concerning the efficiency of connections under fretting corrosion solicitations. The usual wear volume vs. Dissipated energy might be investigated but highlighting protective coatings is failing. Wear volume vs. open circuit potential drop (first hundred seconds of fretting) is classifying clearly every coating on metallic material. However another issue is coming related to stick/slip during the fretting process. Finally the wear volume is replaced by the A ratio, dissipated energy over total energy. When some stick, even under high normal load, is occurring, A ratio is decreasing and there is no relative displacement between materials in contact. Various combinations of materials/coatings have been investigated and the evolutions seem evoluate consistently. Some improvements are needed to confirm the tendency.

Coatings for Biomedical and Healthcare Applications
Room On Demand - Session D3

Biointerfaces: Improving the Cell Adhesion and Avoiding Bacteria. What Kinds of Coatings/Surfaces Should be Used?

D3-1 Very Thin Gold Films Deposited Collagen to Improve Skin Wound Healing in Animal Study*, Sheng-Yang Huang (huangmochiqqegg@gmail.com),* Feng Chia University, Taichung Veterans General Hospital, Taiwan*; P. Hsieh, R. Chang,* Feng Chia University, Taiwan*; C. Chou,* Taichung Veterans General Hospital, National Yang-Ming University, Taiwan*; C. Chung,* Central Taiwan University of Science and Technology, Taiwan*; J. He,* Feng Chia University, Taiwan

Collagen has been widely used in different forms for biomedical purposes. In combination with gold element, it may bring synergistic effect for more precise therapy. In this study, very thin gold film deposition on collagen fabric was conducted by high-power impulse magnetron sputtering (HIPIMS). Specimens with different deposition time (0, 6, 12, 24, 48 and 96 seconds) were prepared. Animals of 175-200 gm Sprague Dawley (SD) male rats were chosen for skin wound healing test and grouped according to the created full thickness wounds of back skin. In the experimental group, wounds were covered with coated collagen specimen and sterilized gauze, while wounds were covered with sterilized gauze only in control group. Visual observation for wound recovery was done during renewing dressing on a daily base. Histology study of wounded skin was performed on post-operative day 3, 7 and day 14. In addition to morphological observation, scoring of wound healing, consisting of neovascularization, collagen deposition and inflammatory cell infiltration was also calculated and compared. The results showed that an improved wound healing and less soft tissue fibrosis can be observed in the presence of very thin gold film. This animal study reveals that the use of such gold coated collagen material on skin wound is beneficial and promising.

D3-2 New Cytocompatible and Antibacterial Porous Ta_2O_5 Surface: Dental Implant Prototype*, Luísa Fialho (luisa.gfialho@gmail.com),* University of Minho, Portugal*; L. Grenho,* university of Porto, Portugal*; M. Fernandes,* University of Porto, Portugal*; L. Forte Martins,* Private dental practice - Dental Verde clinic, Portugal*; S. Carvalho,* University of Minho, Portugal

An innovative surface able to overcome the failures of the dental implants used nowadays, regarding their bioactivity and consequent capacity for osseointegration, was developed. The first functional treatment (plasma electrolytic oxidation (PEO)) develop a tantalum oxide (Ta_2O_5) surface in order to mimic the bone morphology and chemistry and consequently enhancing the surface bioactivity. Thereby, the anodizing parameters were optimized in order to achieve a porous structure enriched with calcium (Ca) and phosphorous (P), such as Ca/P ratio near to 1.67 (theoretical value of hydroxyapatite). The second treatment endows this surface with antibacterial activity. With this purpose, zinc nanoparticles (Zn NPs) were deposited onto the bioactive surfaces by DC magnetron sputtering with (or without) an additional thin carbon (C) layer, for NPs release control.

The morphological analysis by SEM and STEM revealed the formation of a micro/nano-porous oxide layer with incorporation of Ca and P. The deposition of Zn NPs did not affect the surface morphology and the NPs were around and inside the pores. The additional presence of the C layer slightly covered the nano-pores. The BF-STEM results showed that the Zn NPs had irregular shapes and a core-shell structure with two crystalline phases: HCP Zn and ZnO. The initial osteoblasts adhesion was ensured with a significant proliferation on the surface with Zn NPs. The surfaces with Zn NPs substantially reduced the planktonic bacterial with a greater sessile bacteria inhibition on the surfaces.

Furthermore, a preliminary prototype was created. A PEO-optimized Ta dental implant was developed to reproduce the bone surface morphology and chemical composition. Then, the Ta implants were inserted onto a pork jawbone and, by SEM and X-rays analysis, the surface fracture was analysed. The results showed a good adhesion and mechanical resistance of the anodic layer.

