LAFAD-ASSISTED PLASMA SURFACE ENGINEERING PROCESSES FOR WEAR AND CORROSION PROTECTION: A REVIEW

V. Gorokhovsky
Southwest Research Institute®
San Antonio, Texas, United States

ABSTRACT

The large area filtered arc deposition (LAFAD) process is characterized for deposition of various metal, ceramic and cermet coatings having different architectures: from monolithic ceramic to nano-microlaminated, nanolayered and sub-stoichiometric coatings. Duplex processes, consisting of a bottom ionitrided segment followed by coating layers, have been tested for application in forming tools, dies and molds. The barrier properties of LAFAD coatings are mostly due to its nearly defect-free morphology and smoothness as it was demonstrated in die casting die applications and in the application of protective coatings for solid oxide fuel cell (SOFC) metallic interconnects, operating in oxidizing environment at 800˚C. Ultra-thick ceramic and cermet coatings with thicknesses ranging from 30 to 120 μm have been deposited by one unidirectional dual arc LAFAD vapor plasma source onto substrates installed on a rotating turntable 0.5 m in diameter in an industrial coating system with deposition rates exceeding 5 μm/hr. The operating pressure range of the LAFAD process allows it to be used in plasma-assisted hybrid technologies with conventional magnetron sputtering and electron beam evaporation processes. The industrial applications of LAFAD wear and corrosion resistant coatings; their performance in different applications; and a commercialization strategy for LAFAD technology will be discussed.

INTRODUCTION

The contemporary surface engineering technology has reached the ability to grow layered structures in a controlled way, leading ultimately to a new generation of electronic and optical devices, cutting and forming tools operating at higher speeds, protecting the turbomachinery components against erosion and corrosion in a harsh environment, widening the horizons of new energy related applications from fuel cells to power stations, to automotive and aircraft components operating at high contact stress, among many others. In order to meet requirements for coatings operating in extreme conditions such as high contact stress, hostile environments, high temperatures and vibration, coating properties such as adhesion and cohesion toughness, fracture resistance, corrosion and high temperature oxidation resistance must be improved compared to the present state-of-the-art coatings.

It is well established that assistance of the coating deposition process with bombardment by energetic particles, especially energetic metal ions, can dramatically improve coatings by densifying the depositing materials, reducing the grain size and reducing or completely eliminating the growth defects[4,5,27,58]. It is also a mechanism for improving coating adhesion and cohesion toughness by mixing the substrate atoms with the atoms of the depositing coating, or mixing the atoms of the neighbor sublayers in laminated coating architectures by ion-bombardment assisted deposition processes[1,2,4-9,26,27,57,58]. In coating processes assisted with ion bombardment, the surface layer is affected by a high rate of bombardment by energetic ions, which affects the mobility of depositing metal vapor atoms and in many cases creates metastable structures with unique functional properties[1,4,26,27,57]. In addition, the ion bombardment of the coating surface influences gas adsorption behavior by increasing the sticking coefficient of gases such as nitrogen and changing the nature of adsorption sites from lower energy physisorption sites to higher energy chemisorption sites. This approach is especially productive in deposition of nanostructured nanocomposite coatings with ultra-fine or glass-like amorphous structure[5,9]. The ion-to-atoms arrival ratio represents one of the most important characteristics of such processes[4,8,27,58]. It is essential that this ratio is calculated at the atom

deposition spot. If ion bombardment is provided in a different location of the coating chamber or even at the distant spot and at different times from the atom condensation site, this cannot be considered as ion assisted deposition but rather as a post deposition ion treatment. The reason for this is that the time during which the adatom is fully accommodated to the surface lattice is less than 10^{-13} s (the accommodation time), which requires almost immediate ion- bombardment assistance at the atom condensation spot.

IONIZED VAPOR DEPOSITION TECHNOLOGIES

Conventional physical vapor deposition (PVD) sources, such as electron beam evaporator (EBPVD) and direct current magnetron sputtering (DCMS) sources can provide high deposition rates, but low energy of the metal vapor atoms results in low density, poor adhesion, poor structure and morphology of the coatings with high concentration of growth defects[1,2,4,26,27,58]. In the ion-beam assisted deposition (IBAD) process the flow of condensing metal vapor atoms is assisting concurrently by gaseous ion beam created by a separate ion beam source, such as Kauffman type gridded source or end-Hall griddles source as shown schematically in Figure 1. IBAD processes can provide gaseous ion bombardment assistance; however are not capable of providing metal ion bombardment assistance and are not capable of assisting in the deposition of conformal coatings on components with complex shapes[8]. The advanced plasma enhanced magnetron sputtering (PEMS) process, schematically shown in Figure 2 uses a distant thermionic or hollow cathode for ionizing gaseous environment in magnetron sputtering deposition process. In this process the deposition of sputtered metal atoms is assisted by concurrent ion bombardment from ionized gaseous plasma environment but the metal sputtering flow is mostly non-ionized as in the conventional DCMS process[9,56]. The recently developed high power impulse magnetron sputtering (HIPIMS) process uses high power pulses applied to the magnetron target which results in increased electron emission, and consequently increases the ionization rate of the metal sputtering flow[7]. This process has demonstrated that increased ionization rate of the metal sputtering atoms results in improved coating density and adhesion, and ultimately leads to improved coating properties in the deposition of nitride wear resistant coatings for cutting tools. The limitation of the HIPIMS process is that improved ionization is achieved only during the short pulse time. Since pulse parameters are coupled with magnetron sputtering process parameters in HIPIMS

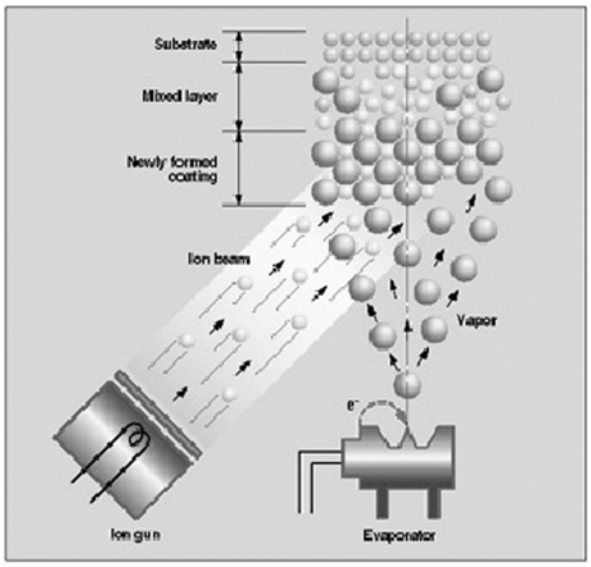

Figure 1. Schematic illustration of IBAD coating process.

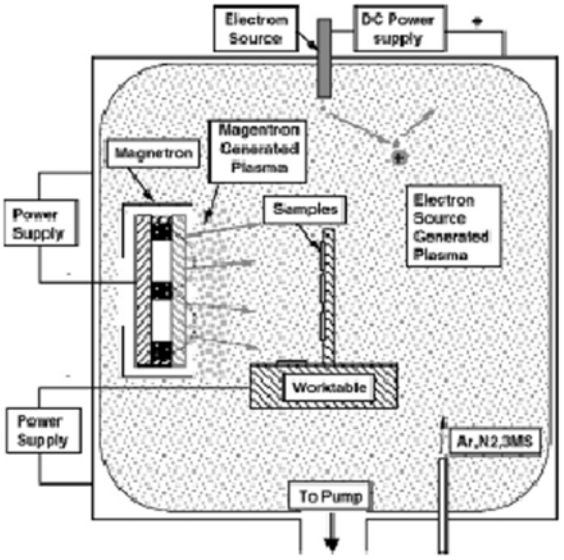

Figure 2. Schematic of plasma enhanced magnetron sputtering (PEMS).

technology, it can adversely affect the sputtering rate which is found three to five times lower than that of the conventional DCMS process[7].

LAFAD AND HYBRID SURFACE ENGINEERING SYSTEMS

The vacuum arc discharge plasma has been used successfully in the last two decades for the deposition of hard coatings for cutting tools and machine parts. In a direct cathodic arc deposition (DCAD) process the highly ionized metal vapor plasma is generated by direct cathodic arc sources (DCAS) in a form of a vapor plasma jet flowing from the cathodic arc spots, which transfers coating material from the target to the substrate surface. A significant disadvantage of this method is the formation of droplets, also known as macro-particles, in the cathodic arc jets, which limit the application of the process to surface coatings that do not require high precision or surface finish. These particles also deleteriously influence critical properties of the coatings as shown illustratively in Figure 3. For instance in the case of TiN coating on cutting tools, the presence of titanium particles in the coating compromises the hardness and wear resistance of the coating[1,2,14,21].

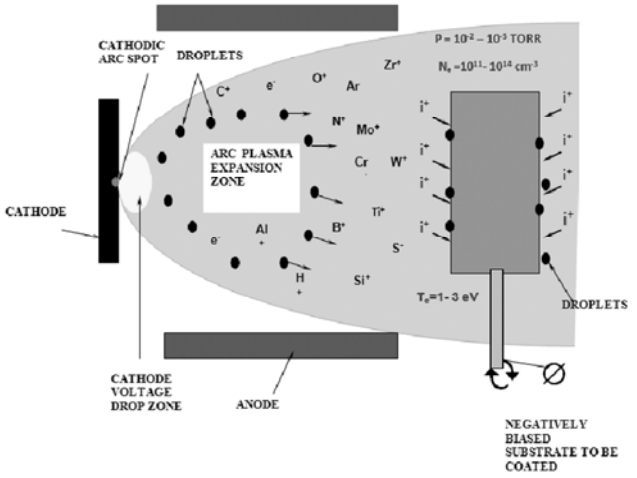

Figure 3. Schematic diagram of direct cathodic arc deposition (DCAD) process.

