S6 Atmospheric Pressure Plasma Jet Treatment of Polymers and Metals for Adhesion Improvement and Thin Film Deposition

U. Lommatzsch[1], J. Ihde[1], D. Pasedag[2], H.-E. Wagner[2]

[1]*Fraunhofer IFAM, Wiener Str. 12, D-28359 Bremen, Germany*
[2]*Institute of Physics, Ernst-Moritz-Arndt University, D-17487 Greifswald, Germany*

Low-temperature (< 1000 K) atmospheric pressure plasmas can be used for improving the adhesion to polymer surfaces, and for the deposition of thin films on metals. Short duration of treatment and lack of vacuum equipment make such plasmas highly attractive for industrial uses. While the activation of surfaces by low-temperature atmospheric plasmas is now established in a variety of industrial applications, the deposition of thin films is in a much less developed stage. In this study a commercially available atmospheric plasma jet is modified for the deposition on thin functional films. An arc-like plasma is generated inside the plasma jet nozzle by kHz-excitation. For deposition siliconorganic precursors are mixed with the plasma at the nozzle exit. The relaxing plasma plume that emerges from the nozzle exit is then used to modify the surface. The system operates without rare gases. Also it does not require the exclusion of the ambient gas atmosphere by encapsulating the treatment zone.

The plasma is characterized by optical emission spectroscopy and temperature measurements. The surface modifications of the polymers PE and PET induced by plasma treatment under non-depositing conditions are studied by XPS and AFM. Thin functional films for corrosion protection and adhesion promotion are deposited on aluminum substrates. The effectiveness of the coatings is studied by corrosion tests and lap shear measurements of adhesive bonded samples.

The spectroscopic characterization of the plasma reveals a strong relaxation inside the plasma plume with increasing distance from the nozzle exit. Active species, like O, OH, NO, and excited NO_2 are identified. The pretreatment of polymers improves adhesive bond strength substantially. This effect is related to chemical and topological modifications of the polymer surface. The modifications are caused by the reactive species and the thermal component of the plasma, and also by post-plasma reactions of the surface with ambient air.

Plasma-polymerized films from organosilicon precursors differing in thickness and chemistry are deposited on aluminum. A dynamic deposition rate of approx. 1000 nm m/min is obtained. Aluminum samples with such a coating show after storage of 250 h in a salt spray environment no signs of corrosion. Adhesive bonded aluminum samples with a very thin plasma-polymeric coating show improved adhesive bond strength after hot water immersion tests in comparison to substrates that were only pretreated.

This research has been supported partially by the Federal Ministry of Economics and Technology and the AiF "Otto von Guericke" under contract IGF-14817 N.

* * *

S6 Microdischarges in Ceramic Foams and Honeycomb Monoliths

K. Hensel, Z. Machala, A. Mizuno

Division of Environmental Physics, Department of Department of Astronomy, Earth Physics and Meteorology, Faculty of Mathematics, Physics and Informatics, Comenius University, Mlynská Dolina F2-39, 842-48 Bratislava, Slovakia

Atmospheric pressure non-equilibrium microplasmas are very attractive for various applications, such as surface modifications, and environmental and biomedical treatment. The atmospheric microplasmas can be generated by various types of electric discharges, including microhollow cathode and capillary plasma electrode discharges, discharges in porous ceramics and capillaries or dielectric barrier or coplanar discharges. The paper presents two types of discharges – a capillary microdischarge in porous ceramic foams and a sliding discharge inside the capillaries of honeycomb monolith – and describes their basic physical properties. Microdischarges inside the ceramics of the specific pore size develop from the surface barrier discharge, in case the amplitude of the applied voltage reaches given threshold. Sliding discharge inside honeycomb capillaries is produced by a combination of AC driven barrier discharge inside catalytic pellet bed coupled in series with DC powered honeycomb monolith. Both discharges produce the relatively cold microplasmas with high level of non-equilibrium. The basic characteristics of the discharges, addressing the effects of the applied voltage, discharge power, pore size, length and diameter of the capillaries, are discussed. The atmospheric microplasmas produced by the presented discharges and utilized in a plasma-catalytic system are considered to have a high potential for effective flue gas treatment.

This research has been supported by the APVT 20-032404, and VEGA 1/3041/06 grants.