In sum up, these findings are promising for biomedical applications.

Keywords: tantalum oxide; zinc oxide nanoparticles; plasma electrolytic oxidation; magnetron sputtering; antibacterial activity; cytocompatibility.

Coatings for Biomedical and Healthcare Applications
Room On Demand - Session DP

Coatings for Biomedical and Healthcare Applications (Symposium D) Poster Session

DP-1 Optimisation of Electrolytic Plasma Oxidation (PEO) Coatings Formed on Magnesium for Biological Applications*, Yue Guo (yue.guo-2@manchester.ac.uk), A. Rogov, B. Mingo, A. Matthews, A. Yerokhin,* The University of Manchester, UK

Magnesium has shown great potential for the next generation of resorbable implant materials. It has well biocompatibility and biodegradability, high strength-to-weight ratio and stiffness similar to that of the human bone. However, magnesium exhibits poor corrosion behaviour, leading to the early deterioration of the implant. Therefore, appropriate surface treatments have to be applied to improve the corrosion resistance of magnesium.

Electrolytic Plasma Oxidation (PEO) is a plasma-assisted technique to form ceramic-like coatings containing oxides comprising constituents of both the parent metal and the electrolyte. PEO coatings can increase corrosion resistance and mechanical properties of the metal substrate, improving the longevity and reliability of the implant. Furthermore, the coating properties can be adjusted by tailoring parameters of the PEO process, such as electrolyte composition and pulsed electrical regime. Previous studies have been mainly focused on the influence of current density, frequency and duty cycle of rectangular pulses, whereas very few works were dedicated to the influence of the pulse shape.

The objective of this work is to investigate a possibility of increasing the corrosion resistance of PEO coatings on Mg by tailoring the current pulse shape. Triangular pulses are given particular attention in comparison with the commonly used rectangular shapes. Two types of rectangular pulses are generated – a Slow ON pulse, where the applied current increases linearly at a certain rate followed by an instant drop of the current; and a Slow OFF pulse, where the applied current increases instantly before decreasing linearly. Characteristics and properties of the coatings produced under different waveform are thoroughly studied. Corrosion tests are performed to evaluate the corrosion resistance. The results have shown a positive effect of the Slow OFF pulse. A more uniform and defect-free coating surface morphology is obtained. The coating exhibits higher corrosion resistance correlated to the better morphology.

DP-2 The Property of Adhesion and Biocompatibility of Silicon and Fluorine Doped Amorphous Carbon Films*, Masafumi Toyonaga (m.tyng.keio@gmail.com),* Keio University, Japan*; T. Hasebe,* Keio University, Tokai University Hachioji Hospital, Japan*; S. Maegawa,* Tokai University Hachioji Hospital, Japan*; T. Matsumoto,* Keio University, Tokai University Hachioji Hospital, Japan*; A. Hotta, T. Suzuki,* Keio University, Japan

Application of nickel-titaniumu (NiTi) alloys to medical implant devices is increasing due to their unique characteristics. To ensure good biocompatibility in the human body, fluorine-doped amorphous carbon (a-C:H:F) coating is a promising candidate. Generally, a-C:H:F coating shows poor adhesion on metallic alloys, so that silicon-incorporated interlayer is introduced between a-C:H:F and metallic alloys. However, this membrane design has a risk of delamination at the outermost interface (a-C:H:F // interlayer), and also there is a practical problem that coating time becomes long because the deposition process in multiple stages is required. Here we develop silicon and fluorine doped amorphous carbon (a-C:H:Si:F) film which exhibits high adhesion and excellent biocompatibility.

The a-C:H:Si:F film and a-C:H:F film (control) were deposited on NiTi substrates using radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) equipment. Chemical compositions and bonding states of the surfaces were determined by X-Ray photoelectron spectroscopy (XPS). Surface free energy was estimated based on Owens-Wendt method using the results of contact angle measurement. Nanoscratch tests were conducted in order to quantify the adhesion strength. Platelet adhesion test and leukocyte adhesion test were conducted in order to evaluate biocompatibility.