One of the first macroparticle filters had a quarter-torus cylindrical electromagnetic plasma guide, and was based on the torus-type plasma traps design, which was developed for the controlled nuclear fusion apparatus such as the Stellarator and the Tokamak. The filter removed the macro-particles, but could operate only with small cathode targets and could not be scaled up due to the difficulty of scaling up the cylindrical magnetic coils[4,11,12,26,27,58]. The main obstacle to using conventional filtered cathodic arc deposition (FCAD) technology is the low productivity of this process, which restricts its usage to semiconductors, optical coatings and some ultra-thin hard coatings used in bio-medical and tribological applications[58]. On the other hand, LAFAD technology overcomes these limitations by providing a highly productive, robust, industry-friendly process which combines the high productivity rate of conventional DCAD and magnetron technologies, with the capability of generating a nearly 100% ionized metal-gaseous vapor plasma with large kinetic energy and with no macroparticles, droplets, multi-atom clusters and other contaminants[1,2,16,21,22,29,30,58]. The unidirectional dual arc LAFAD vapor plasma sources can be used as an alternative to conventional DCAD and magnetron based processes when the high productivity and uniformity needed for most industrial applications must be accompanied by the high ionization and high kinetic energy of atomically clean vapor plasma. Since the LAFAD plasma source operating pressure regimes are overlapping with most of the conventional vacuum vapor deposition technologies such as magnetron sputtering (MS), electron beam physical vapor deposition (EBPVD), thermal evaporation, and plasma assisted chemical vapor deposition (PACVD), it can be used in hybrid processes combining its high deposition and high ionization rates in conjunction with conventional PVD and low pressure PACVD processes as demonstrated from the referenced literature[1,2,15,29,43,47,48,58].

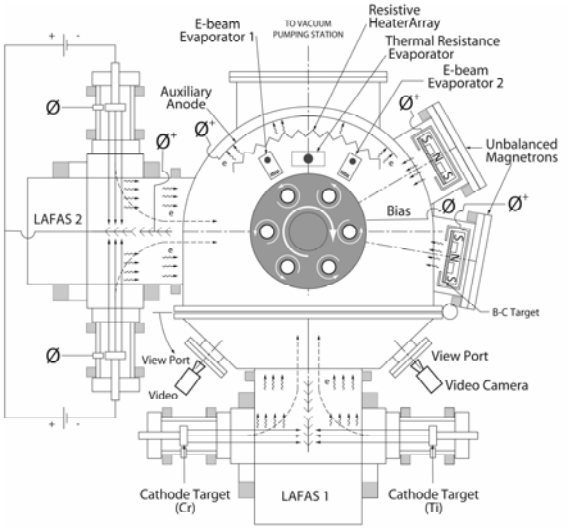

Figure 4. Schematic of filtered arc plasma source ion deposition (FAPSID) surface engineering system.

The hybrid filtered arc plasma source ion deposition (FAPSID) surface engineering system combining LAFAD process with ionitriding, ion implantation and conventional PVD and low pressure PACVD processes is shown schematically in Figure 4. The FAPSID system employs two unidirectional LAFAD dual filtered cathodic arc sources, two unbalanced magnetrons, as well as, electron beam physical vapor deposition (EBPVD) and thermal evaporation sources in one universal vacuum chamber layout[29,43,47,48]. The LAFAD plasma source magnetic deflecting system allows bending of the metal vapor plasma jets at 90˚ toward substrates to be coated, which yields 100% ionized metal vapor plasma flow at the LAFAD source exit and more than 50% ionized gaseous plasma in the coating chamber. Using a vertical rastering magnetic field allows obtaining uniform coating thickness distribution over large deposition areas suitable for industrial PVD coating systems[30]. When the magnetic deflecting subsystem is turned off the LAFAD source can be used in a gas ionization mode as a powerful electron emitter. In this mode the auxiliary arc discharge is ignited between the primary cathodes of the LAFAD source and an auxiliary anode located in the coating chamber as schematically illustrated in Figure 4. Multi-segment coating architecture utilizing segments deposited by LAFAD source followed by segments deposited by other PVD or low pressure PACVD sources, can be deposited by hybrid coating systems similar to that shown in Figure 4[29,43,47,48]. Alternatively, nanocomposite multi-phase, multielemental coatings can be deposited by concurrently using LAFAD with other sources such as unbalanced magnetron (UBM), EBPVD or low pressure PACVD sources[29,43,47,60,61,65,66].

LAFAD-ASSISTED PROCESSES AND APPLICATIONS

Various metal, ceramic and cermet coatings of different architectures where deposited by LAFAD process for different applications. Initially the efforts were directed toward development of hard ceramic coatings and superhard DLCs over large size machine parts or by processing of large number of small components in a fully loaded industrial scale coating chambers. The typical LAFAD process for deposition of monolithic (single layer) titanium nitride ceramic coatings includes pre-heating the components to be coated to 300-400˚C depending on type of substrate material. The pre-heating stage is conducting in argon at the pressure ranging from 0.1 to 1 mtorr. The pre-heating stage is followed by ion cleaning stage. At this stage the dense argon auxiliary arc plasma discharge is established between cathode targets of the two primary direct cathodic arc sources (DCAS) of the LAFAD plasma source and auxiliary anode disposed in a coating chamber. After ion cleaning the high voltage metal ion etching stage is commenced for a duration of 2 to 5 min at argon pressure below 0.1 mtorr. During this stage the substrates to be coated are subjected to intense metal ion bombardment from filtered metal vapor plasma. The substrate bias during the metal ion etching stage is typically setup at 1000 volts resulting in acceleration of metal ions across the plasma sheath to kinetic energies ranging from 1 keV for 1^+ metal ions to 4 keV for 4^+ metal ions. The high voltage metal etching treatment results in formation of ultra-thin surface layer enriched with the coating-forming atoms which dramatically increases the adhesion strength at the coating-to-substrate interface[1,2,4,16,29,57,58]. Note that unfiltered DCAS does not provide sufficient improvement of the adhesion toughness because macroparticles deposited by direct cathodic arc process do not have good adhesive bonding to the substrate[4,11,12,58,27]. In a conventional magnetron sputtering process this stage cannot be provided because of very low ion-to metal atoms arrival ratio in a magnetron sputtering process. The ion-to-

atom arrival ratio in HIPIMS process may exceed 30% which makes this process capable of providing high voltage metal ion etching stage; however, the LAFAD process still has an advantage of being capable of generating 100% ionized metal vapor plasma which is beneficial for metal ion etching. After ion etching, the bias voltage is reduced and the coating deposition process is performed in a reactive gaseous plasma atmosphere. The substrate bias in LAFAD processing of hard ceramic coatings typically ranging from 40 to 100 volts, in most cases does not exceed 40 volts to reduce the substrate temperature, during coating deposition stage, and intrinsic stresses in the coatings. The comparison of conventional TiAlN monolithic coating deposited by DCAD process vs. LAFAD TiAlN coating is shown in Figure 5. It can be seen that the LAFAD coating provides virtually no surface defects while coating deposited by the DCAD process has a large macroparticles density, microdelaminations and pin-holes, which is especially important in such applications as corrosion resistant coatings, diffusion barrier layers and high temperature oxidation resistant coatings[1,2,4,14,24,25,35,41,59,60].

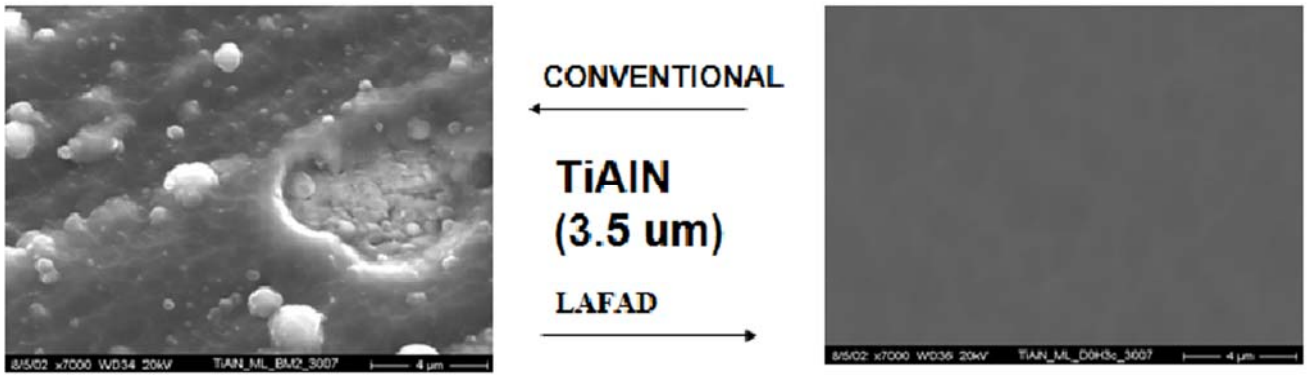

Figure 5. TiAlN monolithic ceramic coating deposited by conventional DCAD process vs. LAFAD coating.

Vacuum cathodic arc evaporation process does not require additional gaseous atmosphere in a vacuum chamber for sustainable operation of vacuum cathodic arc sources[1,2,4,27,58]. The LAFAD process of deposition the hydrogen-free carbon diamond-like carbon coatings (DLC) is performed without adding any plasma carrier gases such as argon[1,2,16]. The continuous carbon vacuum arc is operating at vacuum better than 10^{-5} torr in a self-generated carbon vapor as a plasma carrier gas. The thermal management of substrates during deposition of DLCs has to be able to remove large thermal flux conveyed to the substrates from the carbon plasma stream[1,16]. The energy of carbon ions bombarding the surface of the growing coating cannot exceed 150 eV. Both overheating and ion bombardment by high energy ions can destroy the diamond-like structure and graphitize the coating[1,4,15,16-20]. The HRTEM of 6 μm thick DLC deposited on water-cooled aluminum disk substrate by the LAFAD process[16] is shown in Figure 6. A relatively thick intermediate zone consisting of a mixture of aluminum-carbon atoms can be seen at the carbon DLC-aluminum substrate interface. The formation of this zone is a result of mixing carbon and aluminum atoms under conditions of condensation with intense ion bombardment[16,57]. The hardness of this coating exceeds 70 GPa as illustrated by hardness measurement curves in Figure 7. This hardness is comparable to the

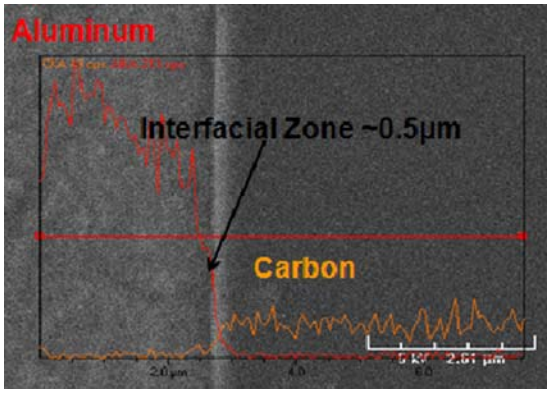

Figure 6. HRTEM cross-section of 6 mm thick DLC deposited by LAFAD process on water-cooled aluminum disk substrate (courtesy of A.Voevodin).

hardness of synthetic diamonds. The filtered arc DLCs also have exceptional corrosion resistance owed by their dense and pin-hole free morphology and chemical inertness[1,67]. The surface displacement-loading curve in nano-hardness indentation has demonstrated almost full recovery which shows high elasticity of hydrogen-free DLCs deposited by the LAFAD process[16]. Different morphology and structure of DLC coatings, deposited by the LAFAD, can be achieved by varying the processing parameters such as substrate bias and currents of the primary DCAD sources. Characterization of LAFAD DLCs of different morphologies resulted in a wide variety of functional properties vs. LAFAD process parameters are discussed in details in[1,15-20]. The many applications of LAFAD DLC coatings include medical and dental instruments, cutting and forming tools, machine parts, magnetic media and optical coatings among others.