* * *

S7 Dust Charging Processes and Their Implications for Space and Laboratory Plasmas

Z. Nemecek, J. Pavlu, I. Richterova, J. Safrankova

Charles University, Faculty of Mathematics and Physics, Prague, Czech Republic

The collection of ions and electrons from the plasma is not the only possible charging mechanism. Electrons can also be emitted from the particle surface due to thermionic, photoelectric, and secondary electron emission processes. These processes are of importance for dust charging in the working body of solid-fuel MHD generators and rocket engines, in the upper atmosphere, in space, and in some laboratory experiments, for instance, in thermal plasmas or in plasmas induced by UV irradiation, with photoelectric charging of dust particles, charging by electron beams, etc.

Dust grains may be charged negatively or positively and both components can coexist in laboratory and space plasmas. Usually, a combination of several charging processes takes place and the resulting grain charge depends on many factors (including the properties of surrounding environments, the grain material, or the grain charging history) that determine which process dominates. A survey of extensive study of dust grain properties influenced by these processes are presented and discussed. It touches electron and ion attachments, secondary and field emissions from grains of different materials and sizes.

Laboratory simulations allow us to separate particular charging/discharging processes that are running in plasma. We can observe a contribution of these processes to the dust grain state, to its inner structure and to the ability to create conglomerates or to split into fragments. Our experimental set-up based on the investigation of single grain levitating in the quadrupole trap allows us to influence this grain by several agents. Moreover, we can choose a material of the grain and its dimension to estimate a relative weight of various processes in different plasma environments.

This research has been supported by the Czech Grant Agency under Contracts 202/08/H057 and by the Research Plan MSM 0021620860.

* * *

S6 Embodiment of Surface-Plasma Metallurgy by Compression Plasma Flows Action on Metals

V. M. Astashynski[1], N. N. Cherenda[2], V. V. Uglov[2]

[1] *Institute of Physics of NAS of Belarus, 68 Nezalezhnastsi Ave., 220072 Minsk, Belarus*
[2] *Belarusian State University, 4 Nezalezhnastsi Ave., 220030 Minsk, Belarus*

Wide opportunities in surface modification of various materials are opened up by using compression plasma flows generated by quasi-stationary plasma accelerators of a new generation. Such accelerators operate in the ion current transfer mode and perform both plasma acceleration in the discharge device and plasma compression due to the interaction between longitudinal components of the “swept-away” current and its azimuthal magnetic field. As a result, at the outlet of the plasma accelerator discharge device a compression plasma flow with parameters much higher than those in the discharge device is created.

The studies conducted have shown the high efficiency of compression plasma flow action on samples in substantial modifications to the surface microstructure and morphology, phase and structure transformations of various materials, which enhance their tribological properties.

In the paper the opportunities of compression plasma flows as applied to embodiment of proposed principles of surface-plasma metallurgy are considered.

Low carbon steel, nickel, aluminium and its alloys were chosen as substrates. Ti, Zr, Cr, Mo, W and Ni layers (about 1-2 mm thick) have been deposited on substrates using the PVD method (vacuum arc vapour deposition).

The compression plasma flow treatment of the coating-substrate system results in both the melting of surface layer and plasma-assisted liquid phase mixing of elements of this system. This process yields a deep modified layer (up to 20 μm for steel and ~ 50 μm for aluminium). Such a layer features enhanced tribological properties due to embedded elements of a coating, a substrate, and a plasma forming gas. These alloying elements are present in the mixed layer at almost constant concentrations. Moreover, the samples treated with 5 pulses of plasma flow show high homogeneity of dopants distribution both across the layer and along the surface.

The main factors ensuring the efficient modification of coating-substrate systems exposed to compression plasma flows were shown to be the rapid heating of the surface due to kinetic energy thermalization of compression plasma flow during its deceleration, melting of both a coating and a substrate, liquid phase mixing under plasma flow pressure, keeping the temperature and pressure at necessary levels until the completion of physicochemical transformations in the surface layer, and the fast cooling and crystallization of the molten layer.

Thus, compression plasma flows can be effectively used for the predictable formation of a variety of alloys in the surface layer of metals by means of coating–substrate system treatment.

This research has been supported by the Belarusian Fund for Fundamental Research (No. F07-275).