First of all, a-C:H:Si:F was deposited from a mixture of TMS ($Si(CH_3)_4$) and C_3F_8 at TMS flow rate of 6.0 sccm and C_3F_8 flow rate of 50 sccm. Although this shows the possibility of new film deposition from a mixture of TMS and C_3F_8, the adhesiveness and biocompatibility of a-C:H:Si:F were not higher than a-C:H:F with Si-interlayer. Therefore, "C_2H_2-doped" a-C:H:Si:F film, which was deposited using a mixcure of TMS, C_3F_8 and C_2H_2 at a TMS flow rate of gradually changed from 6.0 sccm to 0.0 sccm, C_2H_2 flow rate of gradually changed from 0.0 sccm to 3.0 sccm and C_3F_8 flow rate of gradually changed from 0.0 sccm to 50.0 sccm, was newly deposited and this film showed similar chemical composition, bonding state, surface free energy, and higher adhesive strength than a-C:H:F with Si-interlayer, and the same number of adhesive platelets and leukocytes as a-C:H:F.

These results demonstrated that a single film with both adhesion of Si-interlayer and biocompatibility of a-C:H:F was fabricated. Furthermore, this a-C:H:Si:F coating can be anticipated as an effective film coating method in a practical point of view, because the film deposition is completed in one process.

DP-3 *In Vitro* Study of Very Thin Gold Film Deposited Collagen Fabric*, Sheng-Yang Huang (huangmochiqqegg@gmail.com), . Hsieh,* Feng Chia University, Taichung Veterans General Hospital, Taiwan*; R. Chang,* Feng Chia University, Taiwan*; C. Chou,* Taichung Veterans General Hospital, National Yang-Ming University, Taiwan*; C. Chung,* Central Taiwan University of Science and Technology, Taiwan*; J. He,* Feng Chia University, Taiwan

The goal of this study is to test a novel collagen fabric biomedical material with very thin gold film successfully deposited by using high-power impulse magnetron sputtering (HIPIMS). Previous study show that the gold layer is morphologically tunable from island distribution to continuous layer by manipulating deposition time. Here, this study aims to explore the *in vitro* response of the specimens deposited for 0, 3, 6, 51, and 81 seconds, representing the gold layer coverage percentage from 3.07% to 51.22%, respectively. Cell attachment test based on Alamar Blueassay using WS1 fibroblast and antibacterial test based on Kirby-Bauer disk diffusion method were carried out. Experimental results reveal that the gold layer prohibits fibroblast attachment, regardless of the gold layer coverage percentage. Microscopic observation disclosed the fibroblasts inactivation on the gold layer surface. For pseudomonas aeruginosa pathogen, randomly selected specimens with 3 and 6 seconds gold deposition showed inhibition zone of 13 and 11 mm, respectively. The results of this work support the use of this biomedical material in early phase of wound healing for its evidence of fibroblast attenuation and antibacterial effects.

DP-4 e-Poster Presentation: Metallization of Polymers for Medical Applications using HiPIMS*, Aarati Chacko (aarati.chacko@empa.ch), K. Thorwarth, R. Crockett, U. Müller, H. Hug,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

In contrast to wet processes, which require toxic precursors, High Power Impulse Magnetron Sputtering (HiPIMS) is a relatively clean method to achieve polymer metallization. This makes it especially interesting for medical applications such as coating polymer implants. The large proportion of metal ions in the coating discharge, characteristic of HiPIMS, allows a high level of control over film-forming species. This physical vapor deposition method is therefore our method of choice to tailor and study the substrate-film interphase region responsible for adherent and durable coatings.

This study aims to understand the effect of oxygen plasma activation on the surface of a polymer using AFM and XPS. We then relate this to HiPIMS-metallized surfaces and interfaces using ATR-FTIR. The metal-polymer system for this study is titanium on PEEK (Polyetheretherketone), which has shown exemplary adhesion in the case of orthopedic implants for use in spinal fusion surgery. We aim to understand the interactions that lead to this good adhesion to bring further improvements, and also, translate our understanding to other metal-polymer systems.

DP-5 TiZrSiN Coatings, Structural Characterization, and Corrosion Resistance in Ringer's Lactate*, Claudia Patricia Mejía Villagrán (clapamevi21@gmail.com),* Universidad Nacional de Colombia*; M. Chellali,* Karlsruhe Institute of Technology (KIT), Libya*; C. Garzón Ospina,* Universidad Nacional de Colombia*; H. Hahn,* Karlsruhe Institute of Technology (KIT), Germany*; J. Olaya Flórez,* Universidad Nacional de Colombia*; L. Velasco Estrada,* Karlsruhe Institute of Technology (KIT), Germany

TiZrSiN coatings produced by Physical Vapor Deposition in dual condition are characterized. Power density in Zr target was adjusted at three different values (2.0 Wcm^{-2}, 2.9 Wcm^{-2}, and 3.5 Wcm^{-2}), while power density on the TiSi target was fixed (0.55 Wcm^{-2}). As a result, three types of coating were obtained; one with a mostly amorphous structure (2.0 Wcm^{-2}), one with crystalline structure with some amorphous structure (2.9 Wcm^{-2}), and a third one with mostly crystalline structure (3.5 Wcm^{-2}).