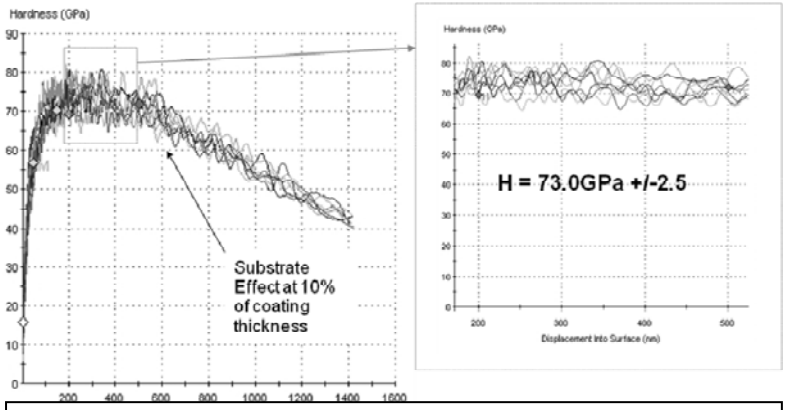

Figure 7. Nanohardness measurement of DLC film shown in Figure 6.

LAFAD process is capable of depositing coatings with multi-elemental compositions and with complex coating architectures. The multilayer metal-ceramic coatings can be deposited by periodically changing the gaseous plasma atmosphere. For instance, multilayer Ti/TiN coating with Ti metallic sublayers having a thickness ~50 nm followed by TiN ceramic sublayers having a thickness ~500 nm is shown in Figure 8**.** This coating is deposited by LAFAD process when nitrogen is added to argon every 20 minutes for deposition of TiN sublayer while during 5 minutes between depositions of nitride sublayers the metallic titanium sublayers are deposited in pure argon gas atmosphere[23,24,36]. When targets made of different metals are installed in the primary cathodic arc sources of LAFAD plasma source the nanolayered ceramic coating can be deposited by periodically exposing the rotating substrates to the metal

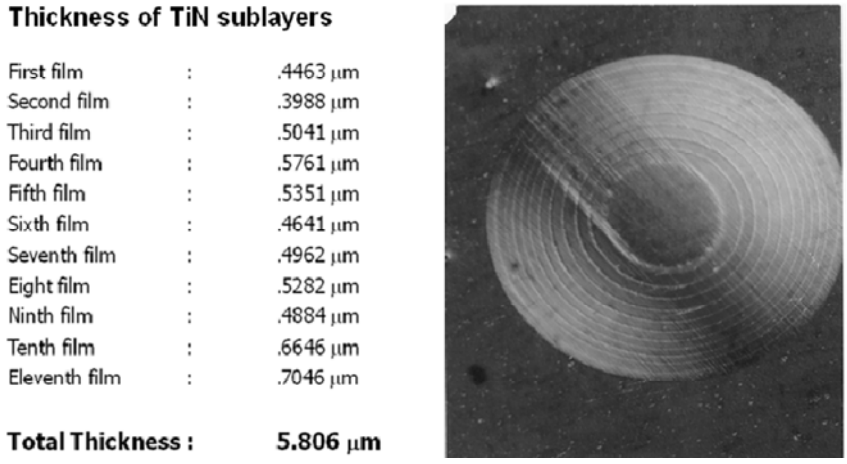

Figure 8. CALO-test wear-scar image of multilayer Ti/TiN coating deposited by LAFAD process.

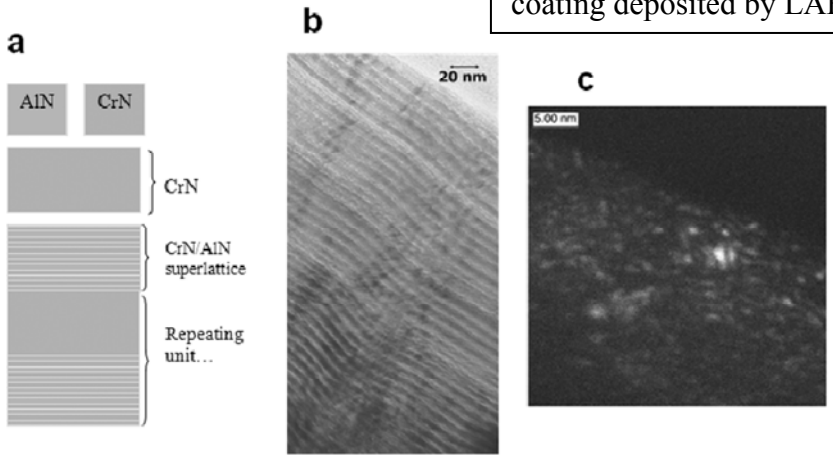

Figure 9. Nanolaminated CrN/CrAlN coating deposited by LAFAD source with primary DCAD sources equipped with Al and Cr targets: a-coating design; b- HRTEM of the coating cross-section; c- ~1 nm size crystals incorporated in nanolaminated coating sublayers.

plasma generating by two opposite DCAD sources. Figure 9 shows CrAlN nano-structured coating complex architecture as deposited by LAFAD process[35,40]. This coating consists of CrN sublayers followed by CrN/AlN superlattice segments. CrN sublayers were deposited when only one primary DCAS, with a chrome target, was working while the opposite DCAS, with aluminum target, was shut off. The CrN/AlN nano-multilayer segments were deposited when rotating substrates were exposed, in turn, to both Cr and Al vapor plasma flows generated by a LAFAD unidirectional source with opposite primary DCAS equipped with chromium and aluminum targets. Thickness of each individual sublayers in CrN-AlN nano-multilayer segments ranged from 3 to 5 nm while nitride nano-crystals in the CrN-AlN nano-multilayer segments did not exceed 1 nm.

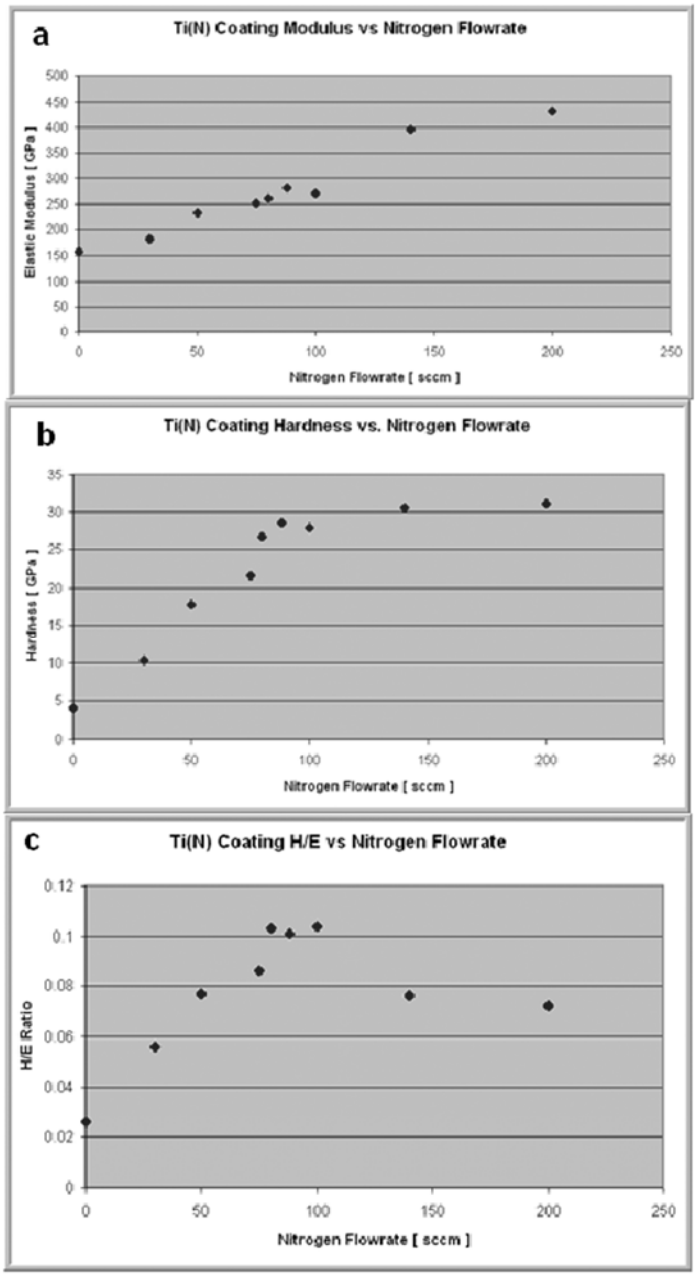

Figure 10. Mechanical properties of sub-stoichiometric TiN coating deposited by LAFAD process vs. nitrogen flowrate.

Ultra-fine grains and almost defectless morphology of LAFAD ceramic coatings are in many cases result in an increase of hardness and elastic modulus while at the same time having increased internal stress and decreased toughness typical for hard ceramic coatings[33,52]. Both chemical composition and coating architecture have been used to optimize the mechanical properties of LAFAD hard coatings. The increase in the Ti layer thickness results in a decrease in the internal stress in both the TiN and Ti layers, and an increase in the grain size and crystallinity of both TiN and Ti phases[52]. Adding Si to TiN coating by using a composite Ti-Si targets for primary DCAD sources of the LAFAD plasma source allows deposition of multiphase coatings consisting of TiN, Si_3N_4 and TiS_2 phases and control of intrinsic stress, grain size and other mechanical properties of the coatings[53,54]. It was found that by adding Si into TiN coatings reduces the grain size significantly from 16.9 to 5.8 nm, changes the orientation from (111) to (220) preferred orientation, and increases the hardness and Young's modulus from 33 and 376 GPa to 51 and 449 GPa, respectively. XPS and XRD results show that the Si/Ti atomic ratio in the coatings is 0.17 and the deposited TiSiN coatings consist of nanosized TiN grains encapsulated by amorphous Si_3N_4 layer, corresponding to the superhardness of the TiSiN coatings. The high plasma density, ion energy, and ion reactivity of the filtered cathodic arc plasma contribute to the formation of the nanocomposite TiSiN coatings at low temperature and low N_2 partial pressure as it does in PEMS process[9,53,54,56].