* * *

S6 Hard Amorphous Si–B–C–N Films with Ultra–High Thermal Stability

J. Vlcek, J. Houska, S. Hreben, J. Capek, P. Zeman, R. Cerstvy

Department of Physics, University of West Bohemia, Univerzitni 22, 306 14 Plzen, Czech Republic

Novel quaternary Si–B–C–N materials attract great attention due to their possible high-temperature and harsh-environment applications (protective coatings, microelectronics and optoelectronics). The Si–B–C–N films were deposited on Si and SiC substrates by dc magnetron co-sputtering using a single C–Si–B or B_4C–Si target in nitrogen–argon gas mixtures. Elemental compositions of the films, their bonding structure, and mechanical and optical properties, together with their oxidation resistance in air, were controlled by compositions of the targets and the gas mixture, by an rf induced negative substrate bias voltage and by a substrate temperature. Extensive molecular–dynamics simulations of these materials were carried out to explain their structure and unique properties. The films (typically 1–7 μm thick) were found to be amorphous in nanostructure with a density of 2.4 – 3.3 gcm^{-3}, very smooth surface (R_a less then 1 nm) and good adhesion to various substrates (Si, SiC, glass and steel) at a low compressive stress (1.0 – 1.6 GPa). They exhibited high hardness (up to 35 GPa), elastic recovery (up to 88 %), optical transparency and wear resistance at extremely high oxidation resistance in air (even above 1500 °C) and stability of the amorphous state (up to a 1700 °C limit imposed by thermogravimetric analysis).

* * *

S6 Physical Aspects of Diaphragm Discharge Creation Using Constant DC High Voltage in Electrolyte Solution

Z. Stará[1], F. Krčma[1], J. Procházková[1], V. Aubrecht[2], P. Slavíček[3]

[1] Faculty of Chemistry, Brno University of Technology, Purkyňova 118, 612 00 Brno, Czech Republic,
[2] Faculty of Electrical Engineering and Communication, Brno University of Technology, Technická 8, 616 00 Brno, Czech Republic
[3] Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic
e-mail: stara@fch.vutbr.cz

Electrical discharges generated in liquids require different initial conditions for their breakdown than electrical discharges in gases. This difference is mainly caused by higher liquid density (and thus particle concentration) and dipole momentum of water molecules (if the discharge is created in water solutions). But there are more factors acting in the discharge initiation. Due to this fact, limited electrode configuration is convenient for discharge generation in water solutions.

This paper describes breakdown moment in so-called diaphragm discharge which is created in a small pin-hole in the dielectric barrier dividing two electrode spaces. As DC high voltage is applied on the electrodes, two kinds of plasma channels propagate from the pin-hole (i.e. the discharge initiation spot) towards electrodes, each on the opposite side of the diaphragm. These plasma streamers differ in their shape, electron velocity as well as in the energy dissipation. Therefore processes consequently initiated in both electrode spaces are strongly influenced by this streamer disparity. Initiation mechanisms of diaphragm discharge breakdown in water solutions can be described by two types of theory: thermal (bubble) and electron theory. The first theory is based on the fact that liquid is intensively heated (by Joule heating) in the region of high electric field that is concentrated in the pin-hole in the diaphragm. When water evaporates breakdown appears in evaporated bubbles due to the substantial voltage gradient on bubble surface (interface between gas and liquid phase). Subsequently, discharge is propagated in liquid phase by electron avalanches like according to Townsend´s theory for electrical discharge in gases. This paper confirms validity of both theories using records made by high speed camera and photograph with high resolution. Formation of bubbles in the pin-hole vicinity was clearly seen in obtained records as well as different shape of plasma streamers on both sides of the diaphragm.

Static electrical characteristics of diaphragm discharge breakdown in electrolyte solutions have been already published in our previous work. This paper extends our study by dynamic characteristics in various electrolyte solutions. Although we used constant DC voltage up to 4 kV, time evaluations of voltage, current and resistance revealed slight pulses in these characteristics. This phenomenon could confirm discharge formation in bubbles (they create and subsequently split).

Diaphragm discharge generation by constant DC voltage was strongly dependent on solution conductivity. Moreover, this parameter significantly changed during the discharge as well as solution pH. Opposite pH evaluation during the discharge in both electrode spaces was observed due to electrolytic reactions on the electrodes. Therefore influence of solution properties on discharge creation and stability was studied by this work.

This research has been supported by the Czech Science Foundation, project No. 202/07/P371.

* * *

S6 H-Mode ICP for PVC Surface Treatment

F. Croccolo, A. Quintini, R. Barni, and C. Riccardi

Università degli Studi di Milano – Bicocca and PLASMAPROMETEO,
Piazza della Scienza 3, I-20126, Milano, Italy
claudia.riccardi@mib.infn.it

Inductively Coupled Plasma (ICP) was previously applied by us in moderate power conditions giving rise to E-mode coupling for surface treatment of a plastic material. The same machine has been modified to be able to apply working powers in the order of 1 kW, thus switching to the real inductive H-mode.

The plasma is generated by applying a 13.56 MHz RF to a $\lambda/4$ antenna outside the plasma chamber in low pressure conditions. The working gas is Argon at working pressures in the range from 10 to 100 Pa.