Corrosion tests using electrochemical impedance while dipping the coatings in ringer's lactate, showed that coatings with TiZrSiN demonstrate better corrosion resistance than their ZrN peers. From all studied conditions, the one with the best resistance to corrosion (2.9 Wcm^{-2}), also demonstrated the highest hardness and the best performance and stability at the tests of electrochemical impedance spectroscopy with time. The improved properties in 2.9 Wcm^{-2} condition/case are attributed to the lattice stabilization for solid solution and adequate portion of silicon content.

DP-6 A Novel Synthesis Method of Carbide Derived Carbon (CDC) Surface Modification for Hip Implants*, Yani Sun (ysun98@uic.edu),* University of Illinois at Chicago, USA*; K. Cheng, M. Mathew,* UIC College of Medicine at Rockford, USA*; M. McNallan,* University of Illinois at Chicago, USA

The inferior tribocorrosion behavior of commonly used biomedical alloys has led to the early failure of total hip replacements (THRs) and serious complications. In 2011, the tribolayer comprising graphitic carbon was found from the retrieved implant, and it was reported as solid lubrication which can reduce the friction between the femoral head and cup. Inspired by this interesting discovery, we have proposed a surface modification method, carbide-derived carbon (CDC), to mimic the tribolayer to improve the tribocorrosion resistance. The results have shown that CDC produced by direct chlorination can provide excellent protection to Ti6Al4V and has high durability.

In this study, a novel method has been developed to synthesize CDC on Ti6Al4V substrates by electrolysis from a low melting point halide salt. Compared to previous preparation processes, this newly developed approach eliminates the exposure to chlorine gas and the requirement of the inert gas environment, which makes the synthesis process more controllable and the CDC layer more uniform. X-ray diffraction (XRD), Raman spectroscopy and scanning electron microscopy (SEM) were utilized for characterization. Based on the results, the produced CDC has a porous structure which may contain nanocrystalline graphite (NCG) and amorphous carbon (a-C). The theoretical thickness of the sample is estimated by a calculation which is approximately 1.44 µm. In addition, the performance of the new coating was tested in a tribocorrosion hip simulator. A system has a pin on ball contact and immersed in bovine calf serum of 30g/L protein concentration, with a pH of 7.6 and a temperature of 37˚C. We applied a normal force of 16N to obtain a contact pressure of around 10MPa and ran the test for 3600 cycles with 1Hz. A Gamry made Potentiostat is connected to the test system, monitoring the electrochemical responses induced by the tribological activity. According to the recordings of normal and tangential forces, the evolution of the friction coefficient is deducted and reported in the results.

The findings have shown that the CDC samples prepared by the electrolysis method exhibit smaller friction coefficient (approximately 0.1), wear loss and potential drop (less than 100 mV compared to 600mV for substrate). Therefore, it is promising that the CDC prepared by the novel electrolysis approach can protect Ti6Al4V substrates from the tribocorrosive damages. For future work, we propose to conduct the adhesion test, the tribocorrosion experiments under potentiostatic mode and the biocompatibility test to fully evaluate CDC's value as a novel material for hip implants.

DP-7 Enhancing Osseointegration on PEEK Spinal Implant by Using Laser Surface Roughening and HIPIMS Titanium Coating*, **Ping-Yen Hsieh (pyhsieh@fcu.edu.tw)**,* Feng Chia University, Taiwan*; H. Tsou,* Taichung Veterans General Hospital, Taiwan*; C. Chung,* Central Taiwan University of Science and Technology, Taiwan*; J. He,* Feng Chia University, Taiwan