TiN coating properties can be also controlled by varying nitrogen content[55]. The mechanical properties of sub-stoichiometric TiN coatings deposited by LAFAD process with different

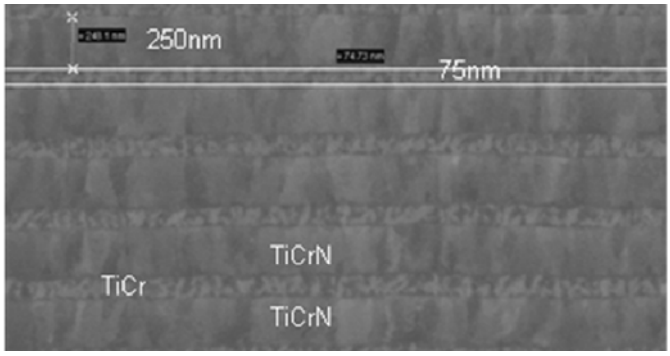

Figure 11. Multilayer TiCr/TiCrN wear and corrosion resistant coating deposited by LAFAD process.

nitrogen flowrate are shown in Figure 10. It can be seen that hardness and elastic modulus increased with the increase of nitrogen flowrate reaching the maximum in stoichiometric coating composition. In a contrast, the H/E ratio associated with coating toughness reached the maximum in under-stoichiometric coating composition[51].

Multilayer TiCrN/TiCr cermet coatings deposited by the LAFAD process have demonstrated a superior corrosion resistance along with low stresses, exceptionally good adhesion and high toughness[1,12,28,44,47]. The cross-section of this coating, having Ti50Cr12N38 composition, is shown in Figure 11[49]. The results of salt fog simulated corrosion testing of M50 steel with 6 μm LAFAD TiCrN/Ti coatings have demonstrated almost a complete elimination of pitting corrosion, as can be seen in Figure 12[49,28].

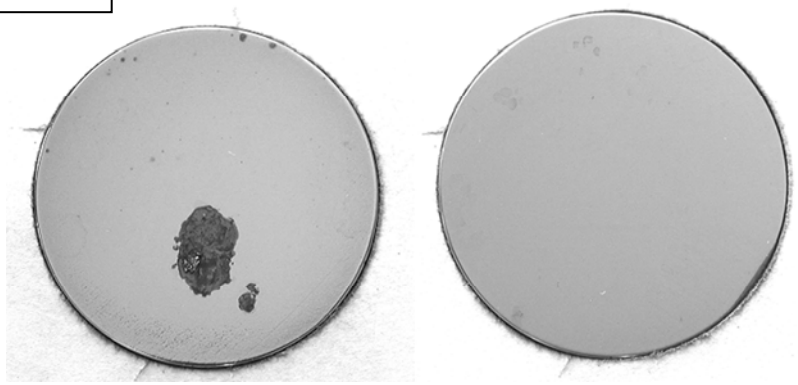

Figure 12. Carburized Pyrowear 675 discs after salt fog testing: left-uncoated; right- with TiCr/TiCrN coating shown in Figure 11.

Further improvement was achieved by using a 2-segment TiCrN/Ti+TiBCN coating deposited by a hybrid LAFAD+UBM process[44,47]. The hybrid FAPSID surface engineering system configuration is capable of depositing LAFAD+UBM coatings with modulated concentrations of one or more components by using LAFAD source in a magnetic shuttering mode. In this mode the deflecting magnetic field is activated and de-activated with repetition frequency ranging from 0.1 to 10 Hz and with a controlled duty cycle. When the deflecting magnetic field is ON, the TiBC coating is deposited by a hybrid LAFAD+UBM process. When deflecting magnetic field is OFF only B_4C sublayer is depositing by UBM source which operates continuously. The HRTEM cross-sectional image of modulated TiBC coating is shown in Figure 13[47]. It can be seen that the bi-layer period in this coating does not exceed 4 nm. The hardness and elastic modulus of TiBC coating deposited by the hybrid

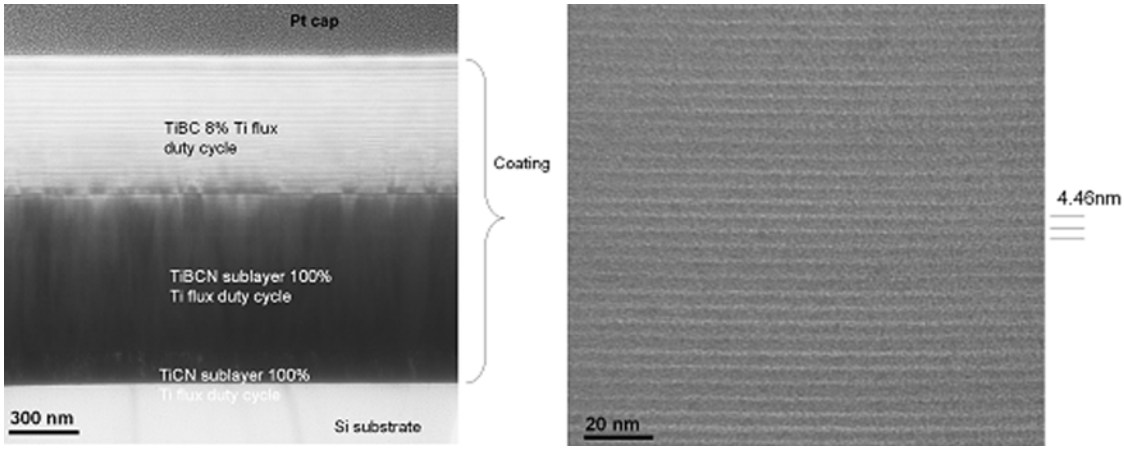

Figure 13. HRTEM cross-sectional image of the TiBC top segment nanolaminated architecture: a- complete top segment architecture; b-magnification of the top end of the TiBC segment.

LAFAD+UBM process in a magnetic shuttering mode depends on the modulating period of Ti-enriched sublayer and Ti concentration in a coating achieving superhard properties with hardness of about 45 GPa at optimized titanium content[47].

The same type of the coating also demonstrated extremely high wear and corrosion resistance in hot perfluoropolyalkylether (PFPAE) corrosion under high load rolling conditions establishing dramatic differences between TiBC coating configurations performance and uncoated Pyrowear 675 samples[28,44,47]. Initial tests were conducted for 2 h at standard test conditions with repeated results, as shown in Figure 14. Testing durations of 2 h demonstrated relatively large, 4–8 μm deep, plastic wear track deformations occurring in the uncoated sample in comparison to the coated samples, which showed only polishing of coating in the form of a local reduction in the coating surface roughness. The multi-phase nanostructured TiBC(N) layer deposited by hybrid LAFAD+UBM process have also demonstrated improved wear resistance in high load contact sliding condition which was attributed to combination of low friction and high adhesion toughness of these coatings[28,44,47].

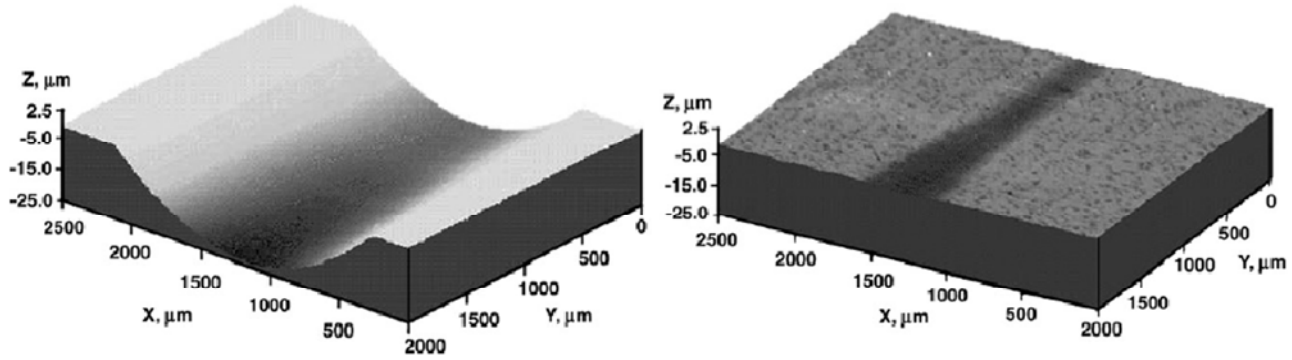

Figure 14. Scanning profilometry image of lubricated sliding wear track, using a 2.0 μm TiCrN/TiCrCN coated ring on an uncoated carburized Pyrowear 675 coupon (left) and on a coupon with TiCrN/TiCrCN+TiBC coating deposited by LAFAD+UBM hybrid process.

The hybrid LAFAD+UBM surface engineering system was used for deposition of both nano-composite and two-segment coatings for cutting tools. The two-segment hard-soft coatings deposited by the LAFAD+MS process, consisted of the first segment hard ceramic coating deposited by the LAFAD source followed by soft, low friction segment deposited by magnetron sputtering deposition process[1,4,58,65,66]. The hard bottom segment was made of TiN, TiAlN, TiC, CrN or TiCN. These ceramic coatings deposited by LAFAD process both multilayers similar to that shown in Figure 8 and monolithic ceramic layers have hardness ranging from 20 to 40 GPa. Various materials were deposited by magnetron sputtering as a top soft low friction coating segment: WS_2, MoS_2 and soft carbon coating[65]. The WS_2 coatings were also deposited by cathodic arc evaporation of tungsten in $Ar+H_2S$ reactive gas atmosphere. The results of testing different cutting tools with 2-segment hard-soft coating have demonstrated increased wear resistance and durability of these tools compared to cutting tools having only hard wear resistant coating[65].

Further improvement of the hard-soft coatings for cutting tools was achieved by using nanocomposite coating systems, employing a soft phase incorporated into the hard phase during LAFAD and a hybrid LAFAD+MS deposition processes[65]. The following nanocomposite mixed hard-soft coatings were deposited and tested for their performance in cutting tools applications: TiC+C, TiN+Ag and TiN+MoS2. The TiN+MoS_2 coatings were deposited both by co-deposition of TiN and MoS_2 during simultaneous operation of LAFAD source with titanium primary arc targets and MoS2 by magnetron sputtering respectfully. It was also deposited by operating of cathodic arc sources with Ti and MoS_2 targets. TiC+C coatings were deposited by LAFAD process using $Ar+CH_4$ as a reactive gas atmosphere. The mixed TiN+Ag hard-soft coatings were deposited by cathodic arc evaporation of

segmented Ti+Ag primary cathodic arc targets of the LAFAD plasma source. In addition, a nanocomposite MoN+Cu coating was deposited by co-evaporation of Mo and Cu primary cathodic arc targets installed in opposite sides of the LAFAD plasma source in nitrogen reactive gas atmosphere. This coating becomes lubricous when undergoes oxidation at high temperatures during cutting[65]. Again, considerable improvement in the tool life was demonstrated.