With this high power source we have been able to perform plasma etching on a PolyVinylChloride (PVC) film. In particular the effect of the plasma is the selective removal of hydrogen and chlorine from the sample surface. The action of the high power plasma on the sample has been proved to be much more effective than that of the low power one. Results obtained with the low power machine at about 300 W for 120 minutes, have been obtained with the high power source at about 600 W for 30 minutes. The final result was the superficial generation of a conductive layer of double C=C bonds. The samples have been also investigated through a FIB microscope revealing the change in charge conductivity.

* * *

S6 TiO_2 Thin Films Deposited by PE CVD Method in Atmospheric Dielectric Barrier Discharge

Y. Klenko, J. Píchal

Department of Physics, Faculty of Electrical Engineering, Czech Technical University, Technicka 2, 166 27 Prague, Czech Republic

Non-thermal discharges under atmospheric pressure have attracted both scientific and practical interest because operating these discharges requires practically no vacuum system. They shorten the treatment time and simplify technological transfer when processes of production are making in continuous mode. These benefits lead to significant reduction of production costs.

One of atmospheric discharges used for various technical applications during many years, recently also for surface treatment, flue gas cleaning and thin film deposition, is the dielectric barrier discharge (DBD). It is applied in diffuse and filamentary mode.

Atmospheric pressure glow discharge (APGD) diffuse mode is characterized by a considerable space charge, current density and formation of the electrode sheaths. By addition of admixtures, e.g. oxygen, into air in the discharge reactor APGD diffuse mode can be altered into the filamentary DBD.

Diffusion character of the discharge is one of the main conditions for its employment in homogeneous thin film growth, with desired structure and chemical compound. Obtaining of diffusion character of DBD in electronegative gas mixture can be also considered as a serious physical and technological challenge. Therefore it is important to study the influence of monomer admixture and its concentration on the character of the barrier discharge.

Contribution takes a step towards the transfer of the well proven PE CVD method into the atmospheric pressure region and discusses the possible application of DBD burning in argon with admixture of titanium tetraisopropoxide (TTIP) and electronegative oxidizer for deposition of TiO_2 thin films with desired physical and chemical characteristics.

Presentation of this contribution was supported by the Czech Technical University in Prague Research Project No. CTU 0814213.

* * *

S5 Effective Gas Heating by Driving of Pulsed Arc

K. Korytchenko, V. Bolyukh, S. Shkirida

NationalTechnikal University "KhPI", 192, Poltavskiy shlyah, Kharkov, Ukraine, entropia@rambler.ru

It is shown the necessity of the electric field strength driving to increase the efficiency of gas heating. The way of the strength calculation is based on assumption that the efficiency grows if there is the balance between electron energy received from the field and energy losses via elastic electron-ion interaction into the pulsed arc. An electric scheme allowing to drive the strength during the pulse arcing was designed. Experimental results of discharge dynamics created by the scheme are presented in the work.

An initial stage of the pulsed arc corresponds to an intensive ionization of the gas under acting of the strong electric field. Thus, plasma passes from weakly-ionized state to highly-ionized one into the discharge channel when the ionization order exceeds 1 %. It is proposed to decrease the electric-field strength when the transition period is coming to create conditions of effective gas heating.

There are a few ways of influence of the strength falling on an energy deposition into arc channel. At first, the reduction of the field strength leads to growth of a frequency of elastic collisions of electrons with ions and, accordingly, an ion temperature increases more quickly. Secondly, due to the electric field decreasing, the electron temperature falls. As a result, a conductivity of the highly-ionized plasma diminishes and the resistance of the arc channel grows. Due to such adjusting it is easily to obtain a condition when the resistance of the channel exceeds the resistance of an external discharge circuit considerably. The last condition means a reduction of the energy losses into the external electric circuit. Thirdly, the limitation of average temperature of electrons allows restricting a growth of the ionization order of the plasma. Such limitation lets to raise a share of discharge energy expending on an increase in gas temperature.

The calculation of optimal strength of the field is done on the basis of a balance equation of electrons energy, a state equation and an equation of Sakha. The two-temperature model of highly-ionized plasma is used where the electrons temperature is differ from ions one. Possibility of an application of the equations related to highly-ionized plasma is checked via a comparison of the frequency of elastic collisions of electrons and atoms (molecules) with the frequency of elastic collisions of electrons with ions. The calculation results show that there is the optimal strength needed to keep quasi-steady if the growth of ions temperature is accompanying an increase of the pressure into the gas-discharge medium that corresponds to the isochoric law. For example, the optimal value of the field strength equals about 300 V/cm into the discharge medium of argon. It is necessary to reduce the strength of the electric field depending on the gas temperature if the pressure is constant during the arcing. It allows decreasing a difference between electrons temperature and ions one.