Current spinal interbody fusion cages are most widely adopted from polyetheretherketone (PEEK) due to its favorable biomechanical properties and X-ray radiolucency characteristics. Unfortunately, the smooth and bioinert surface of PEEK may limit the osseointegration and inhibit bone fusion. Plasma spraying, providing porous and rough titanium layer over the PEEK spinal implant, has been commercialized in clinical application though, this study aims to develop an alternative approach by firstly laser roughening PEEK surface, followed by high power impulse magnetron sputtering (HIPIMS) to deposit a strongly adhered titanium layer for improving osteointegration of PEEK spinal implant. The experimental results showed that properly controlled laser condition gives micrometer-scale topography over the PEEK surface as opposed to the smooth bare PEEK. After HIPIMS deposition, the obtained titanium film presented an adhesion of 5B grade even after immersion in simulated body fluid (SBF) environment for 28 days based on the Scotch-tape adhesion test. Such excellent film adhesion performance is ascribed to the advantage of high ion energy and high-density plasma characteristics of the HIPIMS discharge. In addition, the titanium film on roughened PEEK presented better osteoblast compatibility and osseointegration than the commercial product, so as to provide the high spine stability after implantation. Finally, the long-term assessment results revealed the high stability and no degradation concern for the modified PEEK, which can avoid the malignant reaction between implant and host to ensure the safety after implantation in the human body. In summary, the two-step surface modification on PEEK satisfy the requirements for enhancing osseointegration, suggesting clinical application consideration.

DP-8 Superamphiphobic Stainless Steel Surface Prepared by Femtosecond Laser Patterning and Pulsed Plasma-Polymerization*, C. Lin,* Central Taiwan University of Science and Technology, Taiwan*; C. Chou,* Taichung Veterans General Hospital; National Yang-Ming University, Taiwan*; **Chi-Jen Chung (cjchung@seed.net.tw)**,* Central Taiwan University of Science and Technology, Taiwan*; J. He,* Feng Chia University, Taiwan

Superamphiphobic surfaces, being super-repellent either water or oil, show various applications in self-cleaning, antifouling, non-staining surfaces, spill-resistant, corrosion prevention, and liquid separation. By employing femtosecond laser patterning and pulsed plasma polymerization, this study developed a dual-technique of surface modification to obtain superamphiphobic surfaces on the AISI 304 stainless steel substrates, usually made into dental archwires in orthodontics and dentofacial orthopedics. The characteristics of the superamphiphobic surfaces and *in vitro* wear tests in artificial saliva that mimicked tooth brushing, peanut-chewing, and nougat-chewing modes were performed to determine the durability of the superamphiphobic layer.

The experimental results showed that the water and oil contact angle (WCA and OCA) for bare stainless steel is 65° and 18°, respectively. After dual-technique treatment, the WCA and OCA were 160° and 146°, respectively; namely, both hydrophobicity and oleophobicity were enhanced significantly. It remains WCA and OCA to be 137° and 120°, respectively after 500 times toothbrush wear test. On the other hand, for simulating the food chewing circumstances, the WCA and OCA were, respectively, 129° and 26° for peanut, and 133° and 80° for nougat after 500 times. The peanut-chewing causes much disappearing superamphiphobic behavior than nougat-chewing because the carbohydrate, protein and oil ingredients in peanut transferred onto the surface. This has been verified by SEM, EDS, and FTIR analyses. As a whole, the superamphiphobic surface prepared on the dental stainless steel substrate exhibits good durability, demonstrating the promising applications in dental archwires for orthodontics and dentofacial orthopedics.

DP-9 Light-activated High Efficiency Antimicrobial and Antiviral Coatings*, **Victor Bellido-Gonzalez (victor@gencoa.com)**, P. Killen, T. Sgrilli, D. Monaghan,* Gencoa Ltd, UK*; O. Hernandez-Rodriguez,* IK4-TEKNIKER, Spain

Antimicrobial resistance (AMR) is one of the major global challenges facing healthcare. Prevention of infections acquired in hospitals is the most effective way to fight AMR. Bacteria and other pathogens could be transferred via shared touch surfaces and instrumentation, and unfortunately health centres like hospitals present a breathing ground opportunity for some of the more resistant strains of pathogens. Maintaining an sterile environment is not always easy. Some of the complex instrumentation and equipment in hospitals, like robotics surgery instrumentation, are difficult to undergo through regular complete sterile conditioning protocols as they require complex and expensive cleaning procedure. In some cases the standard sterilasition autoclaving is not possible due to the nature of the instrumentation itself.

An approach which would offer a lower risk of cross contamination in such environments is the use of surfaces which can be “activated” and rapidly kill pathogens. In this paper we will present solutions based on surface coating technology which by light-activation becomes a very effective self-sanitizing surface, able to kill to levels of >99.99% of bacteria.

Recent developments by the authors have provided new analytical techniques for quantifying the ligh-activated antimicrobial efficiency of these coatings. Some of the coatings developed have been able to achieve high sterilisation performance even under “standard office”visible light conditions. Results will be presented.

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