The hybrid LAFAD assisted processes were also used for development of the carbon and boron contained coatings, which were deposited by LAFAD+MS process for cutting tools applications[66]. In these processes titanium and carbon cathodes were used to generate arc plasma. Boron and titanium diboride cathodes were used in the magnetron sources to produce boron containing coatings. The substrates were mounted on a variable speed rotary (two-axis) substrate holder that can be biased to a desired voltage using either a DC or RF power. These coatings have demonstrated improved hardness ranging from 34 GPa to superhard coatings of 65 GPa. The superhard TiBN single layer coating have demonstrated outstanding performance in high speed end milling of hardened tool steels (H-13). It has demonstrated a tool life increase of exceeding 800% over uncoated WC/Co and 25% higher than the second best candidate: multilayer TiBN/TiN[66].

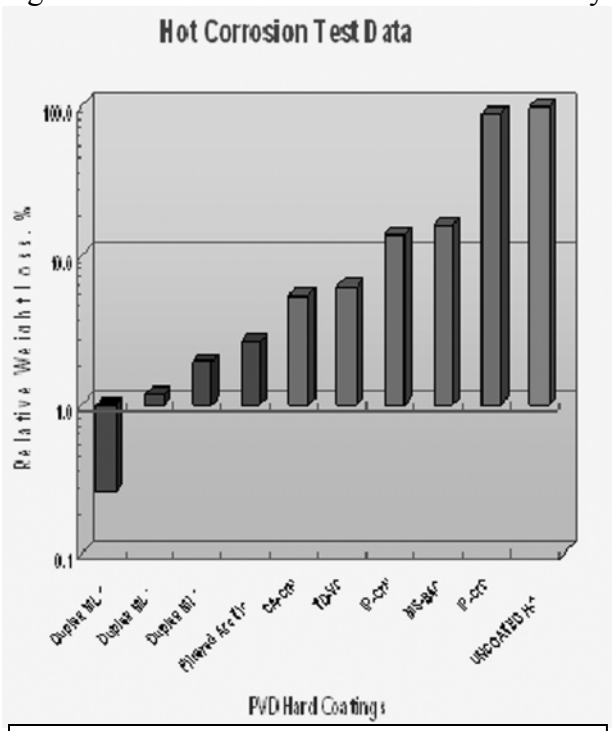

Figure 15. Performance of TiN, TIBN, and TICN multilayer coatings deposited by the filtered-arc method, in a simulated pressure die-casting erosion_corrosion environment, as compared to other commercial coatings: duplex ML1- ionitriding+TiBCN/TiN multilayer (LAFAD); duplex ML2- ion-nitriding+TiN/TiCN multilayer (LAFAD); duplex ML3- ionitriding+Ti/TiN multilayer (LAFAD); CA-CrN, direct cathodic arc deposition; VC- Toyota-diffusion process; IP-CrN, ion-plated CrN; MS-B4C, magnetron-sputtered B_4C; and IP-CrC, ion-plated CrC.

Multi-component LAFAD coatings have demonstrated superior high temperature corrosion and oxidation resistance in a chemically aggressive environment, which makes LAFAD and hybrid LAFAD+UBM and LAFAD+EBPVD processes technologies of choice for wide variety of industrial applications. Duplex coatings consisting of ionitrided layer followed by Ti/TiN/TiNC/TiBNC multilayer, multi-elemental, coatings have demonstrated superior high temperature corrosion resistance in a contact with molten Al-16% Si alloy environment simulating aluminum foundry process using steel made die casting dies[23-25]. The results of weight loss experiments from the erosion-corrosion test in molten aluminum alloy, shown in Figure 15, demonstrate superior performance of LAFAD coating vs. other coatings and surface treatments. The plot is normalized with respect to the weight loss of an uncoated H-13 pin, by assigning this a value of 100, and the results are plotted on a logarithmic scale. Lower weight loss indicates a better performance. The multilayer coatings show a weight loss which is nearly two orders of magnitude smaller than that of the uncoated H-13 pin. It was also demonstrated that multilayer coatings deposited by LAFAD process show minimum ejection forces and thus the minimum adhesion tendency[23-25].

Another example of using LAFAD ceramic coatings for high temperature oxidation resistance applications are coatings for the SOFC interconnects (SOFC IC) made of inexpensive ferritic stainless steels[42,45]. Near defectless morphology and dense structure of LAFAD coatings resulted in their ability to inhibit high temperature oxidation by eliminating

pin holes, voids and porosity as well as reducing the inward/outward mobility of cations/anions. The multielemental oxi-ceramic coatings of CoMnTiCrAlYO system deposited on ferritic steel plates by the LAFAD process have demonstrated its ability to slow the growth of thermally grown oxide scale (TGO) while securing high electrical conductivity and almost completely blocking the chrome outward diffusion, which is poisoning the SOFC cathode[41]. Two-segment coatings were deposited by LAFAD and hybrid LAFAD+EBPVD processes. The bottom segment consists of TiCrAlO layer deposited by LAFAD source with primary DCAD sources equipped with multi-elemental TiCrAlY targets. The elemental composition of TiCrAlYO coating deposited in this process is replicating the cathode target elemental composition with high accuracy[48]. The LAFAD oxi-ceramic coatings, having excellent diffusion barrier properties, were used as the bottom segment of a two-segment coating architecture with a CoMnO top segment deposited by a hybrid LAFAD+EBPVD coating deposition process in the FAPSID surface engineering system[48]. The diffusion barrier performance of this dual-segment coating is illustrated in Figure 16. It can be seen that even a 0.3 μm bottom TiCrAlO adhesive and diffusion

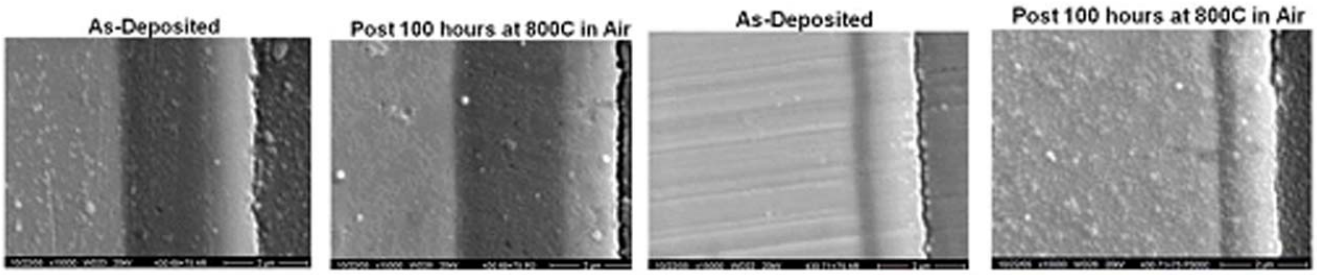

Figure 16. SEM/EDS cross sections of dual segment coating before and after oxidation in 800C air. Top left: 3.0 um CrAlYO + 1 um MnCoO: no chromia TGO scale growth showing no substantial change in coating structure after high temperature exposure. Top right: 0.3 um CrAlYO + 1 um MnCoO: still no chromia TGO scale growth and no substantial change in coating structure after high temperature exposure.

barrier segment provides excellent oxidation protective properties, inhibiting the TGO growth after 1500 hrs of oxidation. In a further development the nanocomposite coating of (Co,Mn)TiCrAlYO system were deposited on ferritic steel substrates by the LAFAD process using primary DCAS targets made of composite (Co,Mn)TiCrAlY alloy[42]. Excellent diffusion barrier properties of LAFAD coatings were also used in deposition of alumina interlayer between bondcoat and top ceramic coating of the TBC system for turbine blade applications. The LAFAD defectless alumina layer having very low oxygen diffusivity was used to slow the formation of TGO scale on bondcoat–to-topcoat interface and demonstrated improvement in stability of TBC against buckling in thermal cycling testing[59,60].

The LAFAD multilayer metal-ceramic coatings similar to that shown in Figure 8 are currently applied for the mass production of dental instruments such as handle and ultra-sonic scalers and curettes[36-39]. Thickness of these coatings deposited on high chromium stainless steel ranged from 2 to 5 microns. This LAFAD process allows to retain the sharpness of the instruments as the radius of curvature at the cutting edge does not exceed coating thickness, which is critically important for this application. The intrinsic stresses and hardness of these coatings is controlled via the ratio of titanium metallic sublayer thickness to ceramic TiN sublayer thickness in these multilayer coatings[36, 52]. The hardness of this coating ranges from 25 to 35 GPa, which allows multiple usage of scalers in periodontal dental operations without re-sharpening. On the other hand, uncoated instruments require re-sharpening after its use for each patient. The absence of macroparticle inclusions and ultra-fine coating morphology are also adding exceptional abrasion resistance which was demonstrated by subjecting dental instruments to vibratory treatment in a contact abrasion media[37-39].

ULTRA-THICK COATINGS AND EFFICIENCY OF LAFAD PROCESS

A record high metal vapor plasma transport efficiency of unidirectional LAFAD source allows deposition of ultra-thick ceramic and cermet coatings of different architectures and compositions as erosion and abrasion wear protection and corrosion resistance coatings for components operating in extreme conditions such as aircraft parts (compressor blades and helicopter rotorblades) and mining tools[49-51]. The thickness of TiN based coatings deposited by one unidirectional LAFAD source on substrates installed in 0.5 m diameter rotary table with single rotation (one side coating) ranged from 20 to 60 μm with deposition rate exceeding 5 μm/hr. In addition, two-segment coatings utilizing either monolithic I,J coatings or multilayer G coating as a bottom segment interfacing the substrate and nano-multilayer K_1 top coating segment were also produced. The cross-section of a two-segment GK_1 coating, deposited during two consecutive coating runs is shown in Figure 17[50,51]. The bottom microlaminated 10-layer G-coating bottom segment was deposited during 10 hrs deposition run with 15 min deposition of metallic titanium sublayers in argon, followed by 45 min deposition of TiN sublayers in nitrogen reactive gas atmosphere. The top nano-microlaminated 40-layer K_1-coating segment was deposited during 11 hrs run with 2 min deposition of metallic titanium sublayers in argon followed by 13 min deposition of TiN sublayers in nitrogen as a reactive gas atmosphere. Good mechanical stability and low stresses in ultra-thick TiN base coatings may be explained by the role of thickness-dependent gradients of point defect density[32].