It is used an electric scheme where the secondary winding of a high-voltage pulse transformer is connected to the discharge gap through a pulse forming network to change the voltage supplied to the gap. The features of the pulse forming network influence on the electric field strength during the arcing. Influence of an inductance of the secondary winding on the arc dynamics is reduced by an achievement of a condition when the transformer core loses its magnetic properties. More over, the active resistance of the winding is minimized.

This research has been supported by the NSC "KhPTI".

S5 Multicomponent Plasma of Electric Arc Discharge

A.I.Cheredarchuk, V.F.Boretskij, P.V.Porytskyy, A.N.Veklich

Taras Shevchenko Kiev National University, Radio Phys. Dept., 64, Volodymirs'ka Str., Kiev, 01033, Ukraine,
e-mail: anri@univ.kiev.ua

Paper deals with investigations of thermal electric arc plasma in complex gas - metal vapour mixtures.

Experimental studies of such kind plasma and calculation of its transport properties were carried out as well.

The arc was ignited between the end surfaces of the non-cooled electrodes. Because of the discharge spatial and temporal instability the method of the single tomographic recording of the spectral line emission was used.

Experimental techniques in the plasma diagnostics were widely discussed. The spatial profiles of temperature and electron density were determined by optical emission spectroscopy. The temperature profiles are obtained from relative intensities of spectral lines. The electron density profiles are obtained from the width of spectral lines in an assumption of Stark broadening.

Plasma composition was calculated in an assumption of the Local Thermodynamic Equilibrium (LTE). The obtained electron density and the temperature in plasma were used as initial parameters in these calculations.

The influence of some mechanisms on plasma state was analysed.

On the base of the Grad’s method the transport properties of the thermal plasma of pure gases (argon, nitrogen, carbon dioxide) and mixtures with copper at atmospheric pressure in the temperature range between 5000 K and 15000K were calculated. The obtained results are compared with recent data calculated by the fourth approximation of Chapman-Enskog’s method. It is concluded that the Grad’s method can be preferable in the studies of the multicomponent plasma of electric arc discharges in comparison with other methods.

This research has been supported by Taras Shevchenko Kyiv National University and Institute for Nuclear Research National Academy of Sciences of Ukraine.

* * *

S5 Modelling of Gasification of Wooden Particles by Steam Plasma Jet in Thermal Plasma Reactor

I. Hirka, M. Hrabovsky

Institute of Plasma Physics, Academy of Sciences, Za Slovankou 3, 182 00, Prague, Czech Republic
email: hirka@ipp.cas.cz

Three-dimensional CFD modelling of gasification of wooden particles by steam plasma jet in thermal plasma reactor has been carried out. Modelling of gasification processes of particles represents computational difficulties. These particles are source of turbulences because they are rapidly gasified. In our modelling they can not be omitted because we also want to model syngas production.

The aim of the paper is to analyze distributions of physical properties (e.g. temperature, density) and distribution of species in the thermal plasma reactor presented as images obtained from the FLUENT code and to compare results obtained from different physical models. In this paper we used steam plasma jet as a heat source where centerline temperature of the jet equals approximately 26 000 K and initial temperature of wooden particles is 300 K. Mean velocity of the jet is approximately 3000 m/s and the mass flow velocity of wooden particles is 2 $g.s^{-1}$. Wooden particles are supplied to reactor chamber with small amount of nitrogen atmosphere (mass flow rate of nitrogen is 0.2 $g.s^{-1}$). These values correspond to real experimental setting of sawdust gasification. Standard, RNG, realizable k-ε models and k-ω models were used in all our simulations. Steam plasma and physical properties of all relevant gases were generated by the ADEP code.

One of the outcomes of the modelling is that backflow of gas mixture is present in the vicinity of the inlet pipe wall what is in good agreement with simpler models and also with real experiment. This backflow is confirmed both by distribution of corresponding velocity vectors aiming in the opposite direction than the plasma flow and also by presence of carbon monoxide in upper parts of the reactor while carbon monoxide is only produced in lower area.

Next important result is distribution of mass fraction of carbon monoxide and also other reactants and products of wood gasification process in whole reactor. Namely in exhaust pipe the mass fraction of CO is nearly 0.6 what corresponds to measurements and mass fraction of CO in anode area is even 0.8.

This research has been supported by the Grant Agency of Czech Republic under project number 202/08/1084.

* * *