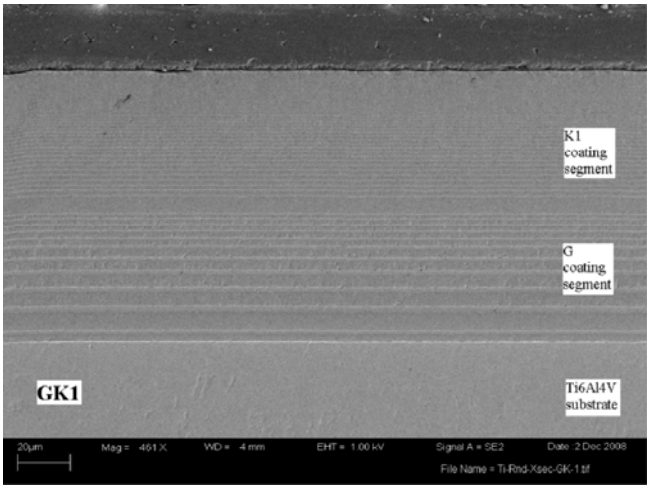

Figure 17. Two-segments nano-microlaminated ultra-thick Ti/TiN coating deposited by LAFAD process.

The current of the primary titanium cathode targets during deposition of G and K1 coatings was 200 amperes resulting in large melting areas surrounding the cathodic arc spots. The maximum deposition rates of LAFAD process has been achieved when the target surface reaches melting temperature in the large area surrounding cathodic arc spots. This condition is achieved during deposition of G and K coatings as can be seen from the Figure 18 photograph depicting the surface of a titanium cathode target exposed to 200 amperes arc current during the deposition of G coating as seen from the titanium target surface. The deposition rates of G and K_1 coatings deposited by LAFAD process with 200 amperes of the primary DCAS current vs. process time in comparison with deposition rate of TiN based coating deposited at lower cathode current of 140 amperes are shown in Figure 19. It can be seen that the deposition rate of TiN coating reaches 10 μm/hr at the beginning of LAFAD deposition process at 200 amperes of primary DCAS sources when the target surface temperature reaches its maximum value near the melting temperature of titanium in areas close to the cathodic arc spots. This deposition rate is almost three times greater than deposition rate of

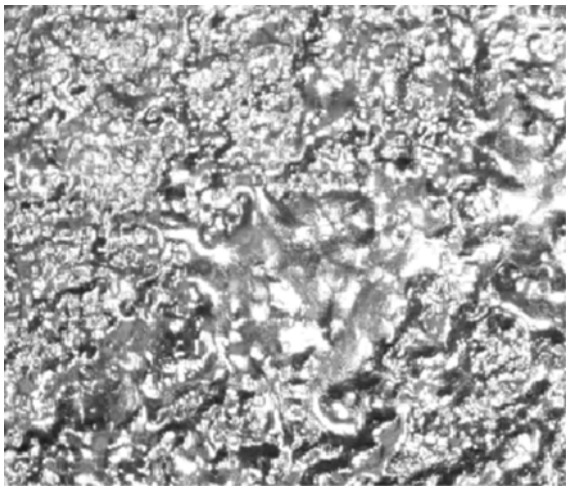

Figure 18. Surface of titanium cathodic arc target subjected to arc evaporation process with 200 amperes arc current.

the TiN coating deposited by a LAFAD source with 140 amperes of the primary DCAS currents. The deposition rate is reduced when the water cooled targets get thinner, resulting in improved water cooling efficiency and reduced integral temperature of the target surface. The uniformity of the coating thickness distribution during deposition of ultra-thick TiN based coatings, with vertical magnetic rastering, is about +/-15% over 12 inches tall coating area and without magnetic rastering, over 6 inches tall deposition area[22,29-31,49]. Using this data the ion current transmission rate in LAFAD process can be calculated. Assuming the value of the average titanium ion charge as $<z_{Ti}>=2.2$[4], the maximum coating deposition rate of 10 μm/hr, and a coating area of 500 cm diameter × 15 cm tall as in G- and K-coating processes, the ion current transmitted from two primary DCAD sources of LAFAD plasma source can be estimated at 16 amperes which corresponds to 4% of the total ion current generated by two DCAS with 200 amperes arc current each. Taking into account that maximum ion current generating in vacuum cathodic arc process is less than 8% of the total arc current[4] it can be seen that LAFAD process is capable of transporting more than a half of the total ion current generating by primary vacuum arc sources toward substrates to be coated along the curvilinear deflecting magnetic field. In contract, the conventional filtered arc deposition processes have efficiency of ion current transmission less than 1%[4,11,12,27,58]. Plasma transport efficiency of the LAFAD process is at least equal or, for many types of commercially available DCAD sources, exceeds the ion transport efficiency of the unfiltered direct arc deposition process. High efficiency of vapor plasma transport in LAFAD process can be explained by concave topology of the deflecting magnetic field of unidirectional dual arc LAFAD plasma source. It is known that diffusion losses are minimal when plasma is confined in concave magnetic field, while plasma diffusion across magnetic force lines is maximal when plasma is confined in convex magnetic field[3]. On the other hand, much greater diffusion losses of vapor plasma were found in a straight vacuum arc column configuration where the arc was confined in an axi-symmetrical longitudinal magnetic field[2,46].

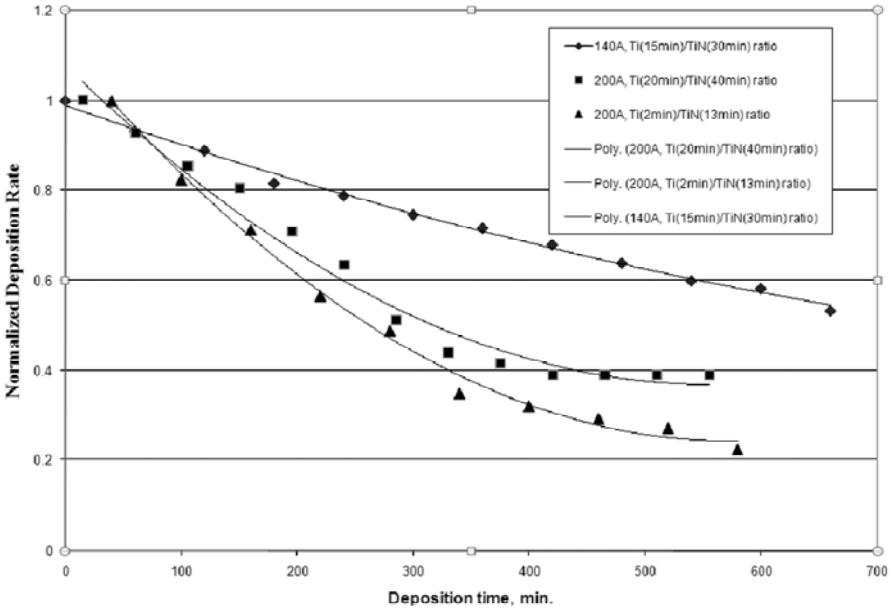

Figure 19. Normalized deposition rates of Ti/TiN multilayer coatings with different architectures deposited by unidirectional dual arc LAFAD metal vapor plasma source on rotating (one side coated) substrates.
Maximum Deposition Rates: 140A, Ti(15min)/TiN(30min)- 2.7um/hr; 200A, Ti(20min)/TiN(40min)- 10.7 um/hr; 200A, Ti(2min)/TiN(13min)- 8.2 um/hr.

Ultra-thick ceramic and cermet coatings deposited by the LAFAD process possess relatively high hardness ranging from 18 GPa for laminated coatings to 35 GPa for monolithic coatings. The high hardness of LAFAD coatings was combined with high fracture resistance, making these coatings capable of erosion protection of turbomachinery components such as compressor blades of turbine engines and protectors for helicopter rotorblades, as well as in abrasive wear applications such as mining and road rehabilitation tools. The laminated architecture is a well known approach to increase toughness of ceramics, cermets and composites[34]. It was found that crack trajectories in ultra-thick

laminated Me/MeN LAFAD coatings that have a relatively thick metallic interlayers are predominantly lateral, arrested in ceramic sublayers, while restricted by two neighboring metallic sublayers; however, in monolithic ceramic coatings the crack pattern is random[51]. Even better fracture resistance can be obtained by using sub-stoichiometric coatings, as illustrated in Figure 20, showing the cross-section of Rockwell 145 kg load indentation of L coating made of TiAl/TiAlN multilayer vs. sub-stoichiometric TiN coating[51]. It can be seen that density of cracks developed in a central area of indentation subjected to high compressive stress in sub-stoichiometric coating having hardness of about 25 GPa is much

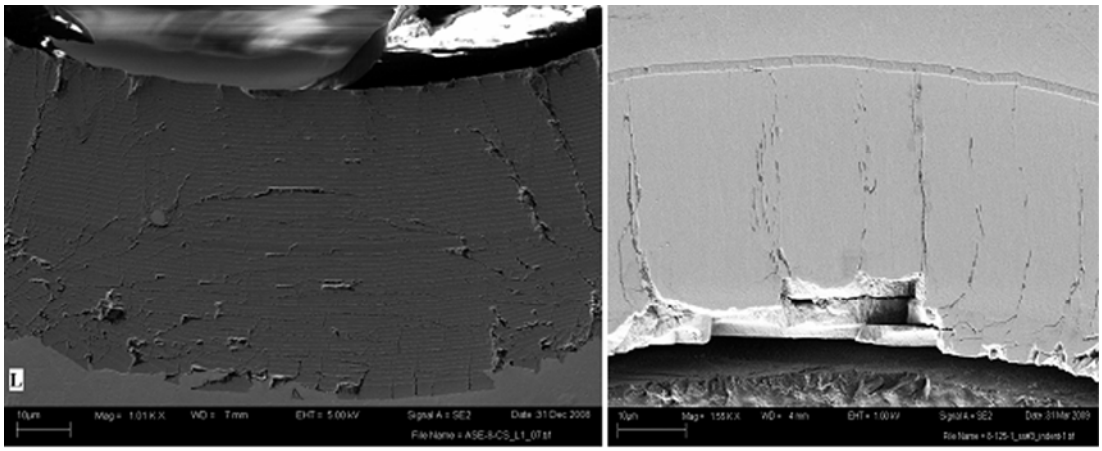

Figure 20. Rockwell (145 kg) indentation cross-sections of ultra-thick TiAl/TiAlN multilayer coating (left) and sub-stoichiometric TiN coating (right) deposited by LAFAD process.

smaller than that of laminated stoichiometric L coating (TiAl/TiAlN multilayer) having about the same hardness and thickness. The combination of high hardness and good fracture resistance in LAFAD ultra-thick ceramic coatings resulted in high erosion resistance. The LAFAD TiN and TiAlN-based ceramic and cermet coatings with thicknesses up to 100 μm, can still provide a smooth surface even with a roughness of RMS<1μm. Thick TiN based coatings deposited by the LAFAD process, both microlaminated Ti/TiN cermet and monolithic TiN ceramics, can provide an order of magnitude improvement of erosion resistance under conditions of impacts with runway sand particulate flow at the speed up to 1200 fps[50]. These properties of the LAFAD process make it an attractive alternative to replace conventional plasma PVD processes for a wide range of applications in turbomachinery.

CONCLUSIONS

The unidirectional dual arc LAFAD vapor plasma source has been characterized as a generator of high-density ion current and mass flow with 100% ionized metal vapor and more than 50% ionized gaseous plasma component. The productivity of the LAFAD plasma source is comparable to, or exceeds, the productivity of conventional DCAD sources and magnetron sputtering sources. For example, one LAFAD source can deposit TiN-based coatings on substrates installed on the 0.5 meter diameter rotating turntable of the industrial size batch coating chamber with an average productivity exceeding 5 μm/hr, yet provide a uniform coating thickness distribution a ~+/-15% over the 12 inches tall deposition area. The efficiency of the LAFAD process is defined by its ability to transport more than half of the total ion current generated by vacuum arc process from the primary DCAS evaporating targets toward substrates to be coated along curvilinear deflecting magnetic field. The LAFAD vapor plasma transport efficiency exceeds more than four times the transport efficiency of the conventional FCAD process and, in many cases, even exceeds the direct cathodic arc deposition process. Cermet

and ceramic coatings of different multielemental multiphase compositions and architectures are featuring near defectless morphology, smooth surface and extremely high adhesion. The operating range of the LAFAD process allows combining it with other PVD processes such as magnetron sputtering and EBPVD, as well as low pressure plasma assistant CVD process, forming hybrid LAFAD plasma assisted surface engineering technologies. Both micro- and nano-laminated ceramic and cermet coatings and nanocomposite coatings deposited by LAFAD process have demonstrated superior functional properties in various applications including wear resistant coatings for cutting and forming tools and medical instruments, erosion resistant coatings for turbomachinery components, high temperature oxidation resistant coatings for SOFC, tribological coatings for gears and bearings operating in extreme conditions. These properties of the LAFAD process make it an attractive alternative to replace conventional plasma PVD processes for a wide range of applications.

REFERENCES

1. V.I. Gorokhovsky, et al., Report on the Investigation of Physics and Chemistry of Chemically Active Plasma Flow for Development of New Synthesis Methods for Composite Superhard Materials and Deposition of Coatings, Report No. 0287-0034250, Institute for Superhard Materials of the Ukrainian Academy of Sciences, Kiev, Ukraine (1983).
2. V.I. Gorokhovsky, V.P. Polistchook and I.M. Yartsev, Process in Plasma-Arc Installation for Vacuum Depositions, Part I: Plasma Generation; Part II: Plasma Propagation, *Surf Coat Tech*, **61**, 101 (1993).
3. N. A. Krall and A. W. Trivelpiece, Principles of Plasma Physics, McGraw-Hill Book Company, New York, USA (1973).
4. R.L. Boxman, D.M. Sanders, and P.J. Martin, *Handbook of Vacuum Arc Science and Technology*. Noyes Publications, Park Ridge, New Jersey, USA (1995).
5. J. Musil, Hard Nanocomposite Films Prepared by Reactive Magnetron Sputtering, in *Nanostructured Coatings*, edited by A. Cavaliero and J. De Hosson, Springer Publishing Co. (2006).
6. S.M. Rossnagel, Directional and Preferential Sputtering-Based Physical Vapor Deposition, *Thin Solid Films* **263**, 1-12 (1995).
7. U. Helmersson, M. Lattermann, J. Bohlmark, A.P. Ehiasarian, and J.T. Gudmundsson, Ionized Physical Vapor Deposition (IPVD): A Review of Technology and Applications, *Thin Solid Films*, **513** 1-24 (2006).
8. M. Klingenberg, J. Arps, R. Wei, J. Demaree, and J. Hirvonen, Practical Applications of Ion Beam and Plasma Processing for Improving Corrosion and Wear Protection, *Surf Coat Tech*, **158-159**, 164-169 (2001).
9. R. Wei, E. Langa, C. Rincon, and J.H. Arps, Deposition of Thick Nitrides and Carbonitrides for Sand Erosion Protection, *Surf Coat Tech*, **201**, 4453-4459 (2006).
10. Q. Luo, W.M. Rainforth, and W.-D. Münz, Wear Mechanisms of Monolithic and Multicomponent Nitride Coatings Grown by Combined Arc Etching and Unbalanced Magnetron Sputtering, *Surf Coat Tech*, **146-147**, 430-435 (2001).
11. A. Aksenov, V. A. Belous, V. G. Padalka, and V. M. Khoroshikh, *Soviet Journal of Plasma Physics*, **4**, 425 (1978).
12. D. Baldwin and S. Falabella, Technical Proceedings of the Annual Meeting of Society of Vacuum Coaters (1995).
13. V.I. Gorokhovsky, T. Kurtinina, and D. Otorbaev, in *Collection of Scientific Papers on Wear Resistant and Protective Coatings*, edited by M.A. Voronkin, Institute of Superhard Materials, Academy of Sciences of the UkrSSR, Kiev [in Russian], (2001).
14. K. Gordashnik, V. Gorokhovsky, and B. Uryukov, Study of Corrosion Stability of Medical Instruments with TiN-Coatings, Proceedings of the International Ion Engineering Congress, ISIAT 83, Institute of Electrical Engineers, Kyoto, Japan (1983).

15. Z. Has, S. Mitura, and V.I. Gorokhovsky, The System for Depositing Hard Diamond-Like Films onto Complex-Shaped Machine Elements in an R.F. Arc Plasma, *Surf Coat Tech*, 47, 106-112 (1991).
16. N. Novikov, V.I. Gorokhovsky, and B. Uryukov, Superhard i-C Coatings Used in Complex Processes of Surface Strengthening of Tools and Machine Parts, *Surf Coat Tech*, **47**, 770 (1991).
17. V. Aleshin, V.I. Gorokhovsky, V. Malnev, E. Pugach, and A. Smekhnov, Structure and Properties of iC-Coatings Deposited from Plasma Phase, *Archive Nauki o Materialach* (Poland), **7**, 105-110 (1986).
18. V. Aleshin, V.I. Gorokhovsky, V. Strel'nitsky, and B. Uryukov, Interaction at the Interface Between Carbon Films and Mmetals, *Soviet Journal of Superhard Materials*, **9**, 19-23 (1987).
19. V.I. Gorokhovsky, Y. Leshchiner, and A. Malyshev, Wear Characteristics of HSS with TiN, CrN and i-C Coating Deposited from Plasma Phase, Proceedings of the International Seminar on Vacuum Coatings for Wear Surfaces of Tools and Machine Parts Using Plasma, Warsaw, Poland (1987).
20. A. Lysenko, V.I. Gorokhovsky, Y. Nikitin, and V. Poltoratsky, Molecular Model of Diamond-Like Carbon Structure Synthesized under Low Pressure, Transactions of the Academy of Sciences of the UkrSSR [in Russian] (1987).
21. V.I. Gorokhovsky, Vacuum Cermet Coatings on Coiled Materials, Proceedings of the Fourth International Conference on Vacuum Web Coating, edited by R. Bakish, Reno, Nevada, USA (1990).
22. V.I. Gorokhovsky, R. Bhattacharya, and D.G. Bhat, Characterization of Large Area Filtered Arc Deposition Technology: Part I-Plasma Processing Parameters, *Surf Coat Tech*, **140**, 82-92 (2001).
23. V.I. Gorokhovsky, D.G. Bhat, R. Bhattacharya, A.K. Rai, K. Kulkarni, and R. Shivpuri, Characterization of Large Area Filtered Arc Deposition Technology: Part II-Coating Properties and Applications, *Surf Coat Tech*, **140**, 215-224 (2001).
24. D.G. Bhat, V.I. Gorokhovsky, R. Bhattacharya, R. Shivpuri, and K. Kulkarni, Development of a Coating for Wear and Cracking Prevention in Die-Casting Dies by the Filtered Cathodic Arc Process, Transactions of the North American Die Casting Association, Twentieth International Die Casting Congress and Exposition, Cleveland, Ohio USA (1999).
25. V. Joshi, K. Kulkarni, R. Shivpuri, R.S. Bhattacharya, S.J. Dikshit, and D. Bhat, Dissolution and Soldering Behavior of Nitrided Hot Working Steel with Multilayer LAFAD PVD Coatings, *Surf Coat Tech*, **146 –147**, 338–343 (2001).
26. P.J. Martin and A. Bendavid, Review of the Filtered Vacuum Arc Process and Materials Deposition *Thin Solid Films*, **394**, 1-15 (2001).
27. D.M. Sanders and A. Anders, Review of Cathodic Arc Deposition Technology at the Start of the New Millennium, *Surf Coat Tech*, **133-134**, 78-90 (2000).
28. www.arcomac.com.
29. V.I. Gorokhovsky, US Patent No. 7,300,559 (November 27, 2007).
30. V.I. Gorokhovsky, C. Bowman, D. VanVorous, and J. Wallace, Deposition of Various Metal, Ceramic and Cermet Coatings by an Industrial-Scale LAFAD Process," *JVST A*, **27**, 1080-1095 (2009).
31. V.I. Gorokhovsky, Characterization of Thick Ceramic and Cermet Coatings Deposited by an Industrial-Scale LAFAD Process, *Surf Coat Tech*, **204**, 1216-1221 (2010).
32. H. Kostenbauer, G.A. Fontalvo, M. Kapp, J. Keckes, and C. Mitterer, Annealing of Intrinsic Stresses in Sputtered TiN Films: The Role of Thickness-Dependent Gradients of Point Defect Density, *Surf Coat Tech* **201**, 4777-4780 (2007).
33. K.J. Ma, A. Bloyce, and T. Bell, Examination of Mechanical Properties and Failure Mechanisms of TiN and Ti-TiN Multilayer Coatings, *Surf Coat Tech*, **76-77**, (1995) 297-302.
34. W. Lee and W.J. Clegg, "The Deflection of Cracks at Interfaces, *Key Engineering Materials*, 1**16-117**, 193-208 (1996).
35. R.J. Smith, C. Tripp, A. Knospe, C.V. Ramana, A. Kayani, V.I. Gorokhovsky, V. Shutthanandan, and D.S. Gelles, Using CrAlN Multilayer Coatings to Improve Oxidation Resistance of Steel Interconnects for Solid Oxide Fuel Cell Stacks, *J Mater Eng Perform*, **13**, 295-302 (2004).

[36.] V.I. Gorokhovsky, B. Heckerman, P. Watson, and N. Bekesch., The Effect of Multilayer Filtered Arc Coatings on Mechanical Properties, Corrosion Resistance, and Performance of Periodontal Dental Instruments, *Surf Coat Tech*, **200**, 5614-5630, (2006).
[37.] V.I. Gorokhovsky, B. Heckerman, and T. Brown, Advanced Surface Engineering Technology for Endodontic Instruments and Related Applications, *Roots*, **Number 2**, 40-50 (2006).
[38.] V.I. Gorokhovsky, B. Heckerman, and T. Brown, Advanced Surface Engineering Technology for Endodontic Instruments and Related Applications, *International Dental Tribune*, Endo Supplement, (2006).
[39.] www.am-eagle.com
[40.] P.E. Gannon, C.T. Tripp, A.K. Knospe, C.V.R. Ramana, M. Deibert, R.J. Smith, V.I. Gorokhovsky, V. Shutthanandan, and D. Gelles, High-Temperature Oxidation Resistance and Surface Electrical Conductivity of Stainless Steels with Filtered Arc Cr-Al-N Multilayer and/or Superlattice Coatings, *Surf Coat Tech*, **188-189**, 55-61 (2004).
[41.] C. Collins, J. Lucas, T.L. Buchanan, M. Kopczyk, A. Kayani, P.E. Gannon, M.C. Deibert, R.J. Smith, D.S. Choi, and V.I. Gorokhovsky, Chromium Volatility of Coated and Uncoated Steel Interconnects for SOFCs, *Surf Coat Tech*, **201**, 4467-4470 (2006).
[42.] A. Kayani, R.J. Smith, S. Teintze, M. Kopczyk, P.E. Gannon, M.C. Deibert, V.I. Gorokhovsky, and V. Shutthanandan, Oxidation Studies of CrAlON Nanolayered Coatings on Steel Plates," *Surf Coat Tech*, **201**, 4460-4466, (2006).
[43.] V.I. Gorokhovsky, C. Bowman, P. Gannon, D. VanVorous, A.A. Voevodin, A. Rutkowski, C. Muratore, R.J. Smith, A. Kayani, D. Gelles, V. Shutthanandan, and B.G. Trusov, Tribological Performance of Hybrid Filtered Arc-Magnetron Coatings, Part I, *Surf Coat Tech*, **201**,3732-3747, (2006).
[44.] V.I. Gorokhovsky, C. Bowman, P. Gannon, D. VanVorous, A. Voevodin, and A. Rutkowski, Tribological Performance of Hybrid Filtered Arc-Magnetron Coatings, Part II," *Surf Coat Tech*, **201**, 6228-6238 (2007).
[45.] L.R. Pederson, P. Singh, and X.-D. Zhon, Application of Vacuum Deposition Methods to Solid Oxide Fuel Cells, *Vacuum*, **80**, 1066-1083 (2006).
[46.] V.I. Gorokhovsky, V.P. Elovikov, P.L. Lizunov, and S.A. Pantyukhin, An Induction Method of Determining Conduction-Zone Size in a Vacuum Arc, *High Temp*, **26**, 170-175 (1988).
[47.] V.I. Gorokhovsky, C. Bowman, P.E. Gannon, D. VanVorous, J. Hu, C. Muratore, A.A. Voevodin, and Y.S. Kang, Deposition and Characterization of Hybrid Filtered Arc-Magnetron Multilayer Nanocomposite Cermet Coatings for Advanced Tribological Applications, *Wear* **265**, 741-755 (2008).
[48.] V.I. Gorokhovsky, P.E. Gannon, M.C. Deibert, R.J. Smith, A. Kayani, M. Kopczyk, D. VanVorous, Z. Yang, J.W. Stevenson, S. Visco, C. Jacobson, H. Kurokawa and S. Sofie, Deposition and Evaluation of Protective PVD Coatings on Ferritic Stainless Steel SOFC Interconnects, *J Electrochem Soc*, **153**, A1886-A1893 (2006).
[49.] V.I. Gorokhovsky, J. Wallace, C. Bowman, P.E. Gannon, J. O'Keefe, V. Champagne and M. Pepi, Large Area Filtered Arc and Hybrid Coating Deposition Technologies for Erosion and Corrosion Protection of Aircraft Components, Proceedings of 32nd International Conference & Exposition on Advanced Ceramics & Composites, Daytona Beach, Florida USA (2008).
[50.] V.I. Gorokhovsky, C. Bowman, J. Wallace, Dave VanVorous, John O'Keefe, Victor Champagne, Marc Pepi, Widen Tabakoff, LAFAD Hard Ceramic and Cermet Coatings for Erosion and Corrosion Protection of Turbomachinery Components, Proceedings of ASME Turbo Expo 2009: Power for Land, Sea and Air, Paper No. GT2009-59391, Orlando, Florida USA (2009).
[51.] V.I. Gorokhovsky, Characterization of Thick Ceramic and Cermet Coatings Deposited by an Industrial-Scale LAFAD Process, Presentation at ICMCT, San Diego, California USA (2008) and published in *Surf Coat Tech*, **204**, 1216-1221 (2010).

[52] Y.H. Cheng, T. Browne, B. Heckerman, J.C. Jiang, E I. Meletis, C. Bowman, and V.I. Gorokhovsky, Internal Stresses in TiN/Ti Multilayer Coatings Deposited by Large Area Filtered Arc Deposition, *J Appl Phys* **104**, 093502 (2008).

[53] Y.H. Cheng, T. Browne, B. Heckerman, J.C. Jiang, E.I. Meletis, C. Bowman, and V.I. Gorokhovsky, Influence of Si Content on the Structure and Internal Stress of the Nanocomposite TiSiN Coatings Deposited by Large Area Filtered Arc Deposition, *J Phys D: Appl Phys* **42** 125415 (2009).

[54] Y.H. Cheng, T. Browne, and B. Heckerman, Nanocomposite TiSiN Coatings Deposited by Large Area Filtered Arc Deposition, *J Vac Sci Tech A*, **27**, 82-88 (2009).

[55] A. Sue, Development of Arc Evaporation of Non-Stoichiometric Titanium Nitride Coatings, *Surf Coat Tech*, **62**, 115-120 (1993).

[56] V.P. Swaminathan, R. Wei, D. Gandy, Nanotechnology Coatings for Erosion Protection of Turbine Components, ASME Paper No. GT2008-50713 (2008).

[57] V.I. Gorokhovsky, A. Zhiglinsky, V. Kuchinsky, and V. Fomichev, Kinetics of Transitional Layer Forming with Precipitation of Surfaces from Ion Beams, *Surface: Physics, Chemistry, Mechanics*, **Number 2** (1991).

[58] V.I. Gorokhovsky and D.G. Bhat, Principles and Applications of Vacuum Arc Plasma-Assisted Surface Engineering Technologies, Proceedings of the GOI-UNDP International Workshop on Surface Engineering and Coatings, Bangalore, India, edited by I. Rajagopal, K.S. Rajam, and R.V. Krishnan, Allied Publishers, Ltd., Mumbai, India (1999).

[59] R. Bhattacharya and B. Majumbar, Improved Thermal Barrier Coating System Based on a Cathodically Deposited Alpha Alumina Sublayer, Report No. AFRL-ML-WP-TR-2001-4099, UES, Inc., Dayton, Ohio USA (2001).

[60] A.K, Rai, Development of Protective Coatings for Single Crystal Turbine Blades, Final Report prepared for The U.S. Department of Energy (Contract No. DE-FG02-03ER83809), UES, Inc. Dayton, Ohio USA (2006).

[61] A.K. Rai, J. Nainaparampil, M. Massey, R.S. Bhattacharya, L.J. Gschwender, C.E. Snyder, Jr., Interaction of Fomblin® Lubricant with Surface Nitrided and/or Coated Bearing (M50) Steel, *Lubric Sci*, **21**, 305-320 (2009).

[62] S.J. Dixit, A.K. Rai, R. Bhattacharya, and S. Guha, Characterization of AlN Thin Films Deposited by Filtered Cathodic Arc Process, *Thin Solid Films*, **398-399**, 17 (2001).

[63] R. Bathe, R.D. Vispute, D. Habersat, R.P. Sharma, T. Venkatesan, C.J. Scozzie, Matt Ervin, B.R. Geil, A.J. Lelis, S.J. Dixit, and R.S. Bhattacharya, AlN Thin Films Deposited by Pulsed Laser Ablation, Sputtering and Filtered Arc Technique, *Thin Solid Films*, **398-399**, 575 (2001).

[64] J.R. Tuck, A.M. Korsunsky, D.G. Bhat, and S.J. Bull, Indentation Hardness Evaluation of Cathodic Arc Deposited Thin Hard Coatings, *Surf Coat Tech*, **139**, 63-74 (2001).

[65] A.K. Rai and R.S. Bhattacharya, Development of Hard-Soft Coatings for Enhanced Machining Performance Employing Large Area Filtered Arc Deposition Technique (CT77), Phase II Final Report prepared for The Edison Materials Technology Center (EMTEC), UES, Inc., Dayton, Ohio USA (2006).

[66] A.K. Rai and R.S. Bhattacharya, Large Area Filtered Arc Deposition of Carbon and Boron Based Hard Coatings, Final Report prepared for The U.S. Department of Energy (Contract No. DE-FG02-99ER82911), UES, Inc., Dayton, Ohio USA (2003).

[67] C.Y. Chan, K.H. Lai, M.K. Fung, W.K. Wong, I. Bello, R.F. Huang, C.S. Lee, and S.T. Lee, Deposition and Properties of Tetrahedral Amorphous Carbon Films Prepared on Magnetic Hard Disks, *J Vac Sci Tech*, **A19**, 1606-1610 (2